THE DISPROPORTIONATION AND COMBINATION
REACTIONS OF BUTYL FREE RADICALS

DISSERTATION

Presented in Partial Fulfillment of the Requirements
for the Degree Doctor of Philosophy in the
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By

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TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. EXPERIMENTATION.	8
A. Experimental Apparatus.	8
1. The High Vacuum System	8
2. The Auxiliary Vacuum System.	15
3. The Photolysis System.	15
4. The Product Transfer System.	17
5. The Reactant Introduction System	18
6. The Optical System	18
7. The Temperature Control System	19
8. The Gas Chromatography System.	21
9. The Calibrated Gas Burette	26
B. Experimental Procedure.	28
1. Chemicals and Reagents	28
2. Analytical Procedures.	31
a. Liquid Nitrogen Non-condensable Fraction	31
b. Liquid Nitrogen Condensates	33
1. Theory of Gas Chroma- tography.	33
2. Gas Chromatographic Analyses	37
3. Filter Transmission.	39
4. Sample Transmissions	39
III. TABULATION OF DATA	41
A. Absorbed Light Intensity.	41
B. Product Analysis.	45
IV. RESULTS AND DISCUSSION	63
A. Sample Calculation.	63
B. Tabulated Results	65
1. Diethyl Ketone Photolysis.	65
2. Di- <u>tert.</u> -butyl Ketone Photolysis	66
3. Di- <u>iso</u> -butyl Ketone Photolysis	66
4. Di- <u>sec.</u> -butyl Ketone Photolysis.	73
5. 2-Methylbutanal Photolysis	73
6. Estimated Quantum Efficiencies for all Products.	73

TABLE OF CONTENTS CON'T

	Page
 (IV. RESULTS AND DISCUSSION - con't)	
C. Discussion of Results	76
1. Proposed Mechanism for Di- <u>tert.</u> -butyl Ketone Photolysis	76
2. Proposed Mechanism for Di- <u>iso</u> -butyl Ketone Photolysis	79
3. Proposed Mechanism for Di- <u>sec.</u> -butyl Ketone Photolysis	80
4. Primary Quantum Efficiencies for Di-butyl Ketones.	83
5. Disproportionation/Combination and H-abstraction Reactions	84
6. Summary.	88

BIBLIOGRAPHY

LIST OF TABLES

Table	Title	Page
1.	Comparison of Ratio of Disproportionation/Combination Rates for Ethyl Radicals	3
2.	Comparison of Ratio of Disproportionation/Combination Rates for <u>n</u> -Propyl Radicals.	4
3.	Comparison of Ratio of Disproportionation/Combination Rates for <u>iso</u> -Propyl Radicals.	5
4.	Mercury Arc Composition and Percentage Transmission. . .	43
5.	Molar Extinction Coefficients for Ketones.	44
6.	Quanta Absorbed as a Function of Pressure and I_0	44
7.	Gas Chromatography Product Volumes from Diethyl Ketone .	46
8.	Gas Chromatography Knowns for Diethyl Ketone	46
9.	Gas Chromatography Product Volumes from Di- <u>tert.</u> -butyl Ketone.	47
10.	Gas Chromatography Knowns for Di- <u>tert.</u> -butyl Ketone. . .	47
11.	Mass Spectrometric Product Volumes from Di- <u>tert.</u> -butyl Ketone.	48
12.	Mass Spectrometric Sensitivities of Knowns for Di- <u>tert.</u> -butyl Ketone	48
13.	Gas Chromatography for Product Volumes from Di- <u>iso</u> -butyl Ketone	49
14.	Gas Chromatography Knowns for Di- <u>iso</u> -butyl Ketone. . . .	50
15.	Mass Spectrometric Product Volumes from Di- <u>iso</u> -butyl Ketone.	51
16.	Mass Spectrometric Sensitivities of Knowns for Di- <u>iso</u> -butyl Ketone	51

LIST OF TABLES CON'T

Table	Title	Page
17.	Gas Chromatography Product Volumes from Di- <u>sec.</u> -butyl Ketone	.52
18.	Gas Chromatography Knowns for Di- <u>sec.</u> -butyl Ketone. . .	.52
19.	Gas Chromatography Product Volumes from 2-Methylbutanal	.53
20.	Diethyl Ketone Photolysis Product Rates	.68
21.	Di- <u>tert.</u> -butyl Ketone Photolysis Product Rates.	.68
22.	Rate of Combination/Disproportionation for Di- <u>tert.</u> -butyl Ketone.	.69
23.	Product Rates as a Function of Pressure for Di- <u>tert.</u> -butyl Ketone.	.69
24.	Product Rates as a Function of I_0 for Di- <u>tert.</u> -butyl Ketone	.70
25.	Product Rates for Di- <u>iso</u> -butyl Ketone	.71
26.	Combination/Disproportionation for Di- <u>iso</u> -butyl Ketone. .	.72
27.	Hydrogen Abstraction/Combination for Di- <u>iso</u> -butyl Ketone.	.72
28.	Rate Products for Propylene, Methane, and CO as a Function of Temperature and I_0 from Di- <u>iso</u> -butyl Ketone	.73
29.	Product Rates for Di- <u>sec.</u> -butyl Ketone and 2-Methylbutanal Photolyses	.74
30.	Product Ratios for Di- <u>sec.</u> -butyl Ketone and 2-Methylbutanal	.74
31.	Quantum Efficiencies of Products for all Ketones.	.75

LIST OF FIGURES

Figure	Title	Page
1.	The Photolysis System	9
2.	The Gas Chromatography System	10
3.	Gas Handling System, Auxiliary System, Photolysis Box . .	11
4.	Photolysis Box and Control Panel.	12
5.	Photolysis Box and Oven	13
6.	Gas Chromatography Apparatus and Recorder	14
7.	Wiring Diagram for Thermal Conductivity Apparatus	22
8.	Wheatstone Bridge Circuit	23
9.	Gas Burette	27
10.	Calibration Graph of Chromatography Column for Diethyl Ketone Products	54
11.	Calibration Graph of Partition Column for Di- <u>tert.</u> -butyl Ketone Products	55
12.	Calibration Graph of Partition Column for Propylene in Di- <u>iso</u> -butyl Ketone Products.	56
13.	Calibration Graph of Partition Column for <u>iso</u> -Butane in Di- <u>iso</u> -butyl Ketone Products.	57
14.	Calibration Graph of Partition Column for <u>iso</u> -Butane in Di- <u>iso</u> -butyl Ketone Products.	58
15.	Calibration Graph of Partition Column for 2,5-dimethyl- hexane in Di- <u>iso</u> -butyl Ketone Products	59
16.	Calibration Graph of Partition Column for Ethylene in Di- <u>sec.</u> -butyl Ketone Products	60

LIST OF FIGURES CON'T

Figure	Title	Page
17.	Calibration Graph of Partition Column for <u>n</u> -Butane and 2-Butene in Di- <u>sec.</u> -butyl Ketone Products	61
18.	Calibration Graph of Partion Column for 1-Butene, Propylene, and 3,4-dimethyl-hexane in Di- <u>sec.</u> -butyl Ketone Products	62
19.	Di- <u>tert.</u> -butyl Ketone Photolysis Products vs. Temperature	78
20.	Di- <u>iso</u> -butyl Ketone Major Photolysis Products vs. Temperature	81
21.	Di- <u>iso</u> -butyl Ketone Minor Photolysis Products vs. Temperature	82
22.	Activation Energy Plot for Di- <u>iso</u> -butyl Ketone	86

I. INTRODUCTION

In the area of gas phase photolysis, considerable interest has developed concerning the combination, disproportionation, H-abstraction, and decomposition reactions of simple alkyl radicals of the type CH_3 , C_2H_5 , $n\text{-C}_3\text{H}_7$, and iso- C_3H_7 ¹. Recent data indicate

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1. For a general review of the literature up to 1953 see, E.W.R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp. (1954).
-

that there is a correlation between the structure of the radical and the relative rates of the disproportionation and combination reactions of these radicals.

The mechanism proceeds as follows for the general type of reaction:

Investigations of diethyl ketone $\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$ by Davis², Dorfman and Sheldon³, and Kutschke, Wijnen and Steacie⁴ have resulted in an acceptance of the general mechanism described above.

-
2. Davis, W., Jr., J. Amer. Chem. Soc., 70, 1868 (1948).
 3. Dorfman, L. M., and Sheldon, Z. D., J. Chem. Phys., 17, 511 (1949).
 4. Kutschke, K. O., Wijnen, M.H.J., and Steacie, E.W.R., J. Amer. Chem. Soc., 74, 714 (1952).
-

The ethyl radicals C_2H_5 formed, both disproportionate and combine by reaction paths 2 and 3, and they abstract hydrogen by reaction path 4. Reaction 4 was further studied by Ausloos and Steacie⁵ using ethyl radicals produced by the photolysis of azoethane $(C_2H_5)_2N_2$ and diethyl ketone. Diethyl ketone was also studied by Brinton and Steacie⁶ over a pressure range of 0.01 to 30 mm., between 100 and

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5. Ausloos, P., and Steacie, E.W.R., Bull. soc. chim. Belg., 63, 87 (1954).
 6. Brinton, R. H., and Steacie, E.W.R., Can. J. Chem., 33, 1840 (1955).
-

250°C. with a variation of 1000 fold of the light intensity. Under conditions where the production of C_2H_4 by decomposition of the pentanonyl radical was negligible, i.e., high light intensity and low ketone pressure, the ratio of $k_2/k_3 = 0.12$ and independent of the temperature. The indication here is that both the disproportionation and combination of ethyl radicals are homogeneous and pressure independent for pressures as low as 0.01 mm. The abstraction reaction showed a definite heterogeneous character for low pressures. A comparison of all published data concerning ethyl radical reactions is made in Table 1.

