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PH BY THE METHOD OF PULSE RADIOLYSIS

DISSERTATION
Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

BY
Bonnie Leonard Gall, B.A.

* * * *

The Ohio State University
1968

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INTRODUCTION

The radiolysis of aqueous solutions has been the subject of innumerable investigations and is now one of the best understood systems in terms of the kinetics in the solutions. The primary species produced by the radiolysis of water$^{1,2}$ are,

\[ \text{H}_2\text{O} \rightarrow \text{H, OH, e}_{aq}^{-}, \text{H}_3\text{O}^{+}, \text{H}_2, \text{H}_2\text{O}_2 \quad (1) \]

where

- $\text{H}$ = hydrogen atom
- $\text{OH}$ = hydroxyl radical
- $\text{e}_{aq}^{-}$ = solvated electron
- $\text{H}_3\text{O}^{+}$ = hydronium ion
- $\text{H}_2$ = hydrogen molecule
- $\text{H}_2\text{O}_2$ = hydrogen peroxide

Within $10^{-15}$ sec after the deposition of energy in the solution by ionizing radiation such as, electrons, x-rays and so on, $\text{H}_3\text{O}^{+}$ has formed.$^3$ The radicals, $\text{H}$ and $\text{OH}$, exist within $10^{-13}$ sec. The solvated electron exists within $10^{-11}$ sec and the molecular products, $\text{H}_2$ and $\text{H}_2\text{O}_2$ have formed within about $10^{-8}$ sec.$^3$ Observation of chemical processes in our systems occurs only after the formation of the primary species.

---


(2) L. M. Dorfman and M. S. Matheson, Progress in Reaction Kinetics, 2, 257 (1965).

Least studied and least understood, however, have been solutions at pH greater than 12. At high pH the hydroxyl radical reacts with hydroxide ion

\[ \text{OH} + \text{OH}^- \rightarrow \text{O}^- + \text{H}_2\text{O} \]  

(2)

Published values for the pK of the hydroxyl radical dissociating to O\(^-\) and H\(_2\)O\(^+\) are 11.9 ± 2\(^1\) and 11.8 ± 2\(^2\). Also at high pH, hydrogen atoms react with hydroxide ions

\[ \text{H} + \text{OH}^- \rightarrow \text{e}_{\text{aq}}^- + \text{H}_2\text{O} \]  

(3)

The published rate constant for reaction (3) is \(1.8 \times 10^7\) M\(^-1\) sec\(^-1\).\(^6\)

The optical absorption spectrum of the solvated electron has been observed.\(^7\)

In oxygenated solutions, both forms of the reducing radical can react with oxygen.

\[ \text{e}_{\text{aq}}^- + \text{O}_2 \rightarrow \text{O}_2^- \]  

(4)

\[ \text{H} + \text{O}_2 \rightarrow \text{HO}_2 \]  

(5)

The published rate constants for these reactions are \(k_4 = 1.88 \times 10^{10}\)

M^{-1} \text{ sec}^{-1} \text{ and } k_5 = 2 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}.^{10} \text{ The absorption spectra of } O_2^- \text{ and } HO_2 \text{ have been reported.}^{11}

The hydroxyl radical does not react with oxygen. Many recent studies,^{11,18-21} however, have been concerned with the investigation of the ozonide ion, O_3^-, formed in the reaction of the oxide radical ion, O^-, with oxygen.

\[
O^- + O_2 \rightarrow O_3^-
\]  


The published rate constant for reaction (6)\textsuperscript{15} is $2.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. The spectrum of ozonide ion has also been reported.\textsuperscript{11,15} The present study continues the investigation of the reactivity of the ozonide ion as well as studying the reactivity of its precursor, the oxide ion, about which very little is known.

Alkali metal ozonides have been prepared from dry powdered alkali metal hydroxides and ozone\textsuperscript{22}. They have been isolated as red solids and are stable in non-aqueous solvents such as liquid ammonia. In liquid ammonia or dimethyl sulfone they have an absorption in the visible with a maximum at 450 nm\textsuperscript{23}. In 1935, Weiss\textsuperscript{24} prepared ozonide ion by bubbling ozone into 7M NaOH solution cooled to $-40^\circ \text{C}$. He observed an absorption in the blue region of the spectrum but erroneously attributed the absorption to $\text{O}_2^-$ rather than to $\text{O}_3^-$. More recently, the same absorption spectrum was observed in the flash photolysis of oxygenated alkaline solution of hydrogen peroxide\textsuperscript{14} and in the pulse radiolysis of oxygenated alkaline solutions\textsuperscript{11,13}. The absorption, with a maximum at 430 nm, has been attributed to the ozonide ion by the authors referred to above for the following reasons. Hydroxyl radical scavengers such as ethanol suppress the formation of the absorbing species which suggests that OH is a precursor. The pH dependent formation\textsuperscript{11,16} of the absorbing species correlates with the

\begin{itemize}
\end{itemize}
conversion of OH to $O^-$. The appearance of the species occurs only above pH 10. The absorption increases until a maximum is reached at approximately pH 13. The absence of the absorption spectrum in deaerated solutions implies that oxygen is a precursor. The formation of the absorbing species is first order in oxygen concentration; the published bimolecular rate constant for the formation is $2.5 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$. Furthermore, the spectrum is similar to that of ozonide in liquid ammonia, as previously mentioned. Finally, the absorption at 430 nm doubles in solutions which also contain nitrous oxide. Nitrous oxide reacts with solvated electron to form the oxide radical ion.

$$N_2O + e_{aq}^- \rightarrow N_2 + O^-$$

The ratio of the optical density at 430 in solutions containing $N_2O$ to the optical density in solutions without $N_2O$ is 1.96 as compared to the calculated ratio of 1.97. This experiment is explained in more detail in the section on Results and Discussion.

Different results have been published for the decay kinetics of the ozonide ion. Czapski and Dorfman found that the absorption at 430 nm exhibited a first order decay. Their experiments were carried out at low pulse intensity so that the initial ozonide concentration was less than $5 \times 10^{-6}$ M. Czapski extended the study in the low intensity region to show an inverse dependence of the first order rate constant on oxygen concentration. Using mixtures of He-$O_2$ and $N_2O-O_2$ to obtain the desired oxygen concentrations, he showed that

---

the presence of \( \text{N}_2\text{O} \) did not affect the decay. Also below pH 13 the rate of decay increased with decreasing pH but above pH 13 the decay was independent of pH.

At higher initial ozonide ion concentrations, \([\text{O}_3^-] > 10^{-5}\), the decay was no longer first order. Adams et al.\textsuperscript{16} reported second order decay of \( \text{O}_3^- \) in oxygenated solutions containing \( \text{N}_2\text{O} \). They reported the rate constant for the reaction,

\[
\text{O}_3^- + \text{O}_3^- \rightarrow \text{products}
\]  

(8)
to be \( 2k_8 = 1.1 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1} \). Further investigations by Felix et al.\textsuperscript{18} showed, however, that the decay of ozonide ion in \( \text{O}_2-\text{N}_2\text{O} \) solutions was mixed first and second order decay. Even for initial \([\text{O}_3^-]\) of \( 2.4 \times 10^{-4} \text{ M} \), the first order decay contributed almost 20% to the initial rate of decay. To obtain the best rate constants, they used an analog computer to do curve fitting over the entire decay curve. They determined that the second order decay also depended on some inverse function of the oxygen concentration. Oxygen stabilized the ozonide ion for both first and second order decay. The mechanism of the decay was not explained, however.

The decay of ozonide ion also depends on the amount of hydrogen peroxide in solution. Two rate constants for the decay which was attributed to the reaction

\[
\text{O}_3^- + \text{HO}_2^- \rightarrow \text{O}_2^- + \text{OH}^- + \text{O}_2
\]  

(9)
have been reported, \( 1.6 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1} \)\textsuperscript{19} and \( 8.9 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1} \)\textsuperscript{18}. Behar and Czapski in current studies have carried out a far more extensive study of the system by studying the ozonide ion decay in the flash photolysis of basic solutions of oxygen and hydrogen peroxide.
They found that oxygen also had an inhibiting effect on rate of decay of $O_3^-$. The following mechanism explained their results.

$$\text{O}^- + \text{O}_2 \rightarrow O_3^- \quad (6)$$

$$O_3^- \rightarrow O^- + \text{O}_2 \quad (10)$$

$$O^- + \text{H}_2\text{O}_2 \rightarrow \text{OH}^- + \text{HO}_2 \quad (11)$$

Since the pK of hydrogen peroxide is 11.8, reaction (11) should probably be written

$$O^- + \text{HO}_2^- \rightarrow \text{OH}^- + \text{O}_2^- \quad (12)$$

The question of which form of hydrogen peroxide is reacting will be discussed in more detail in the section on Results and Discussion.

The results of Behar and Czapski showed that the decay of the ozonide ion actually occurred through the reaction of the oxide radical ion. They obtained the values of $k_{10} = 5 \times 10^3$ sec$^{-1}$ and $k_6/k_{11} = 3.5 \pm 1.5$.

In this investigation the decay of ozonide ion in oxygenated alkaline solutions of benzoate ion, ethanol and methanol has been studied. As was found in the hydrogen peroxide case, ozonide ion underwent no observable reaction with the added solutes. Its disappearance could be explained by its dissociation into oxide radical ion and oxygen and by the subsequent reactions of the oxidizing radical. Therefore, information was obtained concerning the reactivity of the oxidizing radical at high pH. The ozonide ion was quite stable except for its thermal decomposition.

A reasonable mechanism for the decay of ozonide ion in solutions containing solutes with which the oxidizing radical will react is presented. The precise nature of the decay of ozonide ion in oxygenated alkaline solutions containing no other added solutes, however, is still not understood.
EXPERIMENTAL PROCEDURES

The general techniques of pulse radiolysis, described in this text and previously\textsuperscript{27,11,28,29}, have been used in this study. New methods developed during this investigation are described in greater detail.

PULSE IRRADIATION

A Varian V-7715-A linear accelerator was used as a high energy electron source. The machine produces electrons with energies variable from 2 to 6 MeV. The pulse width is continuously variable from 1.6 to 0.005 μsec. For the present investigation 3 to 4 MeV electrons at a current of 300 to 350 mA were used. Irradiation times varied from 1.6 to 0.1 μsec. Figure 1 shows the time profiles of several typical pulses. The decay time of the pulse is approximately 6 nanosec which means that the effects of irradiation do not extend into the time range of the chemical reactivity of the species produced by irradiation. The dose per pulse of a 0.4 μsec pulse of 300 mA is approximately $1 \times 10^{17}$ ev/g.

\begin{enumerate}
\end{enumerate}
Electron Pulse  
4 MEV.  

O.S.U. LINAC  
325 MAMP.  

1.4 µsec  
500 nsec  
20 nsec  

Fig. 1
The cross sectional area of the electron beam can be determined using a sheet of polyvinylchloride which is discolored by the electron beam. The amount of discoloration is an indication of the amount of energy deposited in the sample. When the PVC film is placed at the position of the cell, the area of maximum discoloration is an oval shape approximately 1.5 cm in width and 1 cm in height. If the electron beam first passes through a glass plate 1 mm in thickness, used to simulate the quartz window of the cell, the area of maximum discoloration of the PVC, placed immediately behind the glass plate, increases to 2 cm by 1.5 cm. A smaller amount of energy is deposited outside these limits, however, making the total dimensions of the beam 3 cm by 2.5 cm. Since the cells used had internal dimensions of 2 cm by 1.2 cm, the entire surface of the solution was irradiated approximately uniformly.

Energy deposition was also found to be relatively uniform through the 8 mm depth of the solution using a He-Ne laser as an optical probe. The following procedure was used to check the energy deposition through the depth of the cell. A solution of diphenyl in ethanol was prepared. Irradiation of this solution produces diphenylide ion via the reaction

$$ e_{aq}^- + \phi_2 \rightarrow \phi_2^- $$

(12)
The rate constant for reaction (12) is $4.3 \times 10^3$ M$^{-1}$ sec$^{-1}$. Using a concentration of $2 \times 10^{-3}$ M diphenyl, the formation of diphenylide ion is virtually complete at the end of the pulse. At low pulse intensities

diphenylide ion decays by the pseudo first order process

\[ \Phi_2^- + \text{EtOH} \rightarrow \Phi_2\text{H} + \text{EtO}^- \]  (13)

This system was chosen because diphenylide ion absorbs light in the wavelength region around 630 nm\(^3\). Therefore, a He-Ne laser could be used as a light source. The laser, model 240 from University Laboratories Incorporated, emits light of wavelength 632.8 nm. The laser beam, 2 mm in diameter, was passed through a pinhole 1 mm in diameter. The pinhole could be moved along the depth of the cell to measure the optical density of \( \Phi_2^- \) in the front and back (referring to the direction of the electron beam) of the cell. The measured maximum optical density in the first 2 mm, middle and last 2 mm of the cell were 0.13 ± .01, 0.125 ± .003 and 0.118 ± .001, respectively. Each value is an average of three pulses. The figures show that the fall-off of the dose at the rear of the cell is only about 10%. Figure 2 shows the expected dose distribution for 3 and 4 MeV electrons as a function of depth in water\(^3\). Since the density of quartz\(^3\) is 2.2 times that of water, 1 mm of quartz and 8 mm of water is approximately equivalent to 10 mm of water. Obviously, a sharp drop-off in dose should not be expected.


Figure 2: Dose distribution in water as a function of depth in water, from Brynjolfsson\textsuperscript{32}. 

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.png}
\end{figure}
Boag\textsuperscript{34} has discussed the effect of variations in the concentration of reactive species on the rate constant calculations. The effect on the first order constants should be small as long as the variation in the concentration is not very large. The variation in our solutions is small enough to cause no difficulty in our calculations. This fact is demonstrated in the diphenyl solution since the pseudo first order rate constants calculated for the various positions in the cell were $4.4 \pm 0.2 \times 10^5$ sec$^{-1}$ identical with the published value of $4.4 \pm 0.4 \times 10^5$ sec$^{-1}$\textsuperscript{30}.

The dose given to the solution per pulse was found to be reproducible to within $\%$ so that no pulse monitoring was necessary.

**OPTICAL DETECTION**

Transient species produced by the radiolysis were detected by spectrophotometric measurements of their optical densities. Figure 3 is a schematic representation of the optical system. The light source was a 500-W Osram xenon lamp, type XBO 450W. A remote control shutter was placed in front of the lamp. When light of wavelength 430 nm was monitored, Corning filters type 0-52 or 0-53 were used to remove light of wavelengths less than 300 nm. The light was then passed through the cell at right angles to the electron beam and was reflected back through the cell. When mapping spectra, the light beam was split by a partially reflecting quartz mirror coated with chromium. One monochromator would be used at a reference wavelength setting to correct for pulse intensity variations, although these were generally less than $\%$. The partially

reflecting mirror and the second monochromator were not used when it was necessary to observe only one wavelength.