Table 1. The Comparison of the Ratio of Disproportionation to Combination Rates and the Energy of Activation of Hydrogen Abstraction for Ethyl Radicals.

E_2/E_3	$E_4-1/2E_3$	k_2/k_3	Reference
4.8 kcal(?)	4.1 kcal(?)	.25-82 (56-120°C.)	(3)
0	7.3	0.1 (100-250°C.)	(4)
0	7.5	0.1 (100-250°C.)	(4)
	7.6	0.1 (26-178°C.)	(5)
		0.12 (100-250°C.)	(6)

The majority of the data indicate that the ratio of k_2/k_3 is about 0.1 and temperature independent.

Additional work by Wijnen and Steacie⁷ on partially deuterized

7. Wijnen, M.H.J., and Steacie, E.W.R., Can. J. Chem. 29, 1092 (1951).

diethyl ketone ($\text{CH}_3\text{CD}_2\text{COCd}_2\text{CH}_3$), also confirmed the above mechanism. Furthermore, the isotopic distribution of ethane and ethylene formed indicated that the disproportionation of C_2H_5 radicals occurred by a head-to-tail mechanism:

The photolysis of di-n-propyl ketone, $\text{C}_3\text{H}_7\text{COC}_3\text{H}_7$, has been studied by Bamford and Norrish⁸, Masson⁹ and Whiteway and Masson¹⁰.

8. Bamford, C. H., and Norrish, R.G.W., J. Chem. Soc. 1935, 1504; ibid., 1938, 1531, 1544.

9. Masson, C.R., J. Amer. Chem. Soc., 74, 4731 (1952).

10. Whiteway, S.G., and Masson, C.R., J. Chem. Phys. 25, 233 (1956).

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8. Bamford, C. H., and Norrish, R.G.W., J. Chem. Soc. 1935, 1504; ibid., 1938, 1531, 1544.
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They found that there were two primary processes for di-n-propyl

ketone, paths Ia and Ic, and in the secondary processes radicals combine or disproportionate by reaction paths 2 and 3 and abstract hydrogen by reaction path 4. A comparison of the results obtained for k_2/k_3 from the above studies and the reactions from n-butyraldehyde¹¹ photolysis are given in Table 2.

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11. Blacet, F. E., and Calvert, J. G., J. Amer. Chem. Soc., 73, 661 (1951).
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Table 2. A Comparison of the Ratio of Disproportionation to Combination Rates for n-Propyl Radicals.

Temp. °C.	k_2/k_3	Reference
20	0.13	11
25	0.11	11
100	0.136	10
113	0.21 (?)	9
150	0.118	10

The photolysis of di-iso-propyl ketone (iso-C₃H₇)₂CO has been studied by Heller and Gordon¹² and Whiteway and Masson¹³.

-
12. Heller, C. A., and Gordon, A. S., J. Phys. Chem. 60, 1315 (1956).
 13. Whiteway, S. G., and Masson, C. R., J. Amer. Chem. Soc., 77, 1508 (1955).
-

The results of their work indicated that there was only one primary reaction path, namely Ib. RCO appeared to be stable enough to form trace quantities of isobutyraldehyde. The disproportionation and combination reactions proceeded by paths 2 and 3 for temperatures below

100°C. The abstraction reaction could proceed by either 4a or 4b, and the actual values of the rate constants were not known.

The quantum yield of CO = 1 from 50-150°C. as determined by Whiteway and Masson¹³. A comparison of the data from the above work by Heller and Gordon with the reactions of isobutyraldehyde¹¹, azoisopropane¹⁴, and di-iso-propyl mercury¹⁵ to produce iso-propyl radicals is made in Table 3.

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14. Durham, R. W., and Steacie, E.W.R., Can. J. Chem. 31, 377 (1953).
 15. Chilton, J.T.J., and Gowenlock, B.G., Trans. Faraday Soc., 49, 1451 (1953).
-

Table 3. A Comparison of the Ratio of Disproportionation to Combination Rates for iso-Propyl Radicals.

Source of Radical	k_2/k_3	Temp. °C.	Reference
<u>iso</u> -C ₃ H ₇ CHO	0.49	25	11
(<u>iso</u> -C ₃ H ₇) ₂ N ₂	0.49	30-81	14
(<u>iso</u> -C ₃ H ₇) ₂ CO	0.51	100	12
	0.57	150	12
Hg(<u>iso</u> -C ₃ H ₇) ₂	0.52	255	15

The residual radical (C₃H₆COC₃H₇) produced as a result of the hydrogen abstraction by the iso-propyl radical from di-iso-propyl ketone appeared to be stable at low temperatures and disappeared from the system by combination reactions. Above 100°C., the explanation became considerably more complex due to the onset of many competing reactions. For example, C₃H₆, CO, and C₃H₈ were produced by chain

mechanisms above 200°C.; at temperatures greater than 350°C. the iso-propyl radical C_3H_7 decomposed to yield C_3H_6 and H.

The photolysis of di-sec.-butyl ketone and di-tert.-butyl ketones was previously studied by Glazebrook and Pearson¹⁶ to prove that free radicals participate in the photolysis reactions. The

16. Glazebrook, H. H., and Pearson, T. G., J. Chem. Soc., 1937, 567.

results of this work were only qualitative; therefore, no measure of disproportionation to combination was made.

The only measurement for the rate of disproportionation to combination for butyl radicals has been made by Gruver and Calvert¹⁷ using 2-methylbutanal as a source of sec.-butyl radicals. The

17. Gruver, J. T., and Calvert, J. G., J. Amer. Chem. Soc., 78, 5208 (1956).

secondary reactions for this radical followed the general reaction paths 2 and 3 as do the ketones. The ratio of $k_2/k_3 = 0.61$ at 25°C.

A summary of the best estimates of the ratios for the rates of disproportionation to the combination reactions for the simple alkyl free radicals is as follows:

Radical	k_2/k_3	Temp. °C.
C_2H_5	0.11	100-250
<u>n</u> - C_3H_7	0.13	20-150
<u>iso</u> - C_3H_7	0.52	30-255
<u>sec.</u> - C_4H_9	0.61	25

It is noted that the increasing complexity of the free radical is accompanied by an increase in the rate of disproportionation to combination; i.e., as the molecule has more branching the ratio k_2/k_3 increases. Presumably the increase in the steric hindrance of the more complex radical for combination and the increase in the number of abstractable hydrogen atoms leading to olefin product are the origin of this effect. As a result of the correlation between the structure of the radical and the relative rates of reactions, it was deemed desirable to extend the study to butyl radicals which provided a great range of structural types. The most highly branched radical tert.-butyl and the iso-butyl radical offered an extreme structural difference as related to the disproportionation and combination reactions. In the present work, the photolysis of the dialkyl ketone was used as a source of a given alkyl radical.

II. EXPERIMENTATION

A. Experimental Apparatus

The principal parts of the photolysis, gas transfer and gas chromatography system are diagrammed in Figures 1 and 2 and pictured in Figures 3, 4, 5, and 6.

1. The High Vacuum System.

The high vacuum system consisted of a Welch Duo-Seal Oil Pump, Model 1405H, a three-stage mercury diffusion pump, a 45/50 standard taper joint trap and a 3/8 in. I.D. bore metal vacuum valve (Veeco No. R-25-PSS). The metal valves were connected to the glass components with 3/8 in. O.D. Kovar metal-glass seals.

The Veeco valves were modified by replacing the Neoprene valve seat gaskets with Teflon. The Neoprene "O" rings were replaced with silicone rubber "O" rings and a brass spacer was inserted in the "O" ring groove to give sufficient compression of the "O" rings for high vacuum seals.

The photolysis system was connected to the high vacuum, the sample storage, and the gas transfer systems by means of the manually operated metal valves. The metal valves facilitated the handling of organic vapors without adsorption of the vapors by stopcock grease as used with glass vacuum stopcocks.

The ultimate vacuum for the photolysis system was better than 1.5×10^{-5} mm. of Hg. This represented the maximum pressure in the

FIGURE 1
THE PHOTOLYSIS SYSTEM

FIGURE 2. GAS CHROMATOGRAPHY SYSTEM

FIGURE 3 GAS HANDLING SYSTEM, AUXILIARY SYSTEM, PHOTOLYSIS BOX

FIGURE 4. PHOTOLYSIS BOX AND CONTROL PANEL

FIGURE 5 PHOTOLYSIS BOX AND OVEN

FIGURE 6 GAS CHROMATOGRAPHY APPARATUS AND RECORDER

system, since the McLeod gauge was placed at the farthest point from the vacuum pumps and in the region of poorest vacuum.