Depending on the wavelength region of interest, the following Bausch and Lomb gratings were used: type 33-86-01, 2700 grooves/mm, wavelength region 180-400 nm; type 33-86-02, 1350 grooves/mm, 350-800 nm; type 33-86-07, 1200 grooves/mm, 200-700 nm. The dispersions of the gratings are 3.2, 6.4, 7.4 nm/mm respectively. The gratings were calibrated using the mercury spectral lines produced by a medium pressure mercury lamp. In most cases, the slits on the monochromators were less than 0.3 and 0.2 mm for the entrance and exit slits respectively.

RCA photomultiplier tubes, 1P28, 7200 and 7102 with spectral responses S-5, S-19 and S-1 respectively were used in conjunction with Nexus operational amplifiers. The linearity of the photomultipliers was checked using neutral density filters when 600, 700 or 800 volts were placed on the photomultipliers. Normally, 600 volts were used when light at 430 nm was monitored.

The electronic signals from the amplifier were transmitted to a Tektronix type 555 dual beam oscilloscope. The oscilloscope traces were photographed with a Tektronix C-12 Polaroid five-inch oscilloscope camera onto Polaroid 3000 or 10,000 speed type 107 film.

**Cells**

Rectangular cells made of fused quartz for the body and high purity silica optical windows were used. The internal dimensions of the cells were 8 mm, in the direction of the electron beam, by 12 mm, by 20 mm along the light path. The side facing the electron beam was
Figure 3: Schematic diagram of the optical arrangement.
about 1 mm in thickness although some cells had sides specially ground to 0.5 mm.

Several arrangements for sample introduction were used. For the majority of the experiments, where the solutions were under atmospheric pressure, cell (a) in figure 4 was used. Solutions were introduced using the syringe technique\(^{35}\) which will be described in more detail in section VII.

For solutions pressurized with oxygen, cell (b)\(^{16}\) in figure 4 was used. Complete removal of the Fischer Porter Teflon stopcock (A) allowed introduction of the solution without fear of contamination from the stopcock grease on the standard taper joint (B), used to attach the cell to the vacuum line. Enough solution could be introduced to allow 10 to 15 irradiations of fresh samples of the solution. The solution could be transferred from the reservoir (C) to the cell (D) to the waste bulb (E) with little contamination of the unirradiated portion of the solution.

For studies at other than room temperature, the cell in figure 4 (c)\(^{36}\) was used. The cell was attached to a standard taper joint which determined the position of the cell in a thermostatic box to be described in the next section. A copper constantin thermocouple was cemented to the cell with indium metal.

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(a) Reaction cell for experiments when the liquid sample is saturated with gas at atmospheric pressure;
(b) Reaction cell for experiments when the liquid sample is saturated with gas above atmospheric pressure;
(c) Reaction cell for experiments when the temperature of the solution is other than at room temperature.
TEMPERATURE APPARATUS

The decay of ozonide ion was studied over a temperature range of 2 to 45° C. For temperatures lower than ambient, the temperature was controlled in a thermostatic box by a flow of cooled nitrogen gas. The apparatus and technique have been described by Arai et. al. 36

Figure 5 shows the box which consists of a brass container insulated with styrofoam. It has a thin copper window (A) to admit electrons. Two quartz evacuated cells (B) are used as windows for the analyzing light beam. Nitrogen was cooled by flowing the gas through a copper coil submerged in liquid nitrogen. The flow rate determined the temperature of the gas. Temperature inside and outside the cell were found to agree within 0.2° C. 36

For experiments at temperatures above ambient, heating of the nitrogen gas in order to heat the cell was found to be difficult to control. Instead, the entire solution and the cell were heated in a constant temperature bath. Aliquots of the solution were withdrawn to fill the cell and were irradiated within one minute. Some cooling of the solution in the cell would occur in the time between filling and irradiating. The amount of cooling, however, could be measured. The temperatures used in the calculation were the ones at the time of irradiation.

MATERIALS

Water was triply distilled in a quartz still. The first distillation was from acid dichromate solution, the second from basic permanganate solution and the third with no additives. The following Baker Analyzed
Figure 5: Thermostatic box for kinetic studies at temperatures below ambient; (A) thin copper window, (B) quartz evacuated cells used as windows for the analyzing light beam, (C) reaction cell as shown in figure 4 (c), (D) cooled gas outlet.
Reagents were used without further purification: potassium hydroxide; sodium hydroxide; 30% hydrogen peroxide with no added stabilizers; benzoic acid. Dupont ACS grade concentrated sulfuric acid and U. S. Industrial Chemical Co. ethanol were also used without further purification. Baker Analyzed Reagent ferrous sulfate was recrystallized from triply distilled water. Baker Analyzed Reagent methanol was refluxed with added sulfuric acid and 2,4 dinitrophenylhydrazine and distilled\textsuperscript{37}.

Basic solutions prepared from potassium hydroxide contained carbonate impurities due to about 3% potassium carbonate in the hydroxide. To eliminate this problem, a concentrated solution, 19 M, of sodium hydroxide was prepared and the sodium carbonate, insoluble in the concentrated base, was filtered out. The concentrated base was diluted with triply distilled water to obtain the desired hydroxide ion concentration.

DOSIMETRY

The dosimetry method described by Dorfman and Taub\textsuperscript{38} was used. The solution was the modified Fricke dosimeter containing 10\textsuperscript{−2} M ferrous sulfate and 0.8 N sulfuric acid. The solution was saturated with oxygen and contained no chloride ion.


No pulse monitoring was necessary because the dose to the solution was constant within 3%. The yield of ferric ion for high dose rates is 15.6 molecules/100 eV\textsuperscript{39,40}. The ferric ion was monitored at 356 nm for high intensity pulses and at 304 nm for low intensity pulses. Dose was calculated using 220 M\textsuperscript{-1} cm\textsuperscript{-1} as the extinction coefficient at 25\textdegree C for the ferric ion\textsuperscript{11,38} at 304 nm. The ratio ε\textsuperscript{304}/ε\textsuperscript{366} = 8.9, the mean of the two previously determined values\textsuperscript{11,38}, was used to calculate the extinction coefficient at 366 nm. A temperature correction of 0.79/\textdegree C\textsuperscript{3} was made to the extinction coefficient if the temperature of the solution was other than 25\textdegree C.

**SOLUTION PREPARATION**

A variety of methods was used to prepare solutions for irradiation. Solutes were weighed (accuracy ± 1.5%) and dissolved in triply distilled water. Concentrated NaOH was added to obtain the desired hydroxide ion concentration. If air saturated solutions were being used, the solutions were prepared in 100 ml volumetric flasks and transferred to syringe equipped with an inner standard taper 5/20 joint fused to the exit port through a uranium seal as shown in figure 6 (a). Occasionally, triply distilled water was bubbled with oxygen and used to prepare solutions. This technique did not remove all the nitrogen from solution, however.

When oxygen saturated solutions were used, the solutions were degassed using the syringe technique of Senvar and Hart\textsuperscript{35}. Solutions were injected into a degassing vessel shown in figure 6 (b) through (A)


using the special syringes. The vessel was attached to a vacuum system at (C). The three way stopcock (B) was specially ground and used only triply distilled water as a lubricant to prevent contamination with stopcock grease. Stopcock (C), however, was lubricated with apiezon N vacuum grease.

The bulb was evacuated and shaken vigorously. Oxygen was then bubbled through (A) with stopcock (B) open and (C) closed to the vessel. The procedure was repeated several times. Finally, an excess pressure of oxygen was introduced and used to push the liquid back up through (A) into a syringe. The method was found to be unsuitable for alcohol solutions because the volatile solute would be pumped off in the degassing procedure.

For some experiments, a higher oxygen concentration was desired than could be obtained using the previous procedure. For these situations approximately 40 ml of solution was put into the high pressure cell shown in figure 4 (b). The cell was attached to the vacuum line at (B) and degassed by pumping and shaking. Oxygen was frozen into the solution at liquid nitrogen temperature. Using the known ratio of the volume of the vacuum line to the volume of the cell, the pressure of oxygen in the cell could be calculated from Boyle's Law,

\[ P_a = P_b \left( \frac{V_b}{V_a} \right) \]

where

- \( P_a \) = pressure of \( O_2 \) in the vacuum line
- \( V_a \) = volume of vacuum line
- \( V_b \) = volume of cell above the solution
- \( P_b \) = pressure of \( O_2 \) above the solution
Figure 5:
(a) Modified hypodermic syringe;
(b) Degassing bulb
The concentration of oxygen was calculated assuming Henry's Law. The calculation involved using the equation

\[ y = \beta x \]

where \( y \) = volume of \( \text{O}_2 \) absorbed at \( 25^\circ \text{C} \) and 1 atm pressure 
\( \beta \) = a constant, the bensen absorption coefficient
\( x \) = absolute pressure in atmospheres

The constant \( \beta \) was calculated using the data of Seidell\(^{41} \). He determined the solubility of oxygen in basic solutions in terms of \( l \) which is equal to the volume of gas absorbed at any pressure and temperature divided by the volume of absorbing liquid. The relationship between \( l \) and \( \beta \) is given by the equation

\[ l = (1 + 0.00367t)\beta \]

where \( t \) is the temperature in degrees centigrade.

**ANALYSIS**

Hydroxide ion concentration was determined with 0.100 N hydrochloric acid. The endpoint was determined using phenolphthalein indicator. Accuracy was \( \pm 2.5\% \).

Oxygen concentrations were determined by three different methods. The first method was the calculation described in the previous section assuming equilibrium between the dissolved gas and the gas above the solution at the specified temperature and pressure.

The second method was a direct determination of the oxygen concentration for each individual solution. The apparatus is shown in figure 7. A known volume of solution was introduced into an evacuated bulb (A). The oxygen was removed by pumping with a toeppler pump (C). Water vapor was removed by passing the gas through traps (B) cooled with a dry ice-acetone mixture. The oxygen was then pushed into a gas buret (D) with mercury. Measurements of pressure, volume and temperature allowed calculation of the number of moles of gas using the ideal gas law, \( PV = nRT \), where \( n \) is the number of moles and \( R \) is the ideal gas constant.

The third method was a modification of the second method. The gas buret was replaced by a gas chromatograph analysis system. Samples of known volume were degassed using a modified toeppler pump as shown in figure 8. All gases removed from solution were pushed into a portion of the sample loop (C) with mercury. Helium flowed through part of the sample loop at all times. When a sample of gas was ready for analysis, the stopcocks were turned to allow the helium carrier gas to convey the sample to the gas chromatograph. The chromatograph used was an Aerograph model A-350-B with thermoconductivity detectors. The gases were separated on a Porapak Q, mesh 150-200, column cooled to dry ice temperature, \(-78^\circ \text{C}\). The column would separate nitrogen and oxygen. The water would remain on the column until warmed to room temperature. With a helium flow of about 14 cc/min, nitrogen retention time was 8 minutes and the oxygen retention time was 10 minutes. Figure 9 shows a typical chromatogram.
Figure 7: Apparatus for the direct determination of the oxygen concentration using a gas buret.
Figure 8: Apparatus for the direct determination of the oxygen concentration using a sample loop injection system into a gas chromatograph.
Figure 9: Chromatogram showing the separation of nitrogen and oxygen on a Porapak Q, mesh 150-200, column cooled to -78°C. Helium flow was 14 cc/min. Chart speed was 2 min/inch. Actual size.
Calibration to determine the oxygen concentration from the area under the oxygen peak was carried out each day. This was found to be necessary because small differences in the flow rate of the cooled gas over the detectors significantly affected the response of the detectors. A known volume and pressure of pure oxygen was pumped into the sample loop for the calibration. The area of the oxygen peak was measured by tracing the peak with a planimeter several times. Oxygen concentrations determined in this manner had an uncertainty of ± 5%.

Two methods were used to determine hydrogen peroxide concentrations. At first the peroxide solutions were titrated with ceric sulfate solutions. The endpoint was determined using the yellow color of the Ce(SO₄)₂ solutions. The endpoint was often difficult to see and therefore a second method was used. The peroxide solution which was in the concentration range of 10⁻³ M was diluted to the concentration range of 10⁻⁵ M. To 10 ml of the latter solution, 1 ml of ferrous sulfate solution (0.01 M in 2 N H₂SO₄) and 10 ml of 10 M potassium thiocyanate solution were added. The peroxide would oxidize the ferrous ion to ferric ion. The ferric ion would complex with thiocyanate to form a solution which absorbs around 480 nm. The optical density of the complex was measured and used to calculate the amount of ferric ion formed and hence the amount of peroxide in the original solution. A similar procedure was followed with solutions of known peroxide concentration to calibrate the system.

IRRADIATION PROCEDURE AND ANALYSIS OF DATA

Solution in the cell was seldom pulsed more than once, never more than twice, to avoid build up of reaction products in the cell. When doing competition studies, the maximum optical density of O₃⁻ at 430 nm was the quantity of importance for the calculation. Therefore, the time range of the oscilloscope sweep was selected to insure a good horizontal line. Figure 10 (a) shows such a picture.

Figure 10 (b) shows a decay curve of ozonide ion at 430 nm.

The photograph consists of a base line which corresponds to 0% transmitted light, a 100% transmission line (I₀) and a line for the decay curve of the species absorbing light at the given wavelength. The I₀ line is the complete light transmission reference line for the light beam. Automatic firing of the electron pulse occurred 5 msec after the start of the I₀ trace and was synchronized with the start of the final trace. The result is a display of the time variation of the transmittance (Iₖ) of the solution over the duration of the final trace.

The optical density, Dₜ, at time t and wavelength λ, was calculated using the definition of absorbance

\[ \log(I₀/I₉) = Dₜ^λ \]

The optical density is related to the concentration of the absorbing species if the Beer-Lambert Law is assumed.

\[ Dₜ^λ = ε^λCₜ \]

where

- \( ε^λ \) = extinction coefficient at wavelength
- \( l \) = path length of the light beam
- \( Cₜ \) = concentration of species at time t
Figure 10: Oscilloscope traces of the transmission at 430 nm of the ozonide ion as a function of time; (a) sweep time = 2 msec/division, (b) sweep time = 5 μsec/division.
Often the amount of absorption by the solution was small. For greater accuracy the second channel of the dual-beam oscilloscope was used to expand the signals by 2.5 or 5 times. Both channels required the same calibration for accurate expansion. It was possible to calibrate both channels to within ± 3% of one another.

In the systems studied in this investigation the decay of ozonide ion was always pseudo first order in ozonide ion concentration. The pulse intensity used was always low enough so that no second order type reactions were important. The kinetic equation is

\[
\frac{d[O_3^-]}{dt} = k[O_3^-]
\]

where

\[ [O_3^-] = \text{the concentration of ozonide ion at time } t \]

\[ k = \text{rate constant which may be a complex function of concentrations of solutes and constants} \]

Integration of equation VI from time 0 to time \( t \) gives

\[
\ln[O_3^-]_t - \ln[O_3^-]_0 = -kt
\]

Substituting the optical density of \( O_3^- \) for the concentration as given in equation V gives

\[
\ln D_t - \ln D_0 = -kt
\]

A plot of log \( D_t \) versus time gives a straight line with

slope = \(-k/2.303\)
RESULTS AND DISCUSSION

OZONIDE ION ABSORPTION

Introduction of nitrous oxide into the basic solution converts the solvated electron to the oxide ion.

\[ \text{N}_2\text{O} + e^-_{\text{aq}} \rightarrow \text{N}_2 + 0^- \]  \hspace{1cm} (7)

The rate constant published for reaction (7) is \(8.9 \times 10^9\) M\(^{-1}\) sec\(^{-1}\) \(^{8,43}\). If the intermediate, \(\text{N}_2\text{O}^-\), is formed, its lifetime is either very short or else it must behave kinetically like \(0^-\) \(^{4,16,19,44,45}\). Therefore, the use of nitrous oxide essentially converts the system to a one radical system and the yield of ozonide ion should approximately double in solutions containing \(\text{N}_2\text{O}\) as compared to solutions without \(\text{N}_2\text{O}\). The following calculation illustrates this statement.

The spectrum of ozonide ion was measured using a solution at pH 13.5 and having a ratio of \([\text{N}_2\text{O}] / [\text{O}_2]\) of 20. Therefore, the ratio of the rate of reaction (7) to the rate of reaction (4), where \(k_4 = 1.9 \times 10^{10}\) M\(^{-1}\) sec\(^{-1}\) \(^{8,9}\), was \(k_0[\text{N}_2\text{O}] / k_4[\text{O}_2] = 9.2\). The pulse intensity was


\(\text{(44) P. Neta and L. M. Dorfman, Radiation Chemistry I, A. C. S. Advances in Chemistry, 31, 222 (1968).}\)

\(\text{(45) G. Czapski, Private communication.}\)
sufficiently low to make the rate of
\[ O^- + O^- \rightarrow O_2 \]  \hspace{1cm} (14)

negligible compared to the rate of
\[ O^- + O_2 \rightarrow O_3^- \]  \hspace{1cm} (6)

The amount of hydrogen atom converted to \( O_3^- \) via
\[ H + OH^- \rightarrow e_{aq}^- \]  \hspace{1cm} (3)

followed by reactions (7) and (6) rather than to \( O_2^- \) via
\[ H + O_2 \rightarrow HO_2 \]  \hspace{1cm} (5)
\[ HO_2 + OH^- \rightarrow O_2^- + H_2O \]  \hspace{1cm} (15)

can also be calculated. Since \( k_3 = 1.8 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1} \) and \( k_5 = 2 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1} \), the ratio \( k_3[OH^-]/k_5[O_2] \) was equal to 2. Using
\[ G_{O^-} \rightarrow e_{aq}^- = 3.4 \text{ molecules/100 ev} \]
\[ G_{H + e_{aq}^-} = 3.85 \text{ molecules/100 ev} \]
\[ G_{H^4} = 0.6 \text{ molecules/100 ev at pH 13.5} \]

the yield of \( O_3^- \) in \( N_2O \) solutions is given by the expression

\[ G_{O_3^-} = G_{O^-} + G_{e_{aq}^-} + H\left(\frac{k_7[N_2O]}{k_7[N_2O] + k_4[O_2]}\right) - G_H\left(\frac{k_5[O_2]}{k_3[OH^-] + k_5[O_2]}\right) \times \]

\[ = 3.4 + 3.85 \left(\frac{9.2}{10.2}\right) - 0.6 \left(\frac{1}{3}\right) \]

\[ = 6.7 \text{ molecules/100 ev}. \]

The ratio of \( G_{O_3^-} \) in \( N_2O-O_2 \) solutions to \( G_{O_3^-} \) in \( O_2 \) solutions is

\[ \frac{6.7}{3.4} = 1.97. \]

Optical density measurements of the maximum ozonide ion absorption at 430 nm gave the values of 0.181 for the optical density in \( N_2O-O_2 \) solution and 0.0924 for the optical density in \( O_2 \) solution.

Each value is an average of 6-8 pictures. The measured ratio of

optical densities is 1.96 in excellent agreement with the calculated value of 1.97.

Figure 11 shows the absorption spectrum in N₂O-O₂ solutions as compared to the spectrum in O₂ solutions.

The nature of the electronic transition can be qualitatively discussed by comparison with an isoelectronic molecule such as ClO₂ which has 19 valence electrons. Ozonide ion also has 19 valence electrons. The spectrum of ClO₂ in the gas phase has been studied and reliable assignments have been made for the transitions⁴⁷,⁴⁸,⁴⁹. ClO₂ shows an absorption from 522.5 to 260 nm with a maximum at approximately 330 nm⁴⁷. The extinction coefficient at 330 nm is 2000 M⁻¹ cm⁻¹⁴⁷. Walsh⁴⁸ has discussed the nature of the transition. Using a Walsh diagram⁴⁹ for molecule type AB₂ as shown in figure 12, the relative order of the orbital energies as well as the change in the relative order as the BAB angle changes from 90° to 180° is shown. The symbolism is defined as follows. The molecule lies in the zy plane with the z axis bisecting the BAB angle. Rotation by 180° around the z axis is represented by C₂(z) and reflection through the xz plane is represented by the symbol σᵥ(y). A + sign indicates that the orbital does not change sign after the operation has been performed and a -

Figure 11: Spectrum of the ozonide ion; ○ Spectrum in oxygenated alkaline solutions from Czapski and Dorfman; ● Spectrum in oxygenated alkaline solutions with N₂O added.
sign indicates that the orbital does change sign. The four types of orbitals are represented by the following:

\[
\begin{align*}
C_2(z) & \quad \sigma_v(y) \\
{a_1} & \quad + \\
{a_2} & \quad + \\
{b_1} & \quad - \\
{b_2} & \quad - \\
\end{align*}
\]

Finally, a prime indicates the orbital is symmetric with respect to reflection through the plane of the molecule. A double prime indicates that it is antisymmetric after this operation.

The transition which gives rise to absorption of ClO\(_2\) in the visible and near UV is

\[
\ldots (a_2'')(b_2')^2(b_1'')^2(a_2'')(b_2')(a_1'')^2 (b_1'').
\]

Figure 13 shows the atomic \(p_x\) orbitals of the ClO\(_2\) molecule which are used to make up the \(a_2''\) and \(b_1''\) orbitals. Since ClO\(_2\) is isoelectronic with O\(_3^-\) and an absorption of O\(_3^-\) is observed in the same spectral region as ClO\(_2\) absorption, the transition may involve the same orbitals for the O\(_3^-\) transition.

Referring to the Walsh diagram, the energy difference between the orbitals \(a_2''\) and \(b_1''\) decreases as the BAB angle decreases. The OC\(_3\) angle is approximately 116.5° \(^{48}\) while the 000 angle in ozonide ion is 100° \(^{22}\) determined by x-ray studies on solid KO\(_3\). The angle may change in solution, however. The maximum, however, of the absorption spectrum would be expected to be more toward the visible in the case of O\(_3^-\) as compared to ClO\(_2\). Unfortunately, this kind of argument is only qualitative.
Figure 12: Walsh diagram for AB$_2$ molecules, from Walsh$^{48}$ and Herzberg$^{49}$. 
Figure 13: Schematic representation of the shapes of the molecular orbitals in terms of the linear combinations of the atomic $p_x$ orbitals involved in the proposed electronic transition observed for the ozonide ion.
The molar extinction coefficient of ozonide ion at 430 nm was determined by measuring the optical density in oxygen saturated solutions. The Fricke dosimeter described in the experimental section was used for dosimetry measurements. The maximum optical density of $O_3^-$ at 430 nm and the ferric ion formation curves were measured for 0.4, 0.8, and 1.6 μsec pulses. Figure 14 shows a typical ferric ion formation curve at 304 nm. A typical oscilloscope trace used to calculate the optical density of $O_3^-$ at 430 nm is shown in figure 10 (b).

The extinction coefficient of ozonide ion was then calculated from the expression

$$
\epsilon_{O_3^-} = \frac{G_{Fe^{3+}} \epsilon_{Fe^{3+}} D_{O_3^-}^0}{G_{O^-} D_{Fe^{3+}}^0}
$$

where the $\epsilon$'s represent the extinction coefficients, $D$'s represent the maximum optical density and the $G$ values are $G_{Fe^{3+}}^{33,40} = 15.6$ molecules/100 ev and $G_{O^-}^{46} = 3.3$ molecules/100 ev at pH 13.1. The results are shown in Table I.

**TABLE I: Extinction Coefficient of $O_3^-$ at 430 nm**

<table>
<thead>
<tr>
<th>Pulse (sec)</th>
<th>$\epsilon_{O_3^-} 430$ (M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>1980</td>
</tr>
<tr>
<td>0.8</td>
<td>1850</td>
</tr>
<tr>
<td>0.4</td>
<td>1700</td>
</tr>
<tr>
<td>0.4</td>
<td>2030</td>
</tr>
</tbody>
</table>
Figure 14: Oscilloscope trace of the formation of ferric ion at 304 nm in the irradiation of the modified Fricke dosimeter. Sweep time = 5 seconds per division.
The average value is \(1900 \pm 120 \text{ M}^{-1} \text{ cm}^{-1}\) which agrees within experimental error with \(2000 \pm 40 \text{ M}^{-1} \text{ cm}^{-1}\) from Adams et al.\(^{16}\) Uncertainties in the \(G\) values, however, are not included in the error limit.

**REACTIVITY OF THE OXIDE ION**

There have been many studies of the reactions of the OH radical\(^{2,44,50}\). Only a few \(O^-\) reactions have been studied, however. Most of these systems will be discussed in the following text. To compare the reactivity of the two forms of the oxidizing radical, more information must be obtained on the reactivity of the oxide ion.

It was decided to study the reactions of \(O^-\) with benzoate ion (an addition reaction to the aromatic ring), methanol and ethanol (H abstraction reactions). The rate constants for the reactions of OH with these three solutes\(^{44}\) as well as the rate constant for the reaction of OH with benzoic acid\(^{51}\) have been determined recently in this laboratory. A basis for comparison, therefore, was already established.

The reaction of \(O^-\) with benzoate ion

The rate constants for the reactions

\[
\text{OH} + \text{C}_6\text{H}_5\text{COOH} \rightarrow (\text{OH})\text{C}_6\text{H}_5\text{COOH} \quad (16)
\]

\[
\text{OH} + \text{C}_6\text{H}_5\text{COO}^- \rightarrow (\text{OH})\text{C}_6\text{H}_5\text{COO}^- \quad (17)
\]

are \(k_{16} = 4.3 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}\)\(^{51}\) and \(k_{17} = 6.0 \pm .7 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}\)\(^{44}\), were determined by direct observation of the formation of the product.

---


of the reactions around 330 nm. Therefore, the first attempt to study the rate of the reaction

$$O^- + \phi COO^- \rightarrow (O^-)C_6H_5COO^- \quad (18)$$

was to study the rate of formation of species absorbing in this spectral region. Preliminary studies showed the formation was pseudo first order in $O^-$ concentration. The pseudo first order rate constant did not depend on the benzoate ion concentration in any simple way. It was, therefore, decided to try to obtain the rate constant for reaction (18) by competition with reaction (6)

$$O^- + O_2 \rightarrow O_3^- \quad (6)$$

The amount of ozonide ion formed in such competition studies should be reduced if other solutes are added with which $O^-$ can react at comparable rates. The competition equation, derived in Appendix II, is

$$\frac{D^o}{D} = 1 + \frac{k_{18}[O^-][\phi COO^-]}{k_8[O^-][O_2]}$$

$$= 1 + \frac{k_{18}[\phi COO^-]}{k_8[O_2]} \quad \text{(XI)}$$

where

- $D^o$ = maximum optical density at 430 nm when only $O_2$ is present
- $D$ = maximum optical density when both $O_2$ and $\phi COO^-$ are present in solution

For this equation to be valid, no species in this system other than $O_3^-$ can absorb at 430 nm. When the concentration of benzoate ion is large compared to the concentration of oxygen, the solvated electron will react with $\phi COO^-$

$$e_{aq}^- + \phi COO^- \rightarrow (\phi COO^-)^- \quad (19)$$
to form the adduct which absorbs with a maximum at 440 nm. The adduct reacts rapidly with oxygen, however, to form a species which no longer absorbs in this region. Within 2 to 4 μsec after the pulse it has completely disappeared. The absorption at 430 nm that remains is the ozonide ion absorption. Therefore, no precautions were taken to remove the solvated electron in order to avoid reaction (19).

Figure 15 shows a plot of $D^0/D$ against $[\phi COO^-]/[O_2]$. Competition occurs, but there is a large decrease in slope as the pH increases. The competition data fits, instead, the expression

$$D^0/D = 1 + k([\phi COO^-]/[O_2] \times [OH^-])$$

where $k$ may represent a combination of constants. Figure 16 is a plot of $D^0/D$ against $[\phi COO^-]/[O_2] \times [OH^-]$. Although there is scatter in the data, most points lie within experimental error of the average slope. Experimental error is approximately 10% for the concentration ratio and 5% in the optical density ratio. Each calculated optical density is an average of 3-4 pulses. Table II gives the experimental data which is used to determine the points in Figure 16.

Very large ratios of $[\phi COO^-]/[O_2]$ are needed for benzoate ion to compete with oxygen for the oxidizing species. The known rate constant for the reaction of OH with $\phi COO^-$ is high, $6.0 \times 10^8$ M$^{-1}$ sec$^{-1}$.