2. The Auxiliary Vacuum System.

The auxiliary vacuum system consisted of a Welch Duo-Seal Oil Pump, Model 1400B, a two-stage oil diffusion pump, type VMF-10 (CVC), a 45/50 standard taper joint trap, a 12 mm. hollow bore stopcock (V_7) connecting the pumps to the glass vacuum manifold, a thermocouple gauge (T.C.) (RCA No. 1946) and a McLeod gauge. The functions of the auxiliary vacuum system were to operate the mercury manometer (MG) for the Bodenstein gauge (BG) of the photolysis system and to rough pump the gas transfer system and the sample introductory system for the gas chromatography assembly.

Generally this system was operated with only the fore-pump giving an ultimate vacuum of $\sim 5 \times 10^{-4}$ mm. of Hg; the thermocouple gauge (TC) was sufficient as a pressure metering device. When it was necessary to measure the degree of vacuum of the photolysis assembly, the valve to the auxiliary pumping system (V_7) was closed, with the remaining high vacuum, photolysis, gas transfer and auxiliary vacuum systems connected to the vacuum gauge. Under these conditions, the ultimate vacuum at the McLeod gauge was 1.5×10^{-5} mm. of Hg.

3. The Photolysis System.

The system was contained in an air thermostated box and consisted of a photolysis cell, a Bodenstein pressure gauge, a glass in-line circulating pump, a trap, three manually operated metal valves and connecting tubing.

The photolysis cell (PC) was a quartz cylinder, 5.1 cm. O.D. and 30.4 cm. length overall, with connections at the top and bottom of the cell; sealed on the ends were optical grade fused quartz flats.

The Bodenstein gauge (BG) was used for measuring the pressure of the vapor being studied in the vacuum system. The gauge consisted of a hollow quartz spiral with a pointer on one end and connected at the other by a quartz-glass graded seal to the photolysis system. Also attached to the Pyrex tube was another pointer arm used as the reference index for the moving part of the gauge. The spiral and pointer were sealed into a Pyrex jacket which was connected to a mercury manometer (MG). The gauge was used as a null instrument. The null point was observed through an aperture in the side of the box by means of a telescope mounted outside the thermostat box. The manometer could be evacuated through the stopcock (V_4) connected to the auxiliary vacuum system or the pressure could be increased by operating the stopcock(V_5) which opened to the atmosphere. The pressure differential was then read by eye.

The glass in-line circulating pump (P) was constructed of a sealed hollow glass plug filled with soft iron filings and a ground glass valve stem and valve seat. The purpose of this pump was to keep the vapors in the photolysis system moving freely and prevent a build up of products in the photolysis cell while the sample was being irradiated. The pump was operated by energizing a solenoid which was mounted concentric to the magnetic piston. Thus, the piston was pulled

into the field of the solenoid creating a partial vacuum between the valve and piston, and raising the valve from its seat and allowing the vapor to flow into the vacuum momentarily. The valve then seated itself again and as the solenoid field was again de-energized the piston was allowed to fall forcing the vapors to pass around the piston. This cycle was repeated several times per minute resulting in a current of vapors flowing around the photolysis system. The A.C. current to operate the solenoid was supplied and controlled by a Variac and Gem Flasher. A fixed rate of cycling of about 20 cycles/min. was obtained in this fashion.

The glass trap (T_1) was used to freeze-out all condensible vapors after the photolysis run was completed, thus allowing the non-condensable vapors, at liquid nitrogen temperatures, to be pumped off by means of a Toepler pump (TP). The condensible fraction was then allowed to warm and be trapped elsewhere for analysis by gas chromatography.

The three metal Veeco valves (V_1 , V_2 , V_3) were manually operated from outside the thermostat box. These three valves controlled the transport of vapors in the photolysis system.

4. The Product Transfer System.

This system consisted of the trap contained in the photolysis assembly T_1 , valve V_2 , stopcock V_6 , a three-way stopcock V_{11} , the Toepler pump (TP), the gas chromatography sample trap (T_2) and connecting tubing. This system also served as a connection between the photolysis and auxiliary vacuum systems. For the non-condensable

fraction of vapors at liquid nitrogen temperatures the three-way stopcock was opened to the Toepler pump. This fraction of vapors was pumped into a glass reservoir R and stored over mercury until the sample was analyzed by the mass spectrometer. The condensible fraction of the products was trapped in the introductory part of the gas chromatography apparatus as the vapors were driven from the heated photolysis system.

5. The Reactant Introduction System.

This portion of the apparatus (SS) was maintained under partial vacuum at all times with the sample frozen at Dry-ice-acetone temperatures and was isolated by valve V_3 from the photolysis system. To introduce a sample to the photolysis system the Dry-ice-acetone trap was removed from the sample and the sample allowed to warm to room temperature; then the vapor of the sample was driven into the photolysis system by applying hot water to the sample. The vapor pressure was measured by means of the Bodenstein gauge and manometer.

6. The Optical System.

This assembly (Figure 1) consisted of a light source, a shutter, a quartz focusing lens, an optical stop, two quartz flats, the photolysis cell and a glass flat.

The source of radiation was a mercury arc used as a full arc without chromatic filtering.

The light source (LS) was a Hanovia burner Type A., operated at 3.1 amperes and 162 volts from a transformer in series with a

Sorenson A.C. voltage regulator (1000 S). The Sorenson regulator was supplied by line voltage and the output was regulated to ± 0.1 percent. The burner was mounted in a brass cylinder; the exterior wall was wrapped with 1/4 inch copper tubing for water cooling the housing. The light interval was controlled by a shutter mounted at the front aperture of the lamp housing.

The transmitted light was focused by the quartz lens (L), focal length 4 inches, to give a slightly diverging beam through the photolysis cell. The lens mounted in the wall of the thermostat box focused the light and acted as a thermal barrier.

The optical stop (s) used to control the aperture of the lens (L) was mounted on the end of the oven between the lens and the quartz flat (W) which capped the open end of the oven (O).

The quartz flats (W) were mounted on the open ends of the oven to facilitate the regulation of the oven temperature and transmit the light beam.

The glass flat mounted on the inside wall of the thermostat box was used to seal the box and allow observation of the light beam through the photolysis cell.

7. The Temperature Control System.

The entire photolysis system was contained in an air thermostat box. The box was constructed of cement-asbestos (Transite) on the inside and fiberboard (Masonite) on the outside with a 1 in. dead air space between. Two opposing ends of the box were removable and held

in position with wing nuts and screws. The back wall was fitted with a small removable door of the same construction to permit access to the photolysis system trap (T_1). The purpose of this box was to prevent the condensation of vapors in the photolysis system outside the oven by maintaining the temperature at $100 \pm 1^\circ\text{C}$.

Heat was supplied to the box constantly by a 1000 watt (Chromalax) heater. A 75 watt (Chromalax) heater was connected in series with a bimetallic thermoregulator (Fenwal) and placed in the path of the air coming from a circulating fan. The temperature of the box was recorded using an iron-constantan thermocouple.

The oven (O) for thermal control of the photolysis cell was operated independently of the thermostat box. The construction details of this oven are described in Robert M. Smith's dissertation¹⁸.

18. Robert M. Smith, doctoral dissertation., The Ohio State University, (1955), p. 13.

The voltage to the oven was controlled by a Variac supplied by a Sorenson A.C. voltage regulator (1000S) accurate to ± 0.1 per cent. This permitted thermal regulation of the oven and cell to any desired temperature in the region $100\text{--}325^\circ\text{C}$. The degree of regulation was within $\pm 1^\circ\text{C}$. at 325° . Thermocouples were placed at the bottom front and top rear of the photolysis cell so that an average oven temperature could be recorded. The two halves of the oven were mounted on tracks to permit removal of the cell when necessary.

8. The Gas Chromatography System.

This assembly consisted of a helium gas source, a pressure regulator, a manometer, a surge tank, a thermal conductivity cell, a sample introduction system, a gas chromatography column, a spiral glass trap, a flow meter and an electronic strip chart recorder. See Figures 2, 6, 7, and 8.

The flow conditions were controlled by a pressure regulator V_{16} and a metal needle valve V_{15} , and any pressure changes in the system were minimized by the surge tank (ST). The helium pressure of the column was measured by a mercury manometer (MG) with the flow rate of helium through the apparatus measured by a moving bubble flow meter (F).

The sample introduction system was controlled by stopcocks V_{11} , V_{12} , V_{13} , and V_{14} . For normal methods of calibration a sample carrier, described by R. M. Smith¹⁹, containing the sample was connected to the E joint and any air in the system was pumped off by the

19. Robert M. Smith, ibid., (1955) p. 16.

auxiliary vacuum system through the valve V_{11} . After the vacuum had been achieved in the introduction system, as measured by the T.C. gauge, the valve V_{11} was closed. The carrier was opened to the introduction system and liquid nitrogen used to trap the sample in T_2 . The sample was transferred to the gas chromatography column by re-routing the flow of helium through the trap T_2 with simultaneous warming of the trap by a warm water bath at 60°C. Normal positions

FIGURE 8. WHEATSTONE BRIDGE CIRCUIT

for the valves V_{13} and V_{14} were such that the helium by-passed the introduction system unless a sample was introduced to the chromatographic column.

Generally the flow system was from the helium tank through valves V_{16} and V_{15} to the reference side of the thermal conductivity cell (TC) (Gow-Mac Model NRL) then to the gas chromatography column (CC). After passing through the gas chromatography column, the helium gas was returned to side "X" of the thermal conductivity cell and exhausted to the atmosphere by subsequent passage through the trap T_3 and the flow meter (F).

The gas chromatography column (CC) was constructed of 5 mm. I.D. Pyrex glass tubing formed into U-shaped tubes, 1 meter length, connected together with glass and Tygon tubing. The column packing consisted of a solid phase, either activated silica gel or C-22 firebrick (Johns Manville), with a liquid phase (Dow Therm "A"). The column was suspended inside a glass tube (TH), 6.0 cm. I.D., wrapped with flexible heating tape and the entire tube covered with a Magnesite jacket to serve as thermal insulation for the gas column. The heater voltage was controlled by a Variac and the temperature recorded by a thermocouple.

When it was desirable to obtain one of the pure components, liquid nitrogen was applied to the trap T_3 for the period of time needed to remove the vapor from the helium stream. Thus, the vapors separated on the gas chromatographic column could be subsequently studied by the mass spectrometer for further identification of the component.

The electrical schematic for the thermal conductivity apparatus is given in Figures 7 and 8. The components were a Gow-Mac cell, a 100 ohm. and a 2 ohm. potentiometer, a 250 milliampere D.C. meter, a 6 volt storage battery, one six-prong plug and jack, the connecting wiring and a Brown electronic recorder.

The simplified wiring diagram presents the electrical hook-up as a Wheatstone Bridge circuit with the output signal being transmitted to a recorder. The theory of this analytical method is discussed in Part 2b of the Experimental Procedure.

The sensitivity of the recorder and thermal conductivity cell were determined by the position of a two-position three-pole wafer switch mounted on the Brown recorder. The filament current supplied to the cell was controlled by the 100 ohm. potentiometer in series with a 6 volt D.C. battery which was adjusted to operate at 135 milliamperes. The "base line" on the strip-chart recorder was adjusted by the 2 ohm. potentiometer to any desired position.

The calibration of the recorder and thermal conductivity cell can be electrically accomplished by supplying a 5 or 10 millivolt D.C. signal from a Leeds and Northrup portable precision potentiometer, Type 8662, to the two pole double throw switch at position "Y". See Figure 7.

The flow meter (F) consisted of a Pyrex glass tube 11.0 millimeters I.D. with a flanged jet sealed into the bottom which allowed the helium to rise up the tube. The rate of travel was determined

by placing a commercial bubble solution at the bottom of the column and bubbling helium through the solution. The resulting soap film filled the cross-section diameter of the tube and the rate of climb was measured by the time required to sweep out a given volume.

9. The Calibrated Gas Burette.

This system consisted of a sample reservoir, glass vacuum stopcocks, a mercury manometer and a gas burette. See Figure 9.

The gas burette was equipped with two vacuum stopcocks. The volume was calibrated by filling the burette with mercury, emptying the contents and weighing. The purpose of this burette was the quantitative transference of vapors, which had a low vapor pressure, to the gas chromatography column. The normal procedure for obtaining a sample was to place it in the reservoir, freeze out the sample with dry ice or liquid air and evacuate the reservoir, burette and manometer chamber by means of a fore-pump. The reservoir was then closed off and allowed to warm to room temperature. After the sample was equilibrated, the stopcock to the fore-pump was closed off and the stopcock to the reservoir opened, thus, expanding the vapors into the burette and manometer chamber. The vapor pressure was measured by the manometer and the difference observed by a cathetometer. (Wild No. 45). The sample was isolated in the burette by closing the stopcock between the manometer chamber and the burette, thus allowing the gas burette to be disconnected and subsequently connected to the gas chromatography introductory system.

FIGURE 9 GAS BURETTE

B. Experimental Procedure

1. Chemicals and Reagents.

a. Diethyl ketone (3-pentanone) is a product of the Eastman Organic Chemicals Company, Eastman, Tennessee. The ketone was placed in a system of two bulbs which had been thoroughly flushed with helium. Liquid nitrogen was applied to the sample and the sample bulb sealed off from the atmosphere with a hand torch. The system was degassed by pumping the sample at liquid nitrogen temperature for 30 min. After degassing the sample, the valve V_3 was closed to the vacuum system and the sample was warmed to room temperature then further purified by bulb to bulb distillation with a Dry-ice-acetone bath and intermittent pumping of the system.

b. Di-tert.-butyl ketone (2,2,4,4,-tetramethyl-3-pentanone) is a product of the Edcan Laboratories, South Norwalk, Connecticut. The sample was placed in a system of three bulbs which was flushed with argon and sealed off by a hand torch. Liquid nitrogen was applied to the ketone and the system opened to the vacuum pumps through V_3 . After evacuation, the valve was closed and the sample allowed to warm to room temperature before distilling the ketone. The three bulb distillation which followed permitted the middle one-half of the sample to be isolated.

c. Di-iso-butyl ketone (2,6-dimethyl-4-heptanone), Practical grade, is a product of Eastman Organic Chemicals. The purification of the sample was first done by fractional distillation

as carried out by Mr. J. T. Gruver; b.p., 164-167°C. Because the sample obtained had a slight yellow color, a second attempt was made to purify it using a Wheeler column No. GE-118. The boiling range for this second distillation was 166-167°C. As a check, the ketone was given to Dr. George Kyryacos to be run on a polyethylene glycol gas chromatography column. The chromatograph indicated two light weight fractions present but in very small quantity. Therefore, the sample was sufficiently pure for the photolysis studies. The sample was placed in one of two bulbs and the system thoroughly flushed with argon then sealed off by a hand torch. The sample was frozen at liquid nitrogen temperature and pumped, it was then allowed to warm to room temperature, after closing valve V_3 . The sample was frozen by Dry-ice-acetone and pumped again, warmed to room temperature and distilled from one bulb to another. The high boiling fraction was then stored.

d. Di-sec.-butyl ketone (3,5-dimethyl-4-heptanone) is a product of the Edcan Laboratories. The ketone was placed in a system of two bulbs which had been previously flushed with argon. Liquid nitrogen was applied to the sample and the sample bulb sealed off from the atmosphere with a hand torch. The system was degassed by pumping the sample at liquid nitrogen temperature. Valve V_3 was closed to the photolysis system, after degassing the sample, and the sample was warmed to room temperature. A sample was further purified

by a bulb-to-bulb distillation and intermittent pumping. The first 1/3 of the sample, the low boiling fraction, was distilled off and the system sealed.

e. All of the hydrocarbons of CH_4 , C_2H_6 , C_2H_4 , C_3H_6 , iso- C_4H_{10} , n- C_4H_{10} , iso- C_4H_8 , 1- C_4H_8 , cis-2- C_4H_8 , trans-2- C_4H_8 were research grade chemicals, supplied by the Phillips Petroleum Co., Barttesville, Oklahoma. These chemicals were stored over mercury in glass thimbles until needed.

f. The di-tert.-butyl (2,2,3,3,-tetramethyl butane), the di-iso-butyl (2,5,-dimethyl hexane), and the di-sec.-butyl (3,4,-dimethyl hexane) were hydrocarbons furnished from the API Project RF 572 by Dr. K. Greenlee.

g. The CO used for calibrating purposes was a product of the Matheson Co., Inc., Joliet, Illinois. This was also stored over mercury until used.

h. The Dow-Therm "A" used in preparing the gas chromatography columns was supplied by Dr. George Kyryacos, Dept. of Chemistry., O.S.U. This product was analyzed and found to contain 25 percent biphenyl and 75 percent diphenyl ether.

i. The compressed gases, namely nitrogen and helium were supplied by the Linde Air Products Co., and the Air Reduction Co., respectively.

j. 2-Methylbutanal was furnished by Mr. J. T. Gruver, Dept. of Chemistry, O.S.U., who had previously purified the sample.

The aldehyde was transferred to the photolysis sytem through the gas transfer system; then it was trapped in the photolysis system and thoroughly degassed before a pressure measurement was made.

2. Analytical Procedures.

The products of all the photolyses were obtained in two fractions. The liquid nitrogen fraction, namely CO, was subsequently measured with a Arthur H. Thomas Co. Model 6937-A Blacet-Leighton Apparatus for Micro Gas Analysis. The liquid nitrogen condensates were analyzed by gas chromatography.

a. Liquid Nitrogen Non-condensable Fraction

In experiments with diethyl ketone this fraction was analyzed directly by trapping the reactant and products in trap T₂ (Figure 2) of the gas chromatography system; thus, no measure of the quantity of CO was made with the mass spectrometer.