These two facts coupled with the observed hydroxide ion concentration dependence suggest that the competition reactions are

$$O^- + O_2 \longrightarrow O_3^- \quad (6)$$
$$OH + \phi COO^- \longrightarrow (OH)\phi COO^- \quad (17)$$

Figure 15: The ratio of the optical densities at 430 nm in solutions with and without benzoate ion as a function of the concentrations of benzoate ion and oxygen; ○ $[\text{OH}^-] = 0.11$ M and 0.3 µsec pulse; □ $[\text{OH}^-] = 0.11$ M and 0.5 µsec pulse; △ $[\text{OH}^-] = 0.5$ M; ▲ $[\text{OH}^-] = 1.0$ M.
Figure 16: Competition in oxygenated benzoate ion solutions at pH>13. Dependence of the ratio of the optical density at 430 nm in solutions containing no benzoate ion to the optical density at 430 nm in solutions containing benzoate ion as a function of $[$COO$^-$/O$_2$/OH$^-]$. 
<table>
<thead>
<tr>
<th>$[O_2]$ ( \times 10^4 )</th>
<th>([\text{[COO}^-]) ( \times 10^3 )</th>
<th>([\text{OH}^-]) ( \times 10^4 )</th>
<th>(D) at 430 nm</th>
<th>(D^0) at 430 nm</th>
<th>([\text{[COO}^-]) ( \times [\text{OH}^-] \times [O_2])</th>
<th>(D^0)</th>
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<td>6.3</td>
<td>49.6</td>
<td>1.01</td>
<td>.0803</td>
<td>.188</td>
<td>78.2</td>
<td>2.34</td>
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<td>1.04</td>
<td>.122</td>
<td></td>
<td>31.7</td>
<td>1.54</td>
</tr>
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<td>.149</td>
<td></td>
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<td>1.26</td>
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<td>.0542</td>
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The amount of OH in solution is determined by the equilibrium between OH and $\text{O}^-$

$$\text{O}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH} + \text{OH}^- \quad (20)$$

The equilibrium constant

$$K_{20} = \frac{[\text{OH}][\text{OH}^-]}{[\text{O}^-]} \quad \text{XIV}$$

is the hydrolysis constant of $\text{O}^-$ and is equal to $K_w/K_{\text{OH}}$ where $K_w$ is the equilibrium constant for the dissociation of water and $K_{\text{OH}}$ is the dissociation constant for the weak acid, OH.

$$\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{O}^- + \text{H}_3\text{O}^+ \quad (21)$$

$$K_{\text{OH}} = \frac{[\text{O}^-][\text{H}_3\text{O}^+]}{[\text{OH}]} \quad \text{XV}$$

The competition equation is

$$\frac{D^0}{D} = 1 + \frac{k_{17}[\text{OH}][\text{O}^-][\text{COO}^-]}{k_{6}[\text{O}^-][\text{O}_2]}$$

$$= 1 + \frac{k_{17} K_{20}[\text{O}^-][\text{O}^-][\text{COO}^-]}{k_{6}[\text{O}^-][\text{O}_2][\text{OH}^-]}$$

$$= 1 + \frac{k_{17} K_{20}[\text{COO}^-]}{k_{6}[\text{O}_2][\text{OH}^-]} \quad \text{XVI}$$

A plot of $D^0/D$ against $[\text{COO}^-]/[\text{O}_2] \times [\text{OH}^-]$ should, therefore, be a straight line with a slope equal to $k_{17} K_{20}/k_6$ and an intercept of 1. Using the published values for $k_{17} = 6.0 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, and $k_6 = 2.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ and the slope $= 0.0146 \pm 0.0015$ from figure 16.
will be $6.10 \times 10^{-3}$ M. Since $K_W = 1 \times 10^{-14}$ at $25^\circ$ C, $K_{OH}$ will be \(1.64 \times 10^{-12}\) at $25^\circ$ C and $pK_{OH}$ will be $11.8 \pm .2$. This value is in excellent agreement with the published values of $11.9 \pm 2.5$ and $11.8 \pm .2$. This method is slightly different, however. The earlier investigators measured the change in apparent rate constants for the reaction between the oxidizing radical and ferrocyanate$^4$ and carbonate$^5$ ions respectively by direct observation of the products of these reactions.

Two assumptions must be correct for this explanation of the competition to be valid. First the attainment and maintenance of the equilibrium between $O^-$ and $OH$ must be rapid in comparison to the reactions removing these species. Several rate constant values for reaction (2), the reverse reaction in the equilibrium (20),

\[
OH + OH^- \longrightarrow O^- + H_2O
\]  

have been published including $3.6 \times 10^8$ M$^{-1}$ sec$^{-1}$ $^{54}$, $4 \times 10^9$ M$^{-1}$ sec$^{-1}$ $^{55}$, $3 \times 10^9$ M$^{-1}$ sec$^{-1}$ $^{56}$ and $10^{10}$ M$^{-1}$ sec$^{-1}$ $^{45}$. The first three values have been determined experimentally by competition methods. The 4th value is a suggested value for the reaction. Using the value of

---


$3 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ since it falls in the middle of these numerous values, the half life of reaction (2) would be $2 \times 10^{-9}$ sec. The calculation is made using the definition of the half life for a first order reaction

$$\tau_{1/2} = \frac{0.693}{k} \quad \text{XVII}$$

where

$$\tau_{1/2} = \text{half life}$$

$$k = \text{first order rate constant}$$

The rate constant for the forward reaction in (20), $k_{20}$, can be calculated from

$$k_{20} = \frac{k_{20}}{K_{20}}$$

The rate constant $k_{20}$ is $3.2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$. Since the concentration of water is a constant, 55.5 M, the half life for the forward reaction is $3 \times 10^{-8}$ sec. The half life for reaction (17) at the highest value of the $[\phi\text{COO}^-]$ at pH 13, $1.08 \times 10^{-2}$ M, will be $1 \times 10^{-8}$ sec; 33% of the value for the forward reaction (20). The point fits within experimental error with all the others. Therefore, either the calculated value of $k_{20}$ is too low or else other errors cancel out the effect. For the rest of the data, however, the difference in the half lives is much greater so that the equilibrium assumption is valid as long as $k_2$ is not lower than $3 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$.

The second assumption is that other $O^-$ (or OH) reactions can be neglected. For example, at the highest pH and benzoate ion concentrations used, $[\text{OH}^-] = 1.01 \text{ M}$, $[\phi\text{COO}^-] = 4.96 \times 10^{-2}$ M, $[\text{O}_2] = 6.3 \times 10^{-4}$ M, the value of the ratio of the optical densities, $D^0/D$, is 10% higher than the corresponding point which lies on the slope of the plot shown in Figure 16. If this deviation were due to the reaction of $O^-$ with $\phi\text{COO}^-$, reaction (18), the rate constant for reaction (18) would
be $6.0 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$. This value for $k_{16}$ is an upper limit for the rate constant. It should be noted, however, that the 10\% deviation is within experimental error. For other values of benzoate ion concentration and pH reaction (18) is negligible.

Other reactions of $O^-$ or OH which must be avoided are

\begin{align*}
O^- + O^- & \rightarrow O_2^- \quad (14) \\
OH + O^- & \rightarrow HO_2^- \quad (23) \\
OH + O_2^- & \rightarrow OH^- + O_2 \quad (24) \\
O^- + O_2^- & \rightarrow 2OH^- + O_2 \quad (25)
\end{align*}

Initial oxide ion concentration was always less than $10^5 \text{ M}$. An upper limit on the value of $2k_{14}$ is $1.8 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. Therefore, in competition with reaction (6)

\begin{equation}
O^- + O_2 \rightarrow O_3^- \quad (6)
\end{equation}

for the lowest $[O_2]$ the maximum loss due to reaction (14) is $\%$. Most conditions made this ratio much smaller.

The rate constant for reaction (23) is higher, $k_{23} \leq 2.6 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, but the initial concentration of OH is significantly lower (at most, 5\% of $[O^-]$), making the rate of this reaction negligible. The same can be said for the reaction (24) even though the rate constant is high, $k_{24} = 1.0 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. The rate constant for reaction (25) is not known. It is reasonable, to expect $k_{25}$ to be lower than $k_{24}$ by at least a factor of ten. Other electron transfer reactions to $O^-$ are considerably slower than the comparable reaction with OH. For

\begin{flushright}
\end{flushright}
example, both the electron transfer reactions of $O^-$ with ferrocyanate and with carbonate ions have rate constants less than $10^7 \text{ M}^{-1} \text{ sec}^{-1}$ \textsuperscript{4,5}. The comparable OH reactions have rate constants at least 1000 and 50 times greater, respectively.

In conclusion, the two assumptions that the equilibrium between OH and $O^-$ is maintained and that reactions of the oxidizing radical other than with oxygen or benzoate ion can be neglected are valid assumptions.

The results of this experiment were the determination of the $pK = 11.8 \pm .2$ of the hydroxyl radical and the discovery that $O^-$ does not react competitively with benzoate ion as compared to the reaction rates of $O^-$ with $O_2$ and OH with benzoate ion even up to pH 14.

The reactions of $O^-$ with methanol and ethanol

The rate constants for the reactions

$$O^- + C_2H_5OH \rightarrow OH^- + \cdot C_2H_4OH \quad (28)$$

$$O^- + CH_3OH \rightarrow OH^- + \cdot CH_2OH \quad (29)$$

were determined relative to the rate constant for reaction (6). Unlike the benzoate ion case, the rates of these reactions are not negligible. Furthermore, the rate constants for the reactions

$$OH + C_2H_5OH \rightarrow H_2O + \cdot C_2H_4OH \quad (30)$$

$$OH + CH_3OH \rightarrow H_2O + \cdot CH_2OH \quad (31)$$

are known, $k_{30} = 1.83 x 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ \textsuperscript{44} and $k_{31} = 8.4 x 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ \textsuperscript{44}. Reactions (30) and (31) need not be neglected even though they account for only a few percent of the competition. The actual competition
equation becomes

$$\frac{D^0}{D} = 1 + \frac{k_{28}[O^-][EtOH] + k_{30}[OH][EtOH]}{k_e[O^-][O_2]}$$

$$= 1 + \frac{(k_{28} + k_{30}K_{20}([OH^-])[EtOH])}{k_e[O_2]}$$

where $D^0 = \text{maximum optical density at 430 nm with only } O_2 \text{ present in solution}$

$D = \text{maximum optical density at 430 nm with } O_2 \text{ and } EtOH \text{ present in solution}$

$K_{20} = \text{hydrolysis constant for the equilibrium (20) between } O^- \text{ and } OH^-$

An analogous expression can be written for the methanol solutions where methanol concentration is substituted for the ethanol concentration.

Since hydroxide ion concentrations changed from solution to solution, the ratio of $k_{28}$ to $k_e$ was calculated by rearranging equation XIX to

$$\frac{k_{28}}{k_e} = \frac{[O_2]}{[EtOH]} \frac{k_{30}K_{20}}{k_e[OH^-]}$$

using the $k_{30}$ given above, $k_e = 2.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ and $K_{20} = 6.10 \times 10^{-3} \text{ M}$ at 25° C. For the methanol solutions the equation is

$$\frac{k_{28}}{k_e} = \frac{[O_2]}{[MeOH]} \frac{k_{31}K_{20}}{k_e[OH^-]}$$

Table III gives the results for ethanol and Table IV gives the results for methanol. The average value of the ratio $k_{28}/k_e$ is 0.337 ± 0.028 and of the ratio $k_{28}/k_e$ is 0.209 ± 0.014. Adams et al.\textsuperscript{56} did a competition experiment for ethanol without correcting for reaction (30) and determined a ratio of 0.35. Using $k_e = 2.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ and $K_{28} = 8.4 \pm 20\% \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$, $k_{28} = 5.2 \pm 20\% \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$. 
### TABLE III

**OXYGEN AND ETHANOL COMPETITION FOR OXIDE RADICAL ION**

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Average $k_{28}/k_6 = .337 \pm .028$
TABLE IV
OXYGEN AND METHANOL COMPETITION FOR OXIDE RADICAL ION

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<th>[O₂] (10^4) M</th>
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Average \(k_{29}/k_6 = .209 \pm .014\)
The error limits include the scatter in the data due to uncertainty in concentration and optical density measurements as well as uncertainty in the rate constants used for the calculation. The statements about other reactions of O\(^{-}\) discussed in the benzoate ion competition experiments also apply to the alcohol competition experiments. Such reactions are negligible compared to the ones of interest. Furthermore, no other species except O\(_3\)^\(-\) absorbed light at 430 nm. When enough alcohol was added to a solution to scavenge all the O\(^{-}\), no absorption was observed at 430 nm.

**DECAY OF THE OZONIDE ION**

It has been briefly mentioned in the Introduction that the decay kinetics of ozonide ion in oxygenated water at pH > 13 are first order for low initial ozonide ion concentration and mixed first and second order for higher initial [O\(_3\)^\(-\)]. That is, there is increasing on second order contribution as initial [O\(_3\)^\(-\)] increases. Oxygen has a stabilizing effect on the decay. Figure 17 shows the dependence of the ozonide half life for the first order decay on the oxygen concentrations. Dots represent Czapski's\(^{19}\) data. Open circles are values obtained in this study using oxygen pressures greater than 1 atmosphere above the solution. Uncertainty limits are 20% and account for the scatter in the experimental data. Two effects contribute to the uncertainty. The first is the temperature variation in the accelerator room, which as will be seen has a significant effect since at least one reaction in the decay scheme has a large activation energy. The second consideration is that oxygen concentration in this early work was determined by
Figure 17: Dependence of the half life of the first order decay of ozonide ion at 430 nm in oxygenated alkaline solutions at low pulse intensity on the concentration of oxygen; • from Czapski, O from this investigation.
assuming equilibrium with the oxygen above the solution (see Experimental section VII). If equilibrium is not reached, the calculated \([O_2]\) will be greater than the actual \([O_2]\). This source of error would cause values to fall below the slope of the plot in figure 17.

**First order decay in the presence of added solutes**

The decay of ozonide ion was studied in solutions with added benzoate ion, ethanol, methanol and hydrogen peroxide. The first three solutes were chosen because their rates of reaction with OH had just been studied. Hydrogen peroxide is of particular interest because it is produced in the irradiation of water, \(46\text{H}_2\text{O}_2 = 0.6 \text{ molecules/100 ev}\) and is present, albeit in low concentrations in all irradiated solutions.

Our early work in the investigation of the decay of ozonide ion in solutions with added hydrogen peroxide\(^{18}\) was interpreted as a direct reaction between ozonide ion and hydrogen peroxide,

\[
\text{O}_3^- + \text{HO}_2^- \rightarrow \text{products}
\]  

(9)

The same reaction was studied by Czapski\(^{19}\). The published values for \(k_9\) were \(3.9 \pm 1.1 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1} \) \(^{18}\) and \(1.6 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1} \) \(^{19}\).

Subsequent to these investigations, Behar and Czapski,\(^ {21}\) in work concurrent with our own, studied the hydrogen peroxide system in detail using flash photolysis to generate \(\text{O}_3^-\). They showed that the decay depended not only on the peroxide concentration but also on the oxygen concentration. Their results were consistent with the following mechanism.

\[
\text{O}^- + \text{O}_2 \rightarrow \text{O}_3^- 
\]  

(6)

\[
\text{O}_3^- \rightarrow \text{O}^- + \text{O}_2
\]  

(10)

\[
\text{O}^- + \text{H}_2\text{O}_2 \rightarrow \text{OH}^- + \text{HO}_2
\]  

(11)
The main features of the mechanism are the dissociation of ozonide ion and the reaction of 0\(^-\) with peroxide rather than the reaction of O\(_3\)^- with peroxide. Decomposition of O\(_3\)^- to give O\(_2\)^- and O does not explain the experimental observations. If, for example, the oxygen atom reacted with water, the products would be two hydroxyl radical. A chain reaction would be observed and the amount of O\(_3\)^- would increase until all the oxygen in solution was used. If, however, the oxygen atom reacted with O\(_2\) to produce ozone, no inverse oxygen concentration dependence would be observed for the ozonide ion decay.

Assuming a steady state for the oxide ion, the decay equation becomes

\[
\frac{d[O_3^-]}{dt} = \frac{k_{10}k_{11}[H_2O_2]}{k_6[O_2] + k_{11}[H_2O_2]} \times [O_3^-]
\]

The derivation can be found in Appendix III. A plot of 1/k\(_{\text{obs}}\), where k\(_{\text{obs}}\) is the observed pseudo first order rate constant, against [O\(_2\)]/[H\(_2\)O\(_2\)] should be a straight line. Their results confirmed this relationship. They found a value of k\(_{10}\) = 5 \(\times\) 10\(^3\) sec\(^{-1}\) and a value of k\(_6\)/k\(_{11}\) = 3.5 \(\pm\) 1.5. Heidt\(^{17}\) has also studied the flash photolysis of oxygenated hydrogen peroxide solutions at high pH and determined k\(_{10}\) = 2.8 \(\times\) 10\(^3\) sec\(^{-1}\) and k\(_6\)/k\(_{11}\) = 3.7.