When di-tert.-butyl ketone was photolyzed the liquid nitrogen fraction yielded only CO which was pumped off by the Toepler pump and stored over mercury. The volume of CO was then measured by the gas burette and an aliquot sample was analyzed by the mass spectrometer. The mass spectrometer was calibrated with a standard volume of CO and the sensitivity for $m/e = 28+$ was determined as divisions per μ l. of sample. The mass spectra were first corrected for the presence of air (by determining 28/32 for a pure sample of air and multiplying this ratio by the peak height (divisions) of O₂ or 32), and then the remainder was calculated as CO in μ l. The presence of small amounts of air in this fraction can be

attributed to the transfer process in handling the sample after photolysis and not a leak in the photolysis apparatus. The calibration samples were alternated with the unknowns and the average values for the sensitivities of CO were used for the calculations. In the case of the NO inhibition runs, the non-condensable fraction was pumped off completely by the vacuum pumps.

The products obtained from the photolysis of di-iso-butyl ketone for the non-condensable fraction were generally CO, CH₄, and occasionally C₃H₆. Again, the total volume of the sample was measured by the gas burette and an aliquot sample taken for analysis by the mass spectrometer. The peak heights for the mass to charge ratio (m/e), of 41, 32, 28, and 15 corresponding to the species C₃H₅⁺, O₂⁺, N₂⁺ + CO⁺ and CH₃⁺ were measured and compared with those of a standard mixture containing C₃H₆, CO and CH₄ after the unknown spectra were corrected for the presence of air. The presence of C₃H₆ was detected in this fraction whenever the level of liquid nitrogen on trap T₁ was allowed to get too low, usually this volume was $\leq 1 \mu\text{l}$.

The photolysis of di-sec.-butyl ketone yielded C₃H₆, C₂H₆, CO and CH₄ as the non-condensable fraction which was pumped off by the Toepler pump and stored over mercury. A qualitative analysis of the products was made by the mass spectrometer as a quantitative measurement was not deemed necessary in this case.

The products of the non-condensable fraction from the photolysis of 2-methylbutanal were pumped off by the vacuum pumps

since only the condensable products were of interest to this study.

b. Liquid Nitrogen Condensates

The products left behind in trap T_1 (Figure 1) after the non-condensable fraction was pumped away, were allowed to warm to the temperature of the thermostat box and oven while simultaneously pumping trap T_2 (Figure 2) by the auxiliary pumping system. The residual pressure for this system was approximately 10^{-4} mm. of Hg before applying a Dewar of liquid nitrogen to trap T_2 . Valve V_2 was then opened allowing the reactants and products to distill into trap T_2 for a period of approximately one hour. The gas chromatography introduction system was then isolated by valve V_{11} .

1. Theory of Gas Chromatography.

The technique of gas chromatography enters this discussion as a mode of separating mixtures of gases or vapors into their elemental compounds since the products of photolysis are many and varied. As a means of simplifying the analytical procedures involved, gas chromatography or vapor-liquid partition chromatography can be utilized to accomplish the separation in one operation. To clarify the picture, several definitions are in order. The term gas chromatography is loosely used to cover all of those techniques in which the moving liquid phase is replaced by a moving gas. Separations accomplished by this method depend upon repeated distillation of the substances being separated between the moving gas and the fixed phase which constitutes a column packing. The fixed phase may

be further classified either as an adsorbent, as is the case in gas chromatography, or an adsorbent-liquid distributed on the surface of an inert substance as in vapor-liquid partition chromatography.

The first gas chromatographic studies were accomplished by using adsorbent columns and a technique known as elution analysis. This technique consists of the introduction of a sample onto the column and a subsequent sweeping of the sample on the column by a stream of gas commonly known as a "carrier". The resultant chromatogram consists of a series of peaks of vapor concentrations as a function of time.

The most important advance in gas chromatography has been the method developed by James and Martin²⁰ known as vapor-liquid partition chromatography. They used a fixed liquid phase

20. James, A. T., and Martin, A.J.P., *Biochem. J.*, 50, 679 (1952).

of silicone fluid and stearic acid, adsorbed on Kieselguhr, for the separation of a series of volatile compounds. The vapors were carried through the column by a carrier gas of nitrogen and their concentrations determined and recorded by means of an automatic burette. This method has been refined and more elaborate means of vapor detection have been employed, namely thermoconductivity cells connected with electronic recorders, thus, giving a resulting differential peak as a function of time.

to a linear relationship between the heat loss of the wire and the concentration of the vapor. The conventional method of operation is to arrange two of these cells in opposition in a Wheatstone bridge circuit with the vapor free gas passing through the reference cell. Thus, so long as the system is operating under a vapor free condition the bridge is in balance and the recorder operates at its so-called "base line". Whenever a sample is introduced to the column, the vapors swept from the column change the thermoconductivity of the gas flowing through the detector, therefore, changing the bridge from its null point causing a potential difference to exist across the out-put of the bridge. This potential difference is then recorded as a peak height on the strip chart recorder.

The efficient operation of the gas chromatography apparatus is dependent upon the constancy of flow of helium through the column and the temperature of the thermoconductivity cell and column. The time required for a given component to be swept through the column to the recorder is commonly called the, "elution time", and the ability of the system to separate two components one from the other is called the "resolution". Both of these items are dependent upon the flow rate of helium and the temperature of the column which also effects the sensitivity of the apparatus. Consequently, each component may be calibrated in the apparatus for a given set of operating conditions yielding a linear relationship between the quantity of sample present as a vapor and the response of the differential detector.

A comprehensive survey of the field has recently been compiled by Phillips²¹.

21. Phillips, C., "Gas Chromatography", Academic Press, Inc., (1956).

The justification for the use of gas chromatography to study the photolysis of ketone systems is best shown by pointing out that these systems normally consist of a large excess of ketone and a small amount of reaction products. Hence, gas chromatography allows the minor components to pass through the column more rapidly than the reactant, resulting in a complete separation for the system.

2. Gas Chromatographic Analyses.

Any sample trapped in the gas chromatography trap T₂ could now be analyzed by the gas apparatus. In operation, the flow of helium through the gas chromatography by-pass line was started and the filament current to the thermoconductivity cell (TC) was turned on and adjusted to 135 milliamperes. The desired rate for the flow of helium was established by regulator valve V₁₅ and measured by the flow meter F. When equilibrium was obtained for this apparatus, the helium was re-routed through trap T₂, the liquid nitrogen removed, and a warm water bath at 60°C. was applied to the trap. This allowed the products and reactant to vaporize and pass on to the gas chromatography column. The identification of each component and the characteristic elution time for each was measured by putting a pure compound through the gas column and comparing the

peaks directly. Blended mixtures of the identified components were then run through the column and compared with the unknown chromatogram.

The diethyl ketone runs yielded products identified as n-C₄H₁₀, C₂H₆, and C₂H₄. The gas chromatography column consisted of a 10 cm. length of silica gel and was operated at a flow rate of 78 ml./min. The peak height (divisions) of each component was compared with the sensitivity for each in μ liters of pure sample/division. The ketone was eluted from the column after a considerable length of time. It was only possible after heating the column to approximately 80°C.

The di-tert.-butyl ketone photolysis yielded products identified as iso-C₄H₁₀, iso-C₄H₈, and 2,2,3,3,-tetramethyl butane. The vapor-liquid partition column consisted of 4 meters length of fire brick impregnated with Dow-Therm "A" and was operated at a helium flow rate of 36 ml./min. The iso-C₄H₁₀ and iso-C₄H₈ were eluted from the column at room temperature; the octane was eluted at a temperature of 80°C and the ketone was eluted after the octane. The NO inhibition runs yielded only one product identified as iso-C₄H₈.

The di-iso-butyl ketone photolyses yielded products identified as C₃H₆, iso-C₄H₈, iso-C₄H₁₀, and 2,5-dimethyl hexane. The vapor liquid partition column was the same as for the di-tert.-butyl ketone runs with a flow rate of 37 ml./min.

The products C₂H₄, C₃H₆, n-C₄H₁₀, 1-C₄H₈, trans-2-C₄H₈, cis-2-C₄H₈, 3-methyl pentane and 3,4-dimethyl hexane were

obtained from the photolysis of di-sec.-butyl ketone. The same vapor-liquid partition column was used as for the two previous compounds with a flow rate of 20 ml./min. for all compounds from C_2H_4 through the cis-2- C_4H_8 and the column at room temperature. The hexane and octane were eluted from the column by increasing the flow rate of helium from 20 to 37 ml./min. and applying heat to the gas column after the appearance of the butanes.

The photolysis of 2-methylbutanal yielded the same products as the di-sec.-butyl ketone. However, the expected product, 3-methyl pentane, could not be determined as the aldehyde was eluted at the same time. The conditions for operation were the same as for the previous compound.

3. Filter Transmissions.

Two neutral density filters used in the photolysis run were calibrated with the Cary spectrophotometer to determine the percentage transmission as a function of wave length. The spectrophotometer was adjusted to 100% transmission for air and scanned from 2000 to 3800 $\text{\AA}$. The filters were then placed in the sample compartment and the same range scanned again. The filters calibrated were those designated as the 56% (2) and the 38% (1) transmission (Table 4).

4. Sample Transmissions.

The three ketones di-tert.-butyl ketone, di-iso-butyl ketone and di-sec.-butyl ketone were checked for the percentage transmission as a function of wave length. Four drops of each compound were placed in a clean quartz sample tube, 10 cm. length, and

III. TABULATION OF DATA

A. Absorbed Light Intensity

The effect of concentration and light intensity becomes more apparent when the rate data are corrected to constant light absorption. The rate data then become proportioned to the quantum yields of the products. In Tables 4, 5, and 6, these calculations are summarized.

In column 2, of Table 4, the spectral energy distribution, for a Hanovia mercury vapor lamp, Type A (S-500), is tabulated as a function of wavelength. Column 3 ($\Psi_0 \times 10^{-2}$), the relative number of quanta radiated by the source, is a product of columns 1 and 2, Columns 4 and 5 show the per cent transmission as a function of wavelength for each of the filters. In column 6 and 7 are tabulated the products of columns 3 and 4 ($\Psi_1 \times 10^{-2}$), where the transmission is expressed as a fraction, and 3 and 5 ($\Psi_2 \times 10^{-2}$), respectively. These two columns, 6 and 7, thus represent the relative number of quanta (filtered) incident on the photolysis cell.

Table 5 shows the tabulated molar extinction (ϵ) coefficients, for each of the ketones used, as a function of wavelength. The experimental conditions are listed at the bottom of the table; all measurements were made in a 10 cm. cell. The expression used for calculating (ϵ) is:

$$-\log_{10} T = E = \epsilon cl$$

where T = transmission expressed as a fraction, c = the concentration in moles/l., and l = path length through the cell in cm. This expression is a variation of the combined laws of Beer and Lambert generally expressed as:

$$\log_{10} I_0/I = \epsilon cl.$$

By applying the ideal gas laws to the vapor of a compound in a gas cell, it is possible to calculate the concentration of vapor as follows:

$$c = n/V = P/RT$$

where, n/V = the concentration in moles/l., P = pressure of the vapor expressed in atms., R = universal gas constant in liter-atmospheres/mole-degree, and T = temperature expressed in degrees absolute.

Once the values are known, it is then possible to calculate the fraction of absorbed light for different pressures, light intensities, and temperatures. The only assumptions involved in these measurements are that the ϵ is temperature independent, and that the arc intensity is constant.

The calculation of the relative amount of absorbed light by a given compound in a specific run requires the following data:

Sample pressure, hence $[R_2CO] = c$.

Path length through the photolysis cell = 30.4 cm.

T was calculated from the measured ϵ at each wavelength. The following relationship exists between T and the fraction of light absorbed (A):

$$1 - T = A.$$

Once A has been calculated, the number of quanta absorbed can be determined by use of the expression:

$$A \times \Psi \times 10^2,$$

which holds for each wavelength. In the final analysis, $A \times \Psi \times 10^2$ are summed over all wavelengths. This summation represents the relative number of quanta absorbed by the compound over all wavelengths for a given photolysis run.

Table 6 shows the tabulated values of $A \times \Psi \times 10^2$, in column 7, for several runs where pressure and light intensity corrections can be applied to the product rates.

Table 4. Full Mercury Arc Composition and Percentage Transmissions for Incident Light.

Wave-length	Radiated Energy (watts)	$\Psi_0 \times 10^{-2}$	Per cent Transmission		Relative Number of Quanta Incident on Cell/sec.	
			Filter No.			
			1	2	$\Psi_1 \times 10^{-2}$	$\Psi_2 \times 10^{-2}$
3130	15.0	47.0	38.4	55.5	18.2	26.0
3025	8.2	24.8	38.8	55.8	9.7	13.9
2967	5.0	14.8	39.0	56.0	5.9	8.3
2894	1.8	5.2	39.5	56.2	2.0	2.9
2804	2.8	7.8	39.9	56.4	3.1	4.5
2652	4.6	12.2	40.0	56.2	4.8	6.9
2571	1.8	4.6	39.2	54.5	1.8	2.6
2537	5.0	12.7	38.3	53.1	4.8	6.8
2482	2.6	6.4	36.5	50.8	2.2	3.2
2400	2.2	5.3	34.8	48.7	1.9	2.6
2380	2.6	6.2	34.5	48.7	2.1	3.1
2320	2.4	5.6	34.3	49.0	1.9	2.8

Table 5. Molar Extinction Coefficients (ϵ) for Ketones as a Function of Wavelength (λ).

Wavelength	ϵ	ϵ	ϵ
3130	18.4	6.17	6.84
3025	24.3	17.4	11.9
2967	25.3	19.3	14.6
2894	24.6	22.0	16.0
2804	19.4	18.6	16.2
2652	10.5	8.08	11.9
2571	6.91	0.33	9.03
2537	2.35	0.0	8.16
2482	4.31	3.67	7.09
2400	3.87	1.42	6.84
2380	3.87	3.67	7.09
2320	4.75	0.0	8.40
<hr/>			
Ketone	di- <u>tert.</u> -butyl	di- <u>sec.</u> -butyl	di- <u>iso</u> -butyl
c.c.moles/l.	2.04×10^{-4}	1.20×10^{-4}	2.06×10^{-4}
Temp.°C.	21.3	22.3	21.5

Table 6. Relative Number of Quanta Absorbed by Ketones as a Function of Pressure and Light Intensity.

Ketone	Run No.	$R_2CO \times 10^3$ moles/l.	Pmm.	I_0	Temp. °C.	Relative No. of Quanta Absorbed/ sec. $A \cdot T \times 10^{-2}$
DTBK	1	0.905	22.0	100	117	87.9
DTBK	2	0.971	23.5	56	115	50.6
DTBK	3	0.963	23.5	39	118	35.2
DTBK	4	0.410	10.0	100	118	53.1
DTBK	5	1.65	40.5	100	119	113.8
DTBK	6	0.884	28.9	100	251	87.3
DIBK	3	1.00	23.8	100	108	74.3
DIBK	4	1.00	23.8	39	109	28.4
DIBK	6	1.02	29.8	100	194	75.1
DIBK	7	1.74	40.6	100	102	103.5
DSBK	1	0.940	21.8	100	98	61.2
DSBK	2	0.987	23.3	39	105	24.5
DSBK	3	1.60	37.4	100	101	82.2

B. Product Analysis

Tables 7, 9, 13, 17, and 19 contain the measured gas chromatographic peak heights of the characteristic peaks of all the products from the ketones and aldehyde runs and the volumes in $\mu\text{l.}$ at standard conditions. The volumes are calculated from the peak heights of the respective tables and sensitivities (K_n) obtained from the reciprocal slopes of the graphs in Figures 10-18 inclusive. The data for the respective graphs and K_n 's are obtained from Tables 8, 10, 14, and 18. A sample calculation is given below.

From Table 7, Run no. 4, the peak height of $\text{C}_2\text{H}_4 = 9.4$ div. and the sensitivity = $3.67 \mu\text{l./div.}$ Therefore, the volume of C_2H_4 is

$$9.4 \times 3.67 = 34.5 \mu\text{l. (STP).}$$

Tables 11 and 15 show the measured mass spectrometric peak heights of the characteristic peaks of all the products from the non-condensable fractions of the photolysis runs and the volumes in $\mu\text{l.}$ at standard conditions. The volumes are calculated from the respective peak heights and the sensitivities obtained from Tables 12 and 16. A sample calculation follows.

From Table 11, Run no. 1 the 28 peak height CO^+ is 321.0 div. and known number 3 taken from Table 12 has a sensitivity = $.0755 \mu\text{l./div.}$ Therefore, the volume of the CO aliquot is

$$321.0 \times .0755 = 24.3 \mu\text{l. (STP).}$$

This result is shown in Table 11, column 3, designated as (a).

Column 4, designated as (b), is the total volume of CO for the run. The total volume of CO = calculated volume of CO (a) expressed as a percentage of the sample taken for mass spectrometric analysis X total volume of gas obtained from the run and measured by the Blacet-Leighton gas burette. For example, the total volume of CO is

$$\frac{24.3}{50.8} (100) (265.2) = 126.7 \text{ } \mu\text{l. (STP).}$$

Table 7. Gas Chromatography Peak Heights and Volumes ($\mu\text{l. STP}$) of Products in Excess Ketone from the Photolysis of Diethyl Ketone.

Run No.	C_2H_4		C_2H_6		$\text{n-C}_4\text{H}_{10}$	
	Div.	Vol.	Div.	Vol.	Div.	Vol.
3	5.2	18.5	23.6	66.6	13.5	144.0
4	9.4	34.5	43.7	123.2	22.6	241.8

Table 8. Gas Chromatography Peak Heights of Knowns in Excess Ketone for Photolysis of Diethyl Ketone and Volumes ($\mu\text{l. STP}$).

Calibration Run No.	C_2H_4		C_2H_6		$\text{n-C}_4\text{H}_{10}$	
	Div.	Vol.	Div.	Vol.	Div.	Vol.
58	12.5	45.5	32.5	92.0	----	----
59	24.6	92.8	49.3	141.8	5.1	53.3
61	----	----	63.1	175.7	15.3	165.3
62	13.7	50.9	33.7	98.5	----	----
63	2.9	15.2	----	----	----	----
64	12.4	37.1	46.2	126.7	8.9	106.3

Table 9. Gas Chromatography Peak Heights and Volumes (μ l. STP) of the Products in Excess Ketone from the Photolysis of Di-tert.-butyl Ketone.