The work on the peroxide solutions is mentioned at this time because the above interpretation was very helpful in explaining the results obtained in the present investigation of the decay of ozonide ion in solutions containing benzoate ion and the alcohols. The decay of ozonide ion in solutions containing hydrogen peroxide will be discussed in more detail following the discussion of the other three
systems. As an aid in following the lengthy and sometimes complicated discussion of the mechanism of the ozonide ion decay, the reader may wish to consult the Appendixes where lists of reactions and equations can be found.

Benzoate ion solutions

The decay of ozonide ion in oxygenated benzoate ion solutions in the pH range 13 to 13.7 was found to depend on the concentrations of the benzoate ion, oxygen and hydroxide ion. The decay was pseudo first order under all conditions. Figure 18 shows the first order fir for one set of data. If the calculated first order rate constants, each an average of several decay curves, are plotted against 

$$\frac{[\cdot COO^-]}{[O_2]} \times [OH^-],$$

a family of parallel straight lines result, as shown in figure 19. The y intercept represents the first order decay constant in solutions containing no benzoate ion. If the intercept value is subtracted from the observed rate constant in benzoate ion solutions, all the data fall approximately on the same straight line.

At higher ratios of benzoate ion to oxygen concentrations the plot of the observed rate constants against $$\frac{[\cdot COO^-]}{[O_2][OH^-]}$$ is no longer linear. Figure 20 illustrates this observation.

It was determined in the competition experiment that $O^-$ does not react competitively with benzoate ion. Instead an equilibrium exists between OH and $O^-$ and OH reacts with the benzoate ion. A mechanism which fits these observations for the decay of ozonide ion in benzoate ion solutions is one analogous to Behar and Czapski's mechanism for the peroxide system. Ozonide ion itself does not react with the added
Figure 18: Optical density at 430 nm as a function of time in oxygenated benzoate ion solutions at pH>13.

- $[\text{COO}^-] = 0$, $[O_2]=2.61 \times 10^{-4}$ M, $[\text{OH}^-]=0.168$ M;
- $[\text{COO}^-]=1.04 \times 10^{-4}$ M, $[O_2]=2.66 \times 10^{-4}$ M, $[\text{OH}^-]=0.177$ M;
- $[\text{COO}^-]=2.08 \times 10^{-4}$ M, $[O_2]=2.55 \times 10^{-4}$ M, $[\text{OH}^-]=0.174$ M;
- $[\text{COO}^-]=3.12 \times 10^{-4}$ M, $[O_2]=2.48 \times 10^{-4}$ M, $[\text{OH}^-]=0.175$ M.
Figure 19: Dependence of the observed first order rate constant for the ozonide ion decay at 430 nm on the concentrations of benzoate ion, oxygen and hydroxide ion. □ [O₂] = 2.5 x 10⁻⁴ M; △ [O₂] = 4.4 x 10⁻⁴ M; ○ [O₂] = 9.4 x 10⁻⁴ M.
Figure 20: Observed first order rate constant for ozonide ion decay at 430 nm as a function of the concentrations of benzoate ion, oxygen and hydroxide ion, at high \([\text{C}_2\text{O}_4^{2-}]/[\text{O}_2]\) ratios.
solute. Rather it is the reaction of the oxidizing radical with the added solute which results in the decay of the ozonide ion.

\[ O^- + O_2 \rightarrow O_3^- \] (6)
\[ O_3^- \rightarrow O^- + O_2 \] (10)
\[ O^- + H_2O \rightarrow OH + OH^- \] (20)
\[ OH + \phi COO^- \rightarrow (OH)\phi C_6H_5COO^- \] (17)
\[ O^- \rightarrow \text{products} \] (32)

When no benzoate ion is present, the first order decay, as has been noted, can be described by the reactions

\[ O^- + O_2 \rightarrow O_3^- \] (6)
\[ O_3^- \rightarrow O^- + O_2 \] (10)
\[ O^- \rightarrow \text{products} \] (32)

Reaction (32) represents reactions of a type as yet unknown and may include reactions with impurities. The impurity reactions, however, must be pseudo first order in oxide ion concentration and are reproducible within approximately 20% from solution to solution.

Assuming a steady state for the oxide radical ion concentration (and, therefore, for the hydroxyl radical concentration) the rate of decay of ozonide ion is

\[ \frac{d[O_3^-]}{dt} = \frac{k_{10}k_{32} + k_{10}k_{17}K_{20}[\phi\text{COO}^-]/[OH^-]}{k_e[O_2] + k_{32} + k_{17}K_{20}[\phi\text{COO}^-]/[OH^-]} \times [O_3^-] \] XXIII

The derivation is found in Appendix III.

The conditions in most of the experiments were such that the ratio \( k_e[O_2]/k_{17}K_{20}[\phi\text{COO}^-]/[OH^-] \) was greater than 30 and \( k_e[O_2]/k_{32} \) was greater than 20. If the second and third terms in the denominator of XXIII are neglected the expression for the observed decay constant
in the benzoate ion solutions reduces to

\[ k_{\text{obs}} = \frac{k_{10}k_{32} + k_{10}k_{17}K_{20}[\phi\text{COO}^-]/[\text{OH}^-]}{k_6[O_2]} \quad \text{XXIV} \]

The first order decay constant in solutions containing no benzoate ion is given by the expression

\[ k_{\text{obs}}' = \frac{k_{10}k_{32}}{k_6[O_2] + k_{32}} \approx \frac{k_{10}k_{32}}{k_6[O_2]} \quad \text{XXV} \]

A plot of the \( k_{\text{obs}} \) in benzoate ion solutions against \([\phi\text{COO}^-]/[\text{OH}^-][O_2]\) would be linear. At higher benzoate ion concentrations, however, equation XXIV would no longer be valid and such a plot would deviate from linearity as shown in figure 20. All the experimental observations are explained by this mechanism.

It is possible, however, to determine all the terms in equation XXIII except \( k_{10} \) using the experimentally determined decay constants and the published values of \( k_6 = 2.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1} \) and \( k_{17} = 6.0 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1} \). The value of \( K_{20} = 6.10 \times 10^3 \text{ sec}^{-1} \) was determined in the benzoate ion-oxygen competition experiment. Table V shows the results of the calculations. The rate constant for reaction (10) is equal to \((5.3 \pm .3) \times 10^3 \text{ sec}^{-1}\). This value can be compared with Behar and Czapski's value of \( 5 \times 10^3 \text{ sec}^{-1} \) and Heidt's value of \( 2.8 \times 10^3 \text{ sec}^{-1} \).

Decay of ozonide ion in ethanol solutions

The decay kinetics of the ozonide ion in oxygenated ethanol solutions is also pseudo first order. Some decay curves are shown in Figure 21. A plot of the observed rate constants against the ratio
### TABLE V

**DECAY OF OZONIDE ION IN OXYGENATED BENZOATE ION SOLUTIONS**

<table>
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<tr>
<th>$[O_2]$ $M \times 10^4$</th>
<th>$[\text{COO}^-]$ $M \times 10^4$</th>
<th>$[\text{OH}^-]$ $M$</th>
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<th>$k_{10}$ $x 10^{-3}$ sec</th>
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Average $k_{10} = (3.3 \pm .3) \times 10^3$ sec$^{-1}$
Figure 21: Optical density at 430 nm as a function of time in oxygenated ethanol solutions at pH>13:

- [EtOH] = none, [O_2] = 2.39 x 10^{-4} M;  
- [EtOH] = 3.36 x 10^{-4} M, [O_2] = 2.36 x 10^{-4} M;  
- [EtOH] = 6.72 x 10^{-4} M, [O_2] = 2.24 x 10^{-4} M;  
- [EtOH] = 10.08 x 10^{-4} M, [O_2] = 2.51 x 10^{-4} M;  
- [OH\textsuperscript{-}] = 0.46 M for all solutions.
[EtOH]/[O₂] is not linear, however, but a plot of the reciprocal of the observed rate constant against [O₂]/[EtOH] is linear as long as k_{obs} in ethanol solutions is at least 10 times larger than the first order decay constant in solutions containing no ethanol (Figure 22).

An analogous mechanism to the one given for the benzoate ion solutions and the peroxide system\(^{21}\) can be written.

\[
\begin{align*}
O^- + O_2 &\rightarrow O_3^- \\
O_3^- &\rightarrow O^- + O_2 \\
O^- + \text{EtOH} &\rightarrow \text{OH}^- + \cdot \text{C}_2\text{H}_4\text{OH}
\end{align*}
\]

The steady state assumption for oxide ion gives

\[
k_{\text{obs}} = \frac{k_{10}k_{28}[\text{EtOH}]}{k_{28}[\text{EtOH}] + k_0[O_2]}
\]

From the slope of Figure 22 using \(k_{28} = 8.4 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}\), obtained from the competition experiment, \(k_{10}\) is \(3.6 \times 10^3 \text{ sec}^{-1}\). This mechanism ignores, however, two other means of decay which may not be insignificant. First, it has already been determined that \(O^-\) is in equilibrium with \(\text{OH}\) so that some reaction between \(\text{OH}\) and \(\text{EtOH}\) may occur. Secondly, the first order decay not attributed to reaction with ethanol may not be negligible. The expanded mechanism is

\[
\begin{align*}
O^- + O_2 &\rightarrow O_3^- \\
O_3^- &\rightarrow O^- + O_2 \\
O^- + \text{EtOH} &\rightarrow \text{OH}^- + \cdot \text{C}_2\text{H}_4\text{OH} \\
O^- + \text{H}_2\text{O} &\rightarrow \text{OH}^- + \text{OH} \\
\text{OH} + \text{EtOH} &\rightarrow \text{H}_2\text{O} + \cdot \text{C}_2\text{H}_4\text{OH} \\
O^- &\rightarrow \text{products}
\end{align*}
\]
Figure 22: Dependence of the reciprocal of the observed first order rate constant for ozonide ion decay at 430 nm as a function of the concentrations of oxygen and ethanol.
The steady state assumption for the oxide ion gives

\[ \frac{k_{10}(k_{28} + k_{30}K_{20}/[\text{OH}^-])[\text{EtOH}] + k_{32}}{k_{6}[O_2] + (k_{28} + k_{30}K_{20}/[\text{OH}^-])[\text{EtOH}] + k_{32}} \]

(XXVII)

Using \( k_{30} = 1.8 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1} \), \( k_{6} = 2.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1} \), \( k_{28} = 8.4 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1} \) and \( K_{20} = 6.10 \times 10^{-3} \text{ M} \) at 25° C from this work and \( k_{32} \) calculated from the natural first order decay constant, \( k_{10} \) is calculated for each set of experimental conditions. The average value of \( k_{10} \) is \((5.2 \pm 0.2) \times 10^8 \text{ sec}^{-1}\) as shown in Table VI. This value is only 12% lower than the value from the graphical method. Also the value compares very favorably with \( k_{10} = (5.3 \pm 0.3) \times 10^8 \text{ sec}^{-1} \) from the benzoate ion experiment.

The decay of ozonide ion in methanol solutions

The decay of ozonide ion in methanol solutions is exactly analogous to the decay in ethanol solutions. Decay curves are shown in figure 23. A decay mechanism which fits the data is

\[ \text{O}^- + O_2 \rightarrow O_3^- \quad (6) \]

\[ O_3^- \rightarrow O^- + O_2 \quad (10) \]

\[ O^- + \text{MeOH} \rightarrow \text{OH}^- + \cdot \text{CH}_2\text{OH} \quad (29) \]

\[ O^- + H_2O \leftrightarrow \text{OH} + \text{OH}^- \quad (20) \]

\[ \text{OH} + \text{MeOH} \rightarrow H_2O + \cdot \text{CH}_2\text{OH} \quad (31) \]

\[ O^- \rightarrow \text{products} \quad (32) \]

The observed rate constant would be equal to

\[ \frac{k_{10}(k_{28} + k_{31}K_{20}/[\text{OH}^-])[\text{MeOH}] + k_{32}}{k_{6}[O_2] + (k_{28} + k_{31}K_{20}/[\text{OH}^-])[\text{MeOH}] + k_{32}} \]

(XXVIII)

When \( k_{31} = 8.4 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1} \), \( k_{6} = 2.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1} \).
TABLE VI

DECAY OF OZONIDE ION IN OXYGENATED ETHANOL SOLUTIONS

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<tr>
<th>[O_2] M x 10^4</th>
<th>[EtOH] M x 10^4</th>
<th>[OH^-] M</th>
<th>k_{obs} x 10^{-3} sec</th>
<th>k_{10} x 10^{-3} sec</th>
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Average k_{10} = (3.2 ± .2) x 10^3 sec^{-1}
$k_{50} = 5.2 \times 10^9 \text{M}^{-1} \text{sec}^{-1}$ and $k_{20} = 6.10 \times 10^9 \text{sec}^{-1} \text{M}$ at 25°C from this research and $k_{32}$ calculated from the first order decay, $k_{10}$ is calculated to be $(3.3 \pm 0.3) \times 10^3 \text{sec}^{-1}$ as shown in Table VII. Again there is excellent agreement with the results from the benzoate ion and ethanol experiments.

The decay of ozonide ion in hydrogen peroxide solutions

As has already been mentioned, some experiments were carried out on the decay kinetics of ozonide ion disappearance in hydrogen peroxide solutions at high pH. The disappearance had been interpreted as a direct reaction between ozonide ion and hydrogen peroxide$^{18,19}$. The results of Behar and Czapski$^{21}$ and Heidt$^{17}$ show that the decay is also dependent on oxygen concentration. Behar and Czapski's$^{21}$ mechanism is

$$O^- + O_2 \rightarrow O_3^- \tag{6}$$

$$O_3^- \rightarrow O^- + O_2 \tag{10}$$

$$O^- + H_2O_2 \rightarrow OH^- + HO_2 \tag{11}$$

Analogous mechanisms were found to fit the data in the benzoate ion and alcohol solutions. The concentrations of solutes in Behar and Czapski's$^{21}$ work were such that $[H_2O_2]$ was usually greater than $[O_2]$. In the present work the opposite was true. Hydrogen peroxide concentration. The result is that the first order decay of ozonide ion in solutions without hydrogen peroxide is not negligible compared to that in hydrogen peroxide solutions. Reaction (32) must be added to the mechanism.

$$O^- \rightarrow \text{products} \tag{32}$$
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<tr>
<th>[O₂] ( \text{M} \times 10^4 )</th>
<th>[MeOH] ( \text{M} \times 10^4 )</th>
<th>[OH⁻] ( \text{M} )</th>
<th>( k_{\text{obs}} ) ( \times 10^{-3} \text{ sec} )</th>
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<td>.305</td>
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<tr>
<td>9.4</td>
<td>2.15</td>
<td>.326</td>
<td>177</td>
<td>2.81</td>
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</tbody>
</table>

Average \( k_{10} = (3.3 \pm .3) \times 10^3 \text{ sec}^{-1} \)
Furthermore, in this work reaction (11) was written as

$$0^- + H\text{O}_2^- \rightarrow OH^- + O_2^-$$  \hspace{1cm} (27)

since the pK of H\text{O}_2 is 11.8^18. The published rate constant for reaction (27) is \( (7 \pm 3) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1} \) \(^{18} \), determined by competition between \( O_2 \) and \( H\text{O}_2^- \) for \( O^- \). This measured rate constant, however, was found by Rabani\(^{20} \) to be a composite of the rate constants for the reactions between the various combinations of \( OH, O^-, H\text{O}_2^- \) and \( H_2\text{O}_2 \).

$$0^- + H\text{O}_2^- \rightarrow O_2^- + OH^-$$  \hspace{1cm} (27)

$$0^- + H_2\text{O}_2 \rightarrow OH^- + H\text{O}_2$$  \hspace{1cm} (11)

$$OH + H\text{O}_2^- \rightarrow H_2O + O_2^-$$  \hspace{1cm} (26)

By direct observation of the formation of \( O_2^- \) at 260 nm and using computer techniques to analyze the data, he determined \( k_{27} = 2.74 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1} \) \(^{20} \) and \( (k_{11} + 1.42k_{25}) = 1.18 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1} \) \(^{20} \). The pH effect was not discovered in the competition because at pH greater than 13, the change in the rate constant due to change in pH is only 10-20% and is difficult to observe because of uncertainties in the experimental values. The same effect was found in the alcohol competition experiments.