Run No.	<u>iso</u> -C ₄ H ₈		<u>iso</u> -C ₄ H ₁₀		Di- <u>tert.</u> -butyl	
	Div.	Vol.	Div.	Vol.	Div.	Vol.
1	35.4	79.3	40.6	68.6	3.8	9.9
2	22.5	50.4	26.4	44.6	2.9	11.1
3	31.8	71.2	39.9	67.4	4.0	15.3
4	20.7	46.4	22.9	38.7	2.5	9.58
5	49.3	110.4	57.2	96.7	5.0	19.2
6	51.8	116.0	60.3	101.9	6.7	25.7
7	56.8	127.2	65.3	110.4	7.0	26.8
8	20.4	45.7	3.3	5.58	0.6	2.29
9	79.4	177.9	61.0	103.1	4.4	16.9
10	116.0	259.8	140.0	236.6	15.5	59.4
11	60.0	153.0	0.0	----	0.0	---
12	48.9	124.7	0.0	----	0.0	---

Table 10. Gas Chromatography Peak Heights of Knowns in Excess Ketone for Photolysis of Di-tert.-butyl Ketone and Volumes (μ l. STP).

Calibration Run No.	<u>iso</u> -C ₄ H ₈		<u>iso</u> -C ₄ H ₁₀		Di- <u>tert.</u> -butyl	
	Div.	Vol.	Div.	Vol.	Div.	Vol.
66	17.3	39.8	44.2	75.2	---	---
67	40.2	91.0	22.7	38.5	---	---
68	77.2	173.7	89.4	151.4	---	---
72	22.8	52.6	27.4	52.3	18.4	76.4
73	20.8	45.2	26.2	45.2	25.7	95.1
74	----	----	----	----	22.8	88.3
75	24.7	61.1	34.1	61.7	---	---
76	48.7	90.9	28.7	53.0	---	---

Table 11. Mass Spectrometric Peak Heights and Volumes (μl. STP) of CO from the Photolysis of Di-tert.-butyl Ketone.

Run No.	Divisions	Volume		Known No.
		(a)	(b)	
1	321.0	24.3	126.7	3
2	320.0	24.2	68.7	3
3	302.0	22.8	99.9	5
4	239.0	20.3	59.3	6
5	318.0	24.4	144.	7
6	361.0	27.7	137.8	7
7	532.0	40.8	168.	7
8	445.9	20.1	39.1	8
9	1049.4	47.7	209.0	9
10	1221.6	55.6	400.4	9

(a) Measured volume of CO aliquot sample by mass spectrometer.

(b) Total calculated volume of CO for run.

Table 12. Mass Spectrometric Sensitivities of Knowns for the Analyses of CO from the Photolysis of Di-tert.-butyl Ketone.

Known No.	μl. STP/division
3	.0755
5	.0755
6	.0850
7	.0768
8	.0451
9	.0459

Table 13. Gas Chromatography Peak Heights and Volumes (μl. STP) of the Products in Excess Ketone from the Photolysis of Di-iso-butyl Ketone.

Run No.	C ₃ H ₆		<u>iso</u> -C ₄ H ₈		<u>iso</u> -C ₄ H ₁₀		Di- <u>iso</u> -butyl	
	Div.	Vol.	Div.	Vol.	Div.	Vol.	Div.	Vol.
1	10.0	22.9	1.1	3.1	3.4	7.0	1.4	2.7
2	32.4	74.2	1.1	3.1	8.4	17.3	2.3	4.5
3	77.8	178.2	2.0	5.7	15.7	32.3	7.2	14.0
4	86.2	197.4	2.4	6.8	24.2	49.9	7.1	13.8
5	99.2	227.2	9.9	28.2	38.6	79.5	5.8	11.3
6	108.8	302.5	32.4	143.9	71.4	218.5	4.7	22.0
7	129.8	360.8	2.9	12.9	29.4	90.0	11.0	34.4
8	96.0	266.9	1.9	8.4	6.5	19.9	4.1	20.3

Runs 1-5 inclusive were calculated with the results of the early calibration Runs 77-83 inclusive.

Runs 6-8 inclusive calculated with later calibration Runs 84-89 inclusive.

Table 14. Gas Chromatography Peak Heights of Knowns in Excess Di-iso-butyl Ketone and Volumes (μ l. STP).

[illegible]

Table 15. Mass Spectrometric Peak Heights and Volumes (μ l. STP)
of Products from the Photolysis of Di-iso-butyl Ketone.

Run No.	Div.	CO		Div.	CH ₄		Div.	C ₃ H ₆		Known's
		Volume (a)	(b)		Volume (a)	(b)		Volume (a)	(b)	
1	865.2	33.4	33.4	30.5	1.74	1.74	---	---	---	1 and 2
2	993.0	38.3	38.3	71.3	4.1	4.1	11.3	0.7	---	2
3	1605.3	39.3	107.5	22.9	0.9	2.5	6.0	0.2	0.5	3
3	2210.1	29.3	80.1	44.2	0.8	2.2	4.8	0.1	0.3	Avg. 4, 5, 6
4	2498.8	33.1	93.2	35.4	0.63	1.77	---	---	---	Avg. 4, 5, 6
5	2677.6	35.5	151.1	41.3	0.7	3.0	---	---	---	Avg. 4, 5, 6
6	2784.7	36.9	237.0	118.6	2.1	13.5	---	---	---	Avg. 4, 5, 6
7	2765.0	36.6	166.9	32.8	0.6	2.8	---	---	---	Avg. 4, 5, 6
8	2756.6	36.5	123.8	19.0	0.3	1.0	---	---	---	Avg. 4, 5, 6

(a) Measured volume of aliquot sample by mass spectrometer.

(b) Total calculated volume of component.

Table 16. Mass Spectrometric Sensitivities of Knowns for the Analyses of
Products from the Photolysis of Di-iso-butyl Ketone. Expressed
in μ l. STP/division.

Known No.	CO	CH ₄	C ₃ H ₆
1	.0386	---	.0594
2	.0385	.0569	---
3	.0245	.0380	.0382
4	.0121	.0150	.0193
5	.0129	.0183	---
6	.0147	.0198	---

Table 17. Gas Chromatography Peak Heights and Volumes ($\mu\text{l. STP}$) of the Products in Excess Ketone from the Photolysis of Di-sec.-butyl Ketone.

Run No.	C_2H_4		$\text{n-C}_4\text{H}_{10}$		$\text{1-C}_4\text{H}_8$		<u>trans</u> -2- C_4H_8		<u>cis</u> -2- C_4H_8		$(\text{sec.}-\text{C}_4\text{H}_9)_2$	
	Div.	Vol.	Div.	Vol.	Div.	Vol.	Div.	Vol.	Div.	Vol.	Div.	Vol.
1	77.2	158.3	29.0	108.8	12.3	52.4	5.0	25.3	1.3	8.5	6.2	38.6
2	58.4	119.7	22.6	84.8	9.8	41.7	4.2	21.2	1.1	7.2	4.5	28.0
3	105.8	216.9	40.1	150.4	17.1	72.8	9.7	49.0	4.0	26.0	11.0	68.5

Table 18. Gas Chromatography Peak Heights of Knowns in Excess Di-sec.-butyl Ketone and Volumes ($\mu\text{l. STP}$).

Run No.	C_2H_4		$\text{n-C}_4\text{H}_{10}$		$\text{1-C}_4\text{H}_8$		<u>trans</u> -2- C_4H_8		<u>cis</u> -2- C_4H_8		$(\text{sec.}-\text{C}_4\text{H}_9)_2$	
	Div.	Vol.	Div.	Vol.	Div.	Vol.	Div.	Vol.	Div.	Vol.	Div.	Vol.
92	16.4	36.8	8.8	36.8	---	---	---	---	---	---	---	---
93	27.8	61.3	---	---	---	---	---	---	5.9	36.9	---	---
94	---	---	---	---	---	---	7.3	36.9	---	---	---	---
95	---	---	---	---	7.7	36.6	---	---	---	---	---	---
96	80.4	171.0	30.7	118.1	13.9	58.1	5.5	25.3	1.5	9.0	3.4	19.4
97	63.4	126.6	26.1	95.7	---	---	4.3	22.7	---	---	---	---
98	---	---	---	---	10.5	44.6	---	---	1.5	9.6	---	---
100	62.6	121.1	23.7	82.8	10.2	41.5	5.2	23.0	1.5	7.8	5.4	38.1
102	---	---	68.6	230.8	---	---	---	---	---	---	1.8	17.3

Table 19. Gas Chromatography Peak Heights and Volumes (μ l. STP)
of the Products from the Photolysis of 2-Methylbutanal.