The entire mechanism for the system containing \( H_2\text{O}_2 \) is

$$0^- + O_2 \rightarrow O_3^-$$  \hspace{1cm} (6)

$$O_3^- \rightarrow 0^- + O_2$$  \hspace{1cm} (10)

$$0^- + H_2O \leftrightarrow OH + OH^-$$  \hspace{1cm} (20)

$$H\text{O}_2^- + H_2O \leftrightarrow OH^- + H_2\text{O}_2$$  \hspace{1cm} (33)

$$0^- + H\text{O}_2^- \rightarrow O_2^- + OH^-$$  \hspace{1cm} (27)

$$OH + H\text{O}_2^- \rightarrow H_2O + O_2^-$$  \hspace{1cm} (26)
\[ O^- + H_2O_2 \rightarrow OH^- + HO_2 \]  \hspace{1cm} (11)
\[ O^- \rightarrow \text{products} \]  \hspace{1cm} (32)

The equilibrium constant for reaction is given by
\[ K_{33} = \frac{K_W}{K_{34}} \]  \hspace{1cm} XXIX

where \( K_{34} \) is the dissociation constant for hydrogen peroxide
\[ H_2O + H_2O_2 \rightleftharpoons HO_2^- + H_3O^+ \]  \hspace{1cm} (34)

Assuming a steady state for the \( O^- \) and \( OH^- \) concentrations, the observed rate constant should be equal to
\[ k_{obs} = \frac{k_{10}(k_{27} + k_{26}K_{20}/[OH^-] + k_{11}K_{33}/[OH^-])[HO_2^-] + k_{32}}{k_6[O_2] + k_{32} + (k_{27} + k_{26}K_{20}/[OH^-] + k_{11}K_{33}/[OH^-])[HO_2^-]} \]  \hspace{1cm} XXX

Equation XXX is considerably more complex than the \( k_{obs} \) in equation XXII from Behar and Czapski's mechanism but only because reaction (32) is included and the hydrogen peroxide reaction is separated into 3 different reactions, the extent of each depending on pH.

The data obtained in the present study is of little use in obtaining separate values for the rate constants in equation XXX since the pH was 13.5 for all experiments. It is interesting to note, however, that if \( k_{10} \) is taken to be \( 3.3 \times 10^8 \) sec\(^{-1}\), the average of the values obtained in the benzoate ion and alcohol solutions, a composite rate constant for the peroxide reactions, \( k_{27} + k_{26}K_{20}/[OH^-] + k_{11}K_{33}/[OH^-] \), can be calculated to be \( (3 \pm 3) \times 10^8 \) M\(^{-1}\) sec\(^{-1}\) at pH 13.5. This value compares very well with the composite rate constant measured by competition\(^{18} \), \( (7 \pm 3) \times 10^8 \) M\(^{-1}\) sec\(^{-1}\). The data and calculation are shown in table VIII. Finally, from Behar and Czapski's data\(^{21} \), the ratio of \( k_6 \) to the composite hydrogen peroxide rate constant was found to be
### TABLE VIII

**DECAY OF OZONIDE ION IN OXYGENATED HYDROGEN PEROXIDE SOLUTIONS**

<table>
<thead>
<tr>
<th>[O$_2$] $M \times 10^3$</th>
<th>[H$_2$O$_2$] $M \times 10^3$</th>
<th>$k_{obs}$</th>
<th>$k''(O^- + HO_2^-)$ $x 10^{-9}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.58</td>
<td>1.1</td>
<td>779</td>
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</tr>
<tr>
<td>1.86</td>
<td>1.0</td>
<td>674</td>
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</tr>
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<td>1.25</td>
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<td>890</td>
<td>1.15</td>
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<td>1.31</td>
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</tr>
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</tr>
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<td>.48</td>
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<td>.57</td>
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<tr>
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<td>3.6</td>
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<tr>
<td>2.29</td>
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</tr>
<tr>
<td>2.73</td>
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<td>1.74</td>
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</tr>
<tr>
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<td>.77</td>
</tr>
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<td>.48</td>
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<td>.71</td>
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<td>.66</td>
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<td>.74</td>
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<tr>
<td>1.35</td>
<td>.66</td>
<td>390</td>
<td>.68</td>
</tr>
<tr>
<td>2.74</td>
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<td>158</td>
<td>.56</td>
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<td>.51</td>
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<td>1.09</td>
</tr>
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<td>.58</td>
<td>258</td>
<td>.73</td>
</tr>
<tr>
<td>.73</td>
<td>.63</td>
<td>671</td>
<td>.74</td>
</tr>
</tbody>
</table>

Average $k^\prime (O^- + H_2O^-) = (8 \pm 3) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$
3.5 ± 1.5. Using $k_3 = 2.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, the composite rate constant would be $(8 \pm 3) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$. The agreement among the various values is excellent.

Temperature dependence of $O_3^-$ decay

The temperature dependence of the rate of decay of ozonide ion was studied in benzoate ion solutions at high pH. Of particular interest is the temperature dependence of the dissociation of ozonide ion

$$O_3^- \rightarrow O^- + O_2$$

since the rate constant, $k_{10} = 3.3 \times 10^3 \text{ sec}^{-1}$, has a comparatively low value. The observed decay constant, however, is a complex function of rate constants and equilibrium constants

$$k_{\text{obs}} = \frac{k_{10}k_{32} + k_{10}k_{17}K_{20}[\phi\text{COO}^-]/[\text{OH}^-]}{k_0[O_2] + k_{32} + k_{17}K_{20}[\phi\text{COO}^-]/[\text{OH}^-]} \quad \text{XXIV}$$

so that the temperature variation of $k_{\text{obs}}$ may depend not only upon the temperature variation of $k_{10}$, but also upon the variation of the other constants. For example, $K_{20} = K_w/K_{\text{OH}}$. The equilibrium constant of water, $K_w$, depends greatly on temperature.

Competition studies at various temperatures will show how the ratio, $k_{17}K_{20}/k_3$, varies with temperature (refer to equation XVI). Figure 24 shows the results of competition experiments carried out at 45, 35, 25, 12, 7, and 4°C. The slope, which is equal to $k_{17}K_{20}/k_3$, does change with temperature.
Figure 24: Competition for the oxidizing radical in oxygenated benzoate ion solutions at pH > 13 at various temperatures. ○ 45°C; □ 35°C; △ 25°C; □ 12°C; ⬤ 4°C; 25°C line is the slope of figure 16.
Equation XXIV can be rearranged to give

\[
k_{10} = \frac{k_{\text{obs}} \left( 1 + \frac{k_{32}}{k_2[O_2]} + \frac{k_{17}k_{20}[^{18}COO^-]}{k_5[O_2][OH^-]} \right)}{\frac{k_{32}}{k_5[O_2]} + \frac{k_{17}k_{20}[^{18}COO^-]}{k_5[O_2][OH^-]}}
\]

The ratio \(k_{32}/k_5[O_2]\) is related to the observed first order decay constant in solutions containing no benzoate ion.

\[
k_{\text{obs}} \approx k_{32}/k_5[O_2] \quad \text{XXV}
\]

Using successive approximations of \(k_{10}\) to determine \(k_{32}/k_5[O_2]\), the values of \(k_{10}\) were calculated at different temperatures. Table IX gives the results for the temperatures other than ambient.

The activation energy for reaction (10) was calculated using the Arrhenius equation

\[
k = Ae^{(-E_A/RT)} \quad \text{XXXI}
\]

where

\[k = \text{rate constant}\]
\[E_A = \text{activation energy}\]
\[A = \text{pre-exponential factor}\]
\[R = \text{constant, 1.986 cal/mole deg}\]
\[T = \text{temperature in degrees absolute}\]

As long as \(A\) is not temperature dependent, a plot of \(\log k\) against \(1/T\) should be a straight line with a slope equal to \(-E_A/2.303R\). Such a plot for \(k_{10}\) at various temperatures is shown in figure 25. The activation energy is equal to \(11 \pm 3\) kcal and \(A\) is approximately \(10^{12} \pm 10^2\) sec\(^{-1}\).
TABLE IX

TEMPERATURE DEPENDENCE OF OZONIDE ION DECAY

<table>
<thead>
<tr>
<th>[O₂] M x 10⁴</th>
<th>[νCOO⁻] M x 10⁴</th>
<th>[OH⁻] M</th>
<th>k_{obs}</th>
<th>k</th>
<th>k_{10} x 10⁻³</th>
<th>T °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.68</td>
<td>3.02</td>
<td>.143</td>
<td>950</td>
<td>265</td>
<td>6.61</td>
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<td>.143</td>
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<td></td>
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<td>.240</td>
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<td></td>
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<td>.231</td>
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<tr>
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<td>.143</td>
<td>394</td>
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<td>1.26</td>
<td></td>
</tr>
</tbody>
</table>
Figure 25: Arrhenius plot for the determination of the Activation Energy of the reaction, $O_3^- \rightarrow O^- + O_2$. 
Summary of the ozonide ion decay

The decay kinetics of ozonide ion in the presence of hydroxyl radical scavengers and at low pulse intensity is consistent with the following mechanism.

\[ O^- + Q_2 \rightarrow O_3^- \quad (a) \]
\[ O_3^- \rightarrow O^- + O_2 \quad (b) \]
\[ O^- + X \rightarrow \text{products} \quad (c) \]
\[ O^- \rightarrow \text{products} \quad (d) \]
\[ O^- + H_2O \rightleftharpoons OH + OH^- \quad (e) \]
\[ OH + X \rightarrow \text{products} \quad (f) \]

where X represents the added species such as ethanol. Equilibrium between OH and O^- is maintained. During the course of the O_3^- decay, the majority of the oxidizing radical is in the form of O_3^- . The O^- and OH concentrations are small and do not change significantly during the decay so that the steady state approximation can be used for the concentrations of O^- and OH. The decay equation for O_3^- is, therefore,

\[
\frac{d[O_3^-]}{dt} = \frac{(k_b k_c + k_b k_f K_e/[OH^-])[X] + k_b k_d}{k_a [O_2] + (k_c + k_f K_e/[OH^-])[X] + k_d}
\]

If the additive X has more than one form in basic solutions, as in the case of hydrogen peroxide, the equilibrium of X may be included

\[ X + H_2O \rightleftharpoons XH^+ + OH^- \quad (g) \]

along with the reactions between OH and XH^+ and O^- and XH^+.

At low pulse intensities, the fate of the reducing species, e\textsuperscript{-aq}, does not affect the decay of ozonide ion.
Decay in oxygenated alkaline solutions without other additives

A mechanism for the decay of ozonide ion at low pulse intensities is

\[ \text{O}^- + \text{O}_2 \rightarrow \text{O}_3^- \quad (6) \]
\[ \text{O}_3^- \rightarrow \text{O}^- + \text{O}_2 \quad (10) \]
\[ \text{O}^- \rightarrow \text{products} \quad (32) \]

This mechanism explains the inverse oxygen dependence of the observed first order rate constant. The difficulty arises in suggesting a reasonable reaction and products for the disappearance of \( \text{O}^- \). Czapski\(^1\) has already pointed out that reaction (32) is not only an impurity reaction although if impurities are in the solution, their reactions with \( \text{O}^- \) or \( \text{OH}^- \) will be included to make a composite reaction (32). Behar and Czapski suggest that \( \text{O}^- \) and \( \text{H}_2\text{O} \) might react to produce products other than \( \text{OH}^- \) and \( \text{OH}^- \). For example, they suggest the reaction

\[ \text{H}_2\text{O} + \text{O}^- \rightarrow \text{O} + e^-_{\text{aq}} \quad (36) \]

A difference in ozonide ion decay, however, would be expected in solutions containing \( \text{N}_2\text{O} \) than in solutions containing no \( \text{N}_2\text{O} \) due to the reaction

\[ \text{N}_2\text{O} + e^-_{\text{aq}} \rightarrow \text{N}_2 + \text{O}^- \quad (7) \]

which regenerates \( \text{O}^- \). The nature of the first order decay of ozonide ion remains, therefore, open to speculation.

For irradiation of oxygenated basic solutions containing \( \text{N}_2\text{O} \) at high pulse intensity such that the initial \([\text{O}_3^-]\) is greater than \(10^{-5} \text{ M} \), Felix et al.\(^2\) determined that the decay kinetics of ozonide ion could be described as mixed first and second order. They determined the rate constant for the second order process by curve fitting using an analog
The empirical rate equation used was
\[
\frac{d[O_3^-]}{dt} = \frac{k_1}{[O_2]} [O_3^-] + 2k_2[O_3^-]^2 + k_3[HO_2^-][O_3^-] \quad \text{XXXII}
\]

At the time of their experiments, the oxygen concentration dependence of the first order rate constant was known, but the oxygen concentration dependence of the hydrogen peroxide rate constant was not known. Felix et al.\textsuperscript{18} showed that the second order rate constant, \(2k_2\) in equation XXXII, also depended on oxygen concentration. Their data are shown in figure 26 as a plot of \(2k_2\) against \([O_2]\).

Considering the mechanism proposed for \(O_3^-\) decay for the first order decay, a mechanism can be written in which a suitable second order process is added to the series of reactions,

\[
\begin{align*}
o^- + O_2 &\rightarrow O_3^- \\
o_3^- &\rightarrow o^- + O_2 \\
o^- &\rightarrow \text{products}
\end{align*}
\]

Behar and Czapski\textsuperscript{21} have suggested the inclusion of the reaction,

\[
o^- + O_3^- \rightarrow \text{products} \quad \text{(37')}
\]

A second reaction that can be proposed is

\[
o^- + O^- \rightarrow O_2^- \quad \text{(14)}
\]

For simplification of the discussion, it will be assumed that reactions (6) and (10) are in equilibrium. Later in the discussion the kinetic equations for \(O_3^-\) decay will be determined without making this assumption.

If reaction (6) and (10) are in equilibrium, the \(O^-\) concentration is given by the following equation.
Figure 26: Dependence of the measured second order rate constant for the decay of ozonide ion at 430 nm as a function of oxygen concentration, from Felix, Gall and Dorfman.¹⁸
The decay of ozonide ion will be given by the sum of the first and second order decay, reactions (32) and either (37) or (14). The reaction with hydrogen peroxide is ignored at this time because the peroxide concentration is small, amounting to one tenth of the ozonide ion concentration.

Considering reaction (37) as the second order process, the kinetic equation for the ozonide ion decay is

\[ -\frac{d[O_3^-]}{dt} = k_{32}[O_3^-] + k_{57}[O^-][O_3^-] \]

\[ = \frac{k_{32}k_{10}}{k_e[O_2]}[O_3^-] + \frac{k_{57}k_{10}}{k_e[O_2]^2}[O_3^-]^2 \quad \text{XXXIV} \]

In this case the second order rate constant depends on the inverse of the oxygen concentration. If reaction (14) is the second order process, the kinetic equation is

\[ -\frac{d[O_3^-]}{dt} = k_{32}[O^-] + 2k_{14}[O^-]^2 \]

\[ = \frac{k_{32}k_{10}}{k_e[O_2]}[O_3^-] + \frac{2k_{14}k_{10}^2}{k_e^2[O_2]^2}[O_3^-]^2 \quad \text{XXXV} \]

The second order decay constant will be a function of the inverse of the oxygen concentration squared. Figures 27 and 28 show the plots of the inverse of the measured second order rate constants from Felix et al.\textsuperscript{18} against $[O_2]$ and $[O_2]^2$, respectively. The fit appears to be better for the dependence on the oxygen concentration to the first power.
Figure 27: Dependence of the measured second order rate constant on oxygen concentration. Data from Felix et al.\textsuperscript{18}

Figure 28: Dependence of the measured second order rate constant on the square of the oxygen concentration. Data from Felix et al.\textsuperscript{18}
The values of $k_{37}$ and $k_{14}$ calculated from the slope of figure 27 and
the initial slope of figure 28, respectively, are $k_{37} = 1 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ and $2k_{14} = 3 \times 10^{12} \text{ M}^{-1} \text{ sec}^{-1}$ when $k_6 = 2.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$
and $k_{10} = 3.3 \times 10^8 \text{ sec}^{-1}$ from this work. The published value for
$2k_{14}$ is $1.8 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. The calculated value of $k_{14}$ is
considerably greater than the published value. Reaction (14) is,
therefore, not a reasonable reaction to account for the second order
decay of ozonide ion. Reaction (37) is a more likely candidate to
account for the second order decay.

The following calculation is made to show the difference in the
rate equation when a steady state concentration of $O^-$ is calculated
rather than an equilibrium concentration as used above.

The mechanism is

$$0^- + O_2 \rightarrow O_3^- \quad (6)$$
$$O_3^- \rightarrow O^+ + O_2 \quad (10)$$
$$O^- \rightarrow \text{products} \quad (32)$$
$$O^- + O_3^- \rightarrow \text{products} \quad (37)$$

The rate equations are

$$\frac{d[O_3^-]}{dt} = k_{10}[O_3^-] + k_{37}[O^-][O_3^-] - k_6[O^-][O_2] \quad \text{XXXVI}$$

$$\frac{d[O^-]}{dt} = k_6[O^-][O_2] - k_{10}[O_3^-] + k_{32}[O^-] + k_{37}[O^-][O_3^-] \quad \text{XXXVII}$$

If the steady state assumption for $[O^-]$ is valid, $-d[O^-]/dt = 0$, so
that

$$[O^-]_{ss} = \frac{k_{10}[O_3^-]}{k_6[O_2] + k_{32} + k_{37}[O_3^-]} \quad \text{XXXVIII}$$
\[
\frac{d[O_3^-]}{dt} = k_{10}[O_3^-] + \frac{k_{10}k_{37}[O_3^-]^2}{k_3[O_2] + k_{32} + k_{37}[O_3^-]} - \frac{k_5k_{10}[O_3^-][O_2]}{k_3[O_2] + k_{32} + k_{37}[O_3^-]}
\]

Rearrangement gives

\[
\frac{d[O_3^-]}{dt} = \frac{k_{10}k_{32}[O_3^-]}{k_3[O_2] + k_{32} + k_{37}[O_3^-]} + \frac{2k_{10}k_{37}[O_3^-]}{k_5[O_2] + k_{32} + k_{37}[O_3^-]}
\]

If \(k_{32} + k_{37}[O_3^-]\) is much smaller than \(k_5[O_2]\), equation XXXIX reduces to equation XXXIV except for the factor of 2 in the second order term. Therefore, this calculation gives \(k_{37} = 5 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}\). In all of the data of Felix et al.\(^{16}\), the ratio of \([O_2]\) to initial \([O_3^-]\) is at least 10. Therefore, the ratio \(k_5[O_2]/k_{37}[O_3^-]\) is at least 50. The term \(k_{37}[O_3^-]\), is negligible with respect to \(k_5[O_2]\). For some of their experiments, however, \(k_{32}\) was not negligible with respect to \(k_5[O_2]\).

The plot of the inverse of the observed rate constant against the oxygen concentration as shown in figure 27 should be linear. The equilibrium assumption, therefore, does not give the correct expression for the kinetic equation for ozonide ion decay, but it was suitable for the type of discussion for which it was used.

The actual decay equation for ozonide ion is more complex than that given in XXXIX. For example, the hydrogen peroxide reactions are not included. Also if \(O^-\) reacts with \(O_3^-\), then \(OH\) probably reacts with \(O_3^-\) and terms depending on \([OH^-]\) would be included in the kinetic equation. Due to the uncertainty in the data, however, small corrections such as these would not be meaningful.
It can be concluded from this investigation as well as from recent (or current) work of other investigators that $O^-$ is a less reactive radical than OH. While the number of $O^-$ reactions that have been studied are few, some attempt will be made to compare them with analogous OH reactions that have been studied. Four different types of OH reactions have been studied: electron transfer; association with another OH; addition; hydrogen abstraction.

Some electron transfer reactions that have been studied include the reactions of OH with $CO_3^{2-}$, $CNS^-$, $SeO_3^{2-}$, $I^-$, $Br^-$, $Fe(CN)_6^{3-}$, and so on. The published rate constants range from $4.8 \times 10^5$ M$^{-1}$ sec$^{-1}$ for the reaction of OH with $CO_3^{2-}$ to $1 \times 10^{10}$ M$^{-1}$ sec$^{-1}$ for the reaction of OH with $Fe(CN)_6^{3-}$. In contrast, the rate constants for the reactions of $O^-$ with $CO_3^{2-}$ and $Fe(CN)_6^{3-}$ are less than

1 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1} \text{.} \text{ Adams et al.}^{63} \text{ reported the rate constant for the reaction of O}^- \text{ with CNS}^- \text{ equal to } 1.0 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}. \text{ Their analysis, however, is based on the use of a rate constant for the reaction of OH with CNS}^- \text{ which is too low by a factor of 1.7 to 3}^{44,84}. \text{ The effect of using a value which is too low for the rate constant of the OH reaction is to obtain a value of the rate constant for the O}^- \text{ reaction which is too high because a composite rate constant is measured. The composite is then separated into two parts. It therefore, appears as if O}^- \text{ is much less reactive than OH for electron transfer reactions since the comparable rate constants differ by at least a factor of 50-100 or more.}

\text{In the case of the radical reacting with another similar radical, the rate constant for the reaction of OH with OH is greater by at least a factor of 10 than the rate constant for the reaction of O}^- \text{ with O}^-\text{. The published rate constants are } 2k(\text{OH} + \text{OH}) = 1.26 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1} \text{ and } 2k(\text{O}^- + \text{O}^-) \leq 1.8 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}. \text{ The difference in reactivity may perhaps be explained by the repulsion between the negative charge on the oxide radical ion.}

\text{In contrast, the hydrogen abstraction reaction rate constants for O}^- \text{ differ by only a factor of 2. For example, from this work}


\text{(64) J. H. Baxendale and D. A. Scott, Chem. Communications, 699 (1967).}
\[ k(O^- + \text{EtOH}) = 8.4 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1} \text{ while } k(OH + \text{EtOH}) = 1.83 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1} \]

Also \( k(O^- + \text{MeOH}) = 5.2 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1} \)
as compared to
\( k(OH + \text{MeOH}) = 8.4 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1} \)

In the case of the hydrogen peroxide reactions, comparison is more difficult because not all the values of the rate constants have been separated from each other.

Rabani\(^\text{20}\) gives
\[ k(O^- + H_2O_2) + 1.42 k(OH + HO_2^-) = 1.18 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1} \]

and \( k(O^- + HO_2^-) = 2.74 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1} \). The published rate constant for the reaction of OH with \( H_2O_2 \) is only \( 4.5 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1} \). Therefore, while \( k(OH + HO_2^-) \) is greater than \( k(O^- + HO_2^-) \), \( k(O^- + H_2O_2) \) is significantly larger than \( k(OH + H_2O_2) \).

In the case of addition reactions, comparison is again difficult because so few examples are available. Two addition type reactions of \( O^- \) have been studied, the reaction with oxygen and the reaction with benzoic acid.

Oxide radical ion reacts with oxygen to form ozonide ion, \( k(O^- + O_2) = 2.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1} \)\(^\text{15}\), while OH does not appear to react with \( O_2 \)\(^\text{12}\).

This observation is verified also by exchange reactions between \( ^{16}O^{18} \) and \( H_2O^{18} \) initiated by \( \gamma \)-ray irradiation of oxygenated aqueous solutions\(^\text{66}\). The exchange can also be initiated photochemically. The exchange is very slow in neutral solution compared to the rapid exchange found in alkaline solutions\(^\text{65}\). The mechanism for the exchange included the equilibrium, \( \text{OH} \leftrightarrow O^- + H^+ \), and propagation steps, \( O^- + O_2 \leftrightarrow O=O + O_2 \).


and $0^- + \text{OH}^- \rightarrow 0^- + \text{OH}^-$. This mechanism is similar to the one for the ozonide ion decay except that the relatively stable intermediate, $\text{O}_3^-$, is now known to be formed rather than the exchange, $0^- + \text{O}_3^+ \rightarrow 0^- + \text{O}_2$ being a concerted process.

On the other hand, hydroxyl radical reacts readily with benzene and substituted benzene molecules$^{44,27,51,67,68}$. The products of such reactions have been identified as the OH adduct to the aromatic ring. The rates of reaction are fast, having rate constants for the addition reactions in the region $2 \times 10^9$ M$^{-1}$ sec$^{-1}$ $^{44,29,52,69}$. The only reaction of this type which has been studied for $0^-$ is the reaction with benzoate ion. The rate constant for the latter reactions is at least 1000 times smaller than the analogous rate constant for the OH reaction, $k(0^- + \text{COO}^-) \leq 6 \times 10^6$ M$^{-1}$ sec$^{-1}$ and $k(\text{OH} + \text{COO}^-) = 6.0 \times 10^8$ M$^{-1}$ sec$^{-1}$ $^{44}$.

The hydroxyl radical has been found to have strong electrophilic characteristics in aromatic hydroxylation reactions$^{70,71,72}$. Oxide radical ion has already been shown to have much less electrophilic

character than hydroxyl radical from the difference in reactivity in
electron transfer reactions. On the other hand, nucleophilic substi-
tution in the ring is much slower than electrophilic substitution.
The comparative unreactivity of $O^-$ toward the aromatic ring can perhaps
be explained by these considerations.

Table X is a brief summary of the comparative reactions of OH and
$O^-$ as given above.

Reactivity of $O_3^-$

The present investigation and the investigation of Behar and
Czapski show that $O_3^-$ is unreactive toward added solutes such as
benzoate ion, ethanol, methanol and hydrogen peroxide. It is an
unstable species in that it decomposes to $O_2$ and $O^-$ with a rate constant
for the decomposition of $3.3 \times 10^3$ sec$^{-1}$ at $25^\circ$ C and an activation
energy equal to $11 \pm 3$ kcal. The reactive species in oxygenated
alkaline solutions appears to be the oxidizing radical rather than the
ozonide ion.

The evidence that $O_3^-$ decomposes to $O_2$ and $O^-$ arises from the
oxygen concentration dependence of the decay in all systems which have
been studied and the hydroxide ion concentration dependence in the
benzoate ion system. Competition experiments with oxygen and benzoate
ion showed that OH rather than $O^-$ reacts with benzoate ion. In the
study of the decay of ozonide ion, the same hydroxide ion concentration
dependence was observed. Since all the $O^-$ (and OH) should have reacted
with $O_2$ or $\text{C}O\text{O}^-$ within a few microseconds after the pulse, the only
way for the oxidizing radical to be formed again in solution is for the
ozonide ion to decompose.
<table>
<thead>
<tr>
<th>TYPE</th>
<th>REACTION</th>
<th>RATE CONSTANT ( \text{M}^{-1} \text{ sec}^{-1} )</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELECTRON</td>
<td>( \text{OH} + \text{CO}_3^- )</td>
<td>( 4.8 \times 10^8 )</td>
<td>5</td>
</tr>
<tr>
<td>TRANSFER</td>
<td>( \text{O}^- + \text{CO}_3^- )</td>
<td>( &lt; 10^7 )</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>( \text{OH} + \text{Fe(CN)}_6^{4-} )</td>
<td>( 1.0 \times 10^{10} )</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>( \text{O}^- + \text{Fe(CN)}_6^{4-} )</td>
<td>( &lt; 10^7 )</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>( \text{OH} + \text{CNS}^- )</td>
<td>( 2 \times 10^{10} )</td>
<td>44, 64</td>
</tr>
<tr>
<td></td>
<td>( \text{O}^- + \text{CNS}^- )</td>
<td>( &lt; 10^9 )</td>
<td>63</td>
</tr>
<tr>
<td>COMBINATION</td>
<td>( \text{OH} + \text{OH} )</td>
<td>( 1.26 \times 10^{10} )</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>( \text{O}^- + \text{O}^- )</td>
<td>( &lt; 1.8 \times 10^9 )</td>
<td>4</td>
</tr>
<tr>
<td>H ABSTRACTION</td>
<td>( \text{OH} + \text{EtOH} )</td>
<td>( 1.83 \times 10^3 )</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>( \text{O}^- + \text{EtOH} )</td>
<td>( 8.4 \times 10^8 )</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>( \text{OH} + \text{MeOH} )</td>
<td>( 8.4 \times 10^8 )</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>( \text{O}^- + \text{MeOH} )</td>
<td>( 5.2 \times 10^8 )</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>( \text{OH} + \text{H}_2\text{O}_2 )</td>
<td>( 4.5 \times 10^7 )</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>( \text{O}^- + \text{H}_2\text{O}_2 )</td>
<td>( 1.18 \times 10^{10} )</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>( \text{O}^- + \text{HO}_2^- )</td>
<td>( 2.74 \times 10^8 )</td>
<td>20</td>
</tr>
<tr>
<td>ADDITION</td>
<td>( \text{OH} + \text{O}_2 )</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{O}^- + \text{O}_2 )</td>
<td>( 2.5 \times 10^9 )</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>( \text{OH} + \text{COO}^- )</td>
<td>( 6.0 \times 10^9 )</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>( \text{O}^- + \text{COO}^- )</td>
<td>( &lt; 6 \times 10^6 )</td>
<td>this work</td>
</tr>
</tbody>
</table>
The unreactivity of ozonide ion toward added solutes does not imply that $O_3^-$ is unreactive toward other radicals. Therefore, the suggestion that the second order component of the decay is the result of the reaction of $O^-$ with $O_3^-$ is not an unreasonable one.

The most reasonable products for the reaction are

$$O^- + O_3^- \rightarrow 2O_2^-$$  \hspace{1cm} (37)

rather than

$$O^- + O_3^- \rightarrow O^- + O_3$$  \hspace{1cm} (37)

since electron transfer reactions to $O^-$ are slow and seem to have rate constants much less than the one calculated for reaction (37), $5 \times 10^8$ $\text{M}^{-1} \text{sec}^{-1}$. It is not easy to verify the above statement, however, by observing the formation of the product since both $O_2^-$ and $O_3$ as well as $O^-$, $HO_2^-$ and perhaps $O_3^-$ absorb in the spectral region below 300 nm. Solid ozonides decompose slowly over a period of days to the superoxides and oxygen. For example,

$$2KIO_3 \rightarrow 2KO_2 + O_2$$  \hspace{1cm} (38)

Heidt and Landi, however, found that ozone was formed in the flash photolysis of hydrogen peroxide solutions at high pH as well as ozonide ion. Furthermore, ozone absorption appeared to grow in as ozonide absorption disappeared. Therefore, the question of the possible products of reaction (37) is not resolved.

This investigation has resulted in a reasonable explanation for ozonide ion disappearance in solutions with added substituents such as ethanol and benzoate ion but has not identified the exact nature of the first and second order reactions in the decay of ozonide ion in solutions containing no added oxidizing radical scavengers.
CONCLUSIONS

Ozonide ion absorption with a maximum at 430 nm as determined previously\textsuperscript{11,13} was found to double in solutions containing \( \text{N}_2\text{O} \) due to the conversion of the solvated electron to the oxide ion via the reaction with \( \text{N}_2\text{O} \). The extinction coefficient of the ozonide ion at 430 nm was \( 1900 \pm 120 \, \text{M}^{-1} \, \text{cm}^{-1} \) as compared with the value of \( 2000 \pm 40 \, \text{M}^{-1} \, \text{cm}^{-1} \) determined by Adams et al.\textsuperscript{16}

Ozonide ion is unreactive toward added solutes such as ethanol, methanol, benzoate ion and hydrogen peroxide. Ozonide ion does decompose into \( \text{O}_2 \) and \( \text{O}^- \). The rate constant for this reaction was measured in three different systems; oxygenated alkaline ethanol, methanol and benzoate ion solutions. The average value of the rate constant was \( (5.3 \pm 0.4) \times 10^3 \, \text{sec}^{-1} \) at 25\(^\circ\) C. The activation energy of the reaction was found to be 11 \pm 3 kcal/mole. Previously determined values of the decomposition rate constant were \( 2.8 \times 10^3 \, \text{sec}^{-1} \)\textsuperscript{14} and \( 5 \times 10^3 \, \text{sec}^{-1} \)\textsuperscript{21}.

Oxide radical ion was found to be a less reactive radical than hydroxyl radical. Rate constants for the reactions of \( \text{O}^- \) with \( \text{COO}^- \), EtOH, and MeOH were determined relative to the rate constant for the reaction of \( \text{O}^- \) with \( \text{O}_2 \). The rate constants calculated using \( k(\text{O}^- + \text{O}_2) = 2.5 \times 10^9 \, \text{M}^{-1} \, \text{sec}^{-1} \)\textsuperscript{15} are \( k(\text{O}^- + \text{COO}^-) \leq 6 \times 10^8 \, \text{M}^{-1} \, \text{sec}^{-1} \), \( k(\text{O}^- + \text{EtOH}) = 8.4 \times 10^8 \, \text{M}^{-1} \, \text{sec}^{-1} \) and \( k(\text{O}^- + \text{MeOH}) = 5.2 \times 10^8 \, \text{M}^{-1} \, \text{sec}^{-1} \). In the solutions containing \( \text{COO}^- \), the pK of the hydroxyl
radical was determined to be $11.8 \pm 0.2$ at $25^\circ$ C in good agreement with
the previously determined values of $11.8 \pm 0.2^5$ and $11.9 \pm 0.2^4$.

The mechanism for the decay of ozonide ion in solutions with added
solutes such as benzoate ion, ethanol and so on consisted of the
following reactions:

\[
\begin{align*}
0^- + O_2 &\rightarrow O_3^- \quad \text{(a)} \\
O_3^- &\rightarrow 0^- + O_2 \quad \text{(b)} \\
0^- + X &\rightarrow \text{products} \quad \text{(c)} \\
0^- &\rightarrow \text{products} \quad \text{(d)} \\
0^- + H_2O &\rightarrow OH + OH^- \quad \text{(e)} \\
OH + X &\rightarrow \text{products} \quad \text{(f)}
\end{align*}
\]

X represents the added solute. The decay mechanism in solutions
containing no added solute X such as ethanol and so on is thought to
consist of the reactions (a), (b), and (d) for initial ozonide ion
concentration of less than $10^{-5}$ M. The nature of reaction (d) is not
known. For higher initial ozonide ion concentrations and addition
reaction,

\[
0^- + O_3^- \rightarrow \text{products} \quad \text{(g)}
\]

is added to the mechanism consisting of reactions (a), (b) and (d). An
approximate rate constant can be calculated from the data of Felix et
al.$^{16}$ to be $5 \times 10^8$ M$^{-1}$ sec$^{-1}$ for reaction (g).
APPENDIX I

LIST OF REACTIONS FOUND IN THE TEXT

(1) \( \text{H}_2\text{O} \rightarrow \text{H}, e^-_{\text{aq}}, \text{OH}, \text{H}_3\text{O}^+, \text{H}_2, \text{H}_2\text{O}_2 \)

(2) \( \text{OH} + \text{OH}^- \rightarrow \text{O}^- + \text{H}_2\text{O} \)

(3) \( \text{H} + \text{OH}^- + e^-_{\text{aq}} \)

(4) \( e^-_{\text{aq}} + \text{O}_2 \rightarrow \text{O}_2^- \)

(5) \( \text{H} + \text{O}_2 \rightarrow \text{HO}_2 \)

(6) \( \text{O}^- + \text{O}_2 \rightarrow \text{O}_3^- \)

(7) \( \text{N}_2\text{O} + e^-_{\text{aq}} \rightarrow \text{N}_2 + \text{O}^- \)

(8) \( \text{O}_3^- + \text{O}_3^- \rightarrow \text{products} \)

(9) \( \text{O}_3^- + \text{HO}_2^- \rightarrow \text{products} \)

(10) \( \text{O}_3^- \rightarrow \text{O}^- + \text{O}_2 \)

(11) \( \text{O}^- + \text{H}_2\text{O}_2 \rightarrow \text{OH}^- + \text{HO}_2 \)

(12) \( e^-_{\text{sol}} + \phi_2 + \phi_2^- \)

(13) \( \phi_2^- + \text{EtOH} \rightarrow \phi_2\text{H} + \text{EtO}^- \)

(14) \( \text{O}^- + \text{O}^- \rightarrow \text{O} = \)

(15) \( \text{HO}_2 + \text{OH}^- \rightarrow \text{O}_2^- + \text{H}_2\text{O} \)

(16) \( \text{OH} + \phi\text{COOH} \rightarrow (\text{OH})\text{C}_6\text{H}_5\text{COOH} \)

(17) \( \text{OH} + \phi\text{COO}^- \rightarrow (\text{OH})\text{C}_6\text{H}_5\text{COO}^- \)

(18) \( \text{O}^- + \phi\text{COO}^- \rightarrow (\text{O}^-)\text{C}_6\text{H}_5\text{COO}^- \)

(19) \( e^-_{\text{aq}} + \phi\text{COO}^- \rightarrow (\text{C}_6\text{H}_5\text{COO}^-)^- \)

(20) \( \text{O}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{OH}^- \)

(21) \( \text{H}_2\text{O} + \text{OH} \rightarrow \text{O}^- + \text{H}_3\text{O}^+ \)

(22) \( \text{OH} + \text{I}^- \rightarrow \text{OH}^- + \text{I} \)

(23) \( \text{OH} + \text{O}^- \rightarrow \text{HO}_2^- \)
(24) OH + O$_2^-$ → OH$^-$ + O$_2$
(25) O$^-$ + O$_2^-$ → HO$_2^-$ + O$_2$
(26) OH + HO$_2^-$ → H$_2$O + O$_2^-$
(27) O$^-$ + HO$_2^-$ → OH$^-$ + O$_2^-$
(28) O$^-$ + EtOH → OH$^-$ + ·C$_2$H$_4$OH
(29) O$^-$ + MeOH → OH$^-$ + ·CH$_2$OH
(30) OH + EtOH + H$_2$O + ·C$_2$H$_4$OH
(31) OH + MeOH + H$_2$O + ·CH$_2$OH
(32) O$^-$ → products
(33) HO$_2^-$ + H$_2$O → OH$^-$ + H$_2$O$_2$
(34) H$_2$O$_2$ + H$_2$O → HO$_2^-$ + H$_3$O$^+$
(35) e$^-_{aq}$ + HO$_2^-$ → OH$^-$ + O$^-$
(36) O$^-$ → O + e$^-_{aq}$
(37) O$^-$ + O$^-$ → products
(38) 2KO$_3$ → 2KO$_2$ + O$_2$
APPENDIX II
DERIVATION OF THE COMPETITION EQUATION

For a pair of reactions where two different solutes can react with the same species,

\[\begin{align*}
A + X &\rightarrow P & (1) \\
A + Y &\rightarrow \text{products} & (2)
\end{align*}\]

\(A\) = species with which both solutes, \(X\) and \(Y\), can react.

\(P\) = product of interest. The amount of \(P\) formed is the measured quantity.

The competition equation is given by:

\[
\frac{D^0}{D} = 1 + \frac{R_2}{R_1}
\]

\(D^0\) = optical density of \(P\) produced in solutions containing only \(X\).

\(D\) = optical density of \(P\) produced in solutions containing both \(X\) and \(Y\).

\(R_1\) = rate of reaction (1) = \(k_1[A][X]\).

\(R_2\) = rate of reaction (2) = \(k_2[A][Y]\).

In solutions containing both \(X\) and \(Y\), the amount of \(A\) which reacts with \(X\) is given by \(D\) and the amount of \(A\) which reacts with \(Y\) is given by \(D^0 - D\). The last relationship depends on the fact that the amount of \(A\) is produced by the pulse in all the different solutions. The pulse was reproducible to within 3% so that the relationship is valid within experimental error. The ratio of \(D/(D^0 - D)\) is given by the relative rates of reactions (1) and (2).
Therefore,

\[
\frac{D}{D^0 - D} = \frac{R_1}{R_2}
\]

rearranging,

\[
\frac{D^0}{D} = 1 + \frac{k_2[A][Y]}{k_1[A][X]}
\]
APPENDIX III

KINETIC EQUATIONS FOR THE DECAY OF OZONIDE ION

(A) Simple Case: First order decay in solutions containing only oxygen and hydroxide ion.

Mechanism:

\[ \text{O}^- + \text{O}_2 \rightarrow \text{O}_3^- \]  
\[ \text{O}_3^- \rightarrow \text{O}^- + \text{O}_2 \]  
\[ \text{O}^- \rightarrow \text{products} \]

1. Kinetic decay equation for ozonide ion:
\[ \frac{d[\text{O}_3^-]}{dt} = k_2[\text{O}_3^-] - k_1[\text{O}^-][\text{O}_2] \]  

2. Kinetic decay equation for the oxide ion:
\[ \frac{d[\text{O}^-]}{dt} = k_1[\text{O}^-][\text{O}_2] + k_3[\text{O}^-] - k_2[\text{O}_3^-] \]

Assuming a steady state for the oxide radical ion (the concentration of \text{O}^- remains small and does not change significantly during the course of the reaction), then Equation II is equal to zero and the steady state concentration of \text{O}^- is given by
\[ [\text{O}^-]_{ss} = \frac{k_2[\text{O}_3^-]}{k_1[\text{O}_2] + k_3} \]

Substituting Equation III into Equation I:
\[ \frac{d[\text{O}_3^-]}{dt} = k_2[\text{O}_3^-] - \frac{k_1k_2[\text{O}_2][\text{O}_3^-]}{k_1[\text{O}_2] + k_3} \]

Rearrangement gives:
\[ \frac{d[\text{O}_3^-]}{dt} = \frac{k_2k_3[\text{O}_3^-]}{k_1[\text{O}_2] + k_3} \]
(B) Complex Case: First order decay in solutions containing oxygen, hydroxide ion and added solute such as ethanol. The additive will be denoted by the symbol X.

Mechanism:

\[ O^- + O_2 \rightarrow O_3^- \] \hspace{1cm} (1)

\[ O_3^- + O^- + O_2 \] \hspace{1cm} (2)

\[ O^- + X \rightarrow \text{products} \] \hspace{1cm} (3)

\[ O^- \rightarrow \text{products} \] \hspace{1cm} (4)

\[ O^- + H_2O \rightarrow OH + OH^- \] \hspace{1cm} (5)

\[ OH + X \rightarrow \text{products} \] \hspace{1cm} (6)

Kinetic decay equation for ozonide ion decay:

\[ \frac{d[O_3^-]}{dt} = k_2[O_3^-] - k_1[O^-][O_2] \] \hspace{1cm} VI

Kinetic decay equation for the oxide ion:

\[ \frac{d[O^-]}{dt} = k_1[O^-][O_2] - k_2[O_3^-] + k_3[O^-][X] + k_4[O^-] + k_6k_5[X][O^-]/[OH^-] \] \hspace{1cm} VII

Assuming a steady state for the \( O^- \) concentration:

\[ [O^-]_{ss} = \frac{k_2[O_3^-]}{k_1[O_2] + k_3[X] + k_4 + k_6K_5[X]/[OH^-]} \] \hspace{1cm} VIII

Substituting Equation VIII into Equation VI:

\[ \frac{d[O_3^-]}{dt} = \frac{k_1k_2[O_2][O_3^-]}{k_1[O_2] + (k_3 + k_6K_5/[OH^-])[X] + k_4} + k_2[O_3^-] \] \hspace{1cm} IX

Rearrangement gives:

\[ \frac{d[O^-]}{dt} \] \hspace{1cm} (7)

\[ \frac{d[O_3^-]}{dt} = \frac{-k_2(k_3 + k_6K_5/[OH^-])[X] + k_2k_4}{k_1[O_2] + (k_3 + k_6K_5/[OH^-])[X] + k_4} \] \hspace{1cm} IX
BIBLIOGRAPHY