Run No.	<u>n</u> -C ₄ H ₁₀		1-C ₄ H ₈		<u>trans</u> -2-C ₄ H ₈		<u>cis</u> -2-C ₄ H ₈		(sec.-C ₄ H ₉) ₂	
	Div.	Vol.	Div.	Vol.	Div.	Vol.	Div.	Vol.	Div.	Vol.
1	62.2	209.6	2.6	11.1	1.5	7.3	0.6	3.9	1.5	9.4

FIGURE 10 CALIBRATION OF VAPOR CHROMATOGRAPHY COLUMN SILICA GEL. O- C_2H_6 , $\square$ - C_2H_4 , Δ - C_4H_{10} , IN EXCESS DIETHYL KETONE. FLOW RATE = 78 ML./MIN.

FIGURE 11 CALIBRATION OF VAPOR-LIQUID PARTITION COLUMN FIREBRICK C-22 + 45% DOW THERM "A". ○ $i\text{-C}_4\text{H}_{10}$, Δ $i\text{-C}_4\text{H}_8$, □ 2,2,3,3-TETRAMETHYL BUTANE IN EXCESS DITERTIARYBUTYL KETONE. FLOW RATE = 37 ML./MIN.

FIGURE 12 CALIBRATION OF VAPOR-LIQUID PARTITION COLUMN FIREBRICK C-22 + 45% DOW THERM "A". $\circ$ C_3H_6 , EARLY CALIBRATIONS; $\square$ C_3H_6 , LATER CALIBRATIONS. IN EXCESS DIISOBUTYL KETONE. FLOW RATE = 37 ML./MIN.

FIGURE 13 CALIBRATION OF VAPOR-LIQUID PARTITION COLUMN FIREBRICK C-22 + 45% DOW THERM "A" $\circ$ i - C_4H_{10} , EARLY CALIBRATIONS; $\square$ i - C_4H_{10} , LATER CALIBRATIONS, IN EXCESS DIISOBUTYL KETONE. FLOW RATE = 37 ML/MIN.

FIGURE 14 CALIBRATION OF VAPOR-LIQUID PARTITION COLUMN. FIREBRICK C-22 + 45% DOW THERM "A". ○ i -C₄H₈, EARLY CALIBRATIONS; □ i -C₄H₈, LATER CALIBRATIONS. IN EXCESS DIISOBUTYL KETONE. FLOW RATE = 37 ML./MIN.

FIGURE 15 CALIBRATION OF VAPOR - LIQUID PARTITION COLUMN
FIREBRICK C-22 + 45% DOW THERM "A". ○ 2,5-DIMETHYL
HEXANE, EARLY CALIBRATIONS; □ 2,5-DIMETHYL HEXANE,
LATER CALIBRATIONS. IN EXCESS DIISOBUTYL KETONE.
FLOW RATE = 37 ML./MIN.

- 09 -

FIGURE 16 CALIBRATION OF VAPOR-LIQUID PARTITION COLUMN FIREBRICK C-22 + 45% DOW THERM "A"
 C_2H_4 IN EXCESS DISECONDARYBUTYL KETONE Flow rate = 20 ml./min.

- T9 -

FIGURE 17 CALIBRATION OF VAPOR-LIQUID PARTITION COLUMN FIREBRICK C-22 + 45% DOW THERM "A". $\bigcirc$ $n\text{-C}_4\text{H}_{10}$, Δ $2\text{-C}_4\text{H}_8\text{-cis}$, $\square$ $2\text{-C}_4\text{H}_8\text{-trans}$ IN EXCESS DISECONDARY-BUTYL KETONE. FLOW RATE = 20.0 ML/MIN.

- 62 -

FIGURE 18 CALIBRATION OF VAPOR-LIQUID PARTITION COLUMN
FIREBRICK C-22 + 45% DOW THERM "A" O 1-C₄H₈, Δ C₃H₆,
□ 3,4-DIMETHYL HEXANE IN EXCESS DISECONDARYBUTYL
KETONE. FLOW RATE = 20 ML./MIN.

IV. RESULTS AND DISCUSSION

The necessary data for calculation of reaction rates and rate functions are tabulated in Tables 7-19 inclusive. A sample calculation is outlined below.

A. Sample Calculation

A calculation for di-tert.-butyl ketone photolysis, Run no. 4, is made as follows:

Sample pressure of ketone = 10.0 mm. of Hg.

Temperature of oven = 118.1°C. or 391.3°K.

The original concentration of ketone $[R_2CO]$ in moles/c.c. is calculated by use of the ideal gas law,

$$[R_2CO] = \frac{n}{V} = \frac{P}{R \cdot T} \frac{\text{moles}}{\text{c.c.}}$$

where P is the pressure in atmospheres, R is the gas constant in c.c.-atms./mole-degree K, and T is the oven temperature in degrees absolute or Kelvin. Therefore,

$$\begin{aligned} [R_2CO] &= \frac{10.0}{(760) (82.06) (391.3)} \\ &= .410 \times 10^{-6} \frac{\text{moles}}{\text{c.c.}} \end{aligned}$$

The rate of product formation again uses the ideal gas law for calculation, i.e.,

$$R_x = \frac{n}{V_c \cdot t}$$

where n, is the number of moles of product formed in t seconds

in a reaction cell of volume V_c (in c.c.) and $n = P V / R T$,
therefore, the expression obtained is,

$$R_x = \frac{P \cdot V}{R \cdot T \cdot V_c \cdot t} \frac{\text{moles}}{\text{c.c. sec.}}$$

Data from gas chromatography Run no. 4, Table 9 is tabulated below:

Substance	Volume (μ l. STP)
<u>iso</u> -C ₄ H ₈	46.4
<u>iso</u> -C ₄ H ₁₀	38.7
DTB	9.58

When this data is substituted into the above rate equation with
the additional data,

$$V_c = 420 \text{ c.c.}$$

$$t = \text{irradiation time in seconds} = 600.0 \text{ sec.}$$

we obtain,

$$R_{\text{iso-C}_4\text{H}_{10}} = \frac{(1)(38.7) \times 10^{-6}}{(.0806)(273.2)(420)(600)}$$

$$= \frac{(1)(38.7) \times 10^{-6}}{5.64 \times 10^{-6}}$$

$$= 6.86 \times 10^{-12} \frac{\text{moles}}{\text{c.c. sec.}}$$

$$R_{\text{iso-C}_4\text{H}_8} = \frac{(1)(46.4) \times 10^{-6}}{5.64 \times 10^{-6}}$$

$$= 8.23 \times 10^{-12} \frac{\text{moles}}{\text{c.c. sec.}}$$

$$R_{\text{DTB}} = \frac{(1)(9.58) \times 10^{-6}}{5.64 \times 10^{-6}}$$

$$= 1.70 \times 10^{-12} \frac{\text{moles}}{\text{c.c. sec.}}$$

The rates calculated above are tabulated in Table 21.

A calculation of the estimated quantum efficiency Φ for the same run is also given. Table 6 gives $A \cdot \Psi \times 10^2 = 53.1$ and from Table 21 the rate of formation of CO, $R_{CO} = 10.5 \times 10^{-12}$ moles/c.c. sec. The quotient,

$$\frac{R_{CO}}{A \cdot \Psi} = \frac{10.5 \times 10^{-12}}{53.1 \times 10^{-2}} = 1.98 \times 10^{-14} \frac{\text{moles}}{\text{quanta c.c. sec.}}$$

may be described as the relative quantum efficiency. Referring again to Table 31, note that this has been done for six additional runs and similar results were obtained. These numbers were then averaged with the assumption that $\Phi_{CO} = 1.0$ for di-tert.-butyl; the average value obtained = 23.3×10^{-14} . All of the relative quantum efficiencies calculated by the above expression $R_x/A \cdot \Psi$ were then normalized by dividing the quotients by 23.3×10^{-14} . Thus, the estimated overall quantum efficiencies Φ 's

$$\Phi_n = \frac{R_x}{A \cdot \Psi} / 23.3 \times 10^{-14}$$

were calculated and are tabulated in Table 31.

B. Tabulated Results

1. Diethyl Ketone Photolysis.

The product rates for these runs are tabulated in Table 20, and the ratio of the rate of disproportionation to combination is included. This ratio,

$$k_2/k_3 = R_{C_2H_4}/R_{C_4H_{10}},$$

has an average value of 0.135.

2. Di-tert.-butyl Ketone Photolysis.

The product rates for these runs are given in Table 21 and plotted in Figure 19; as the rate of product formation versus the temperature, °C. In Table 22, the ratio of the rate of combination to disproportionation is tabulated as a function of temperature, light intensity and ketone concentration. This ratio of

$$k_3/k_2 = R_{C_8H_{18}} / \text{average value of } R_{C_4H_8} \text{ and } R_{C_4H_{10}}$$

has an average value of 0.22. Table 23 gives the tabulated results for the rate of product formation as a function of pressure. The starred values (*) were NO pressurized runs made to decide whether the reaction proceeded by a free radical mechanism or involved an intramolecular mechanism. Table 24 gives the rates of product formation as a function of light intensity(I_0).

3. Di-iso-butyl Ketone Photolysis.

The product rates are given in Table 25 and plotted in Figures 20 and 21 versus the temperature, °C. The ratio of combination to disproportionation (i.e., k_3/k_2) is tabulated in Table 26, as a function of temperature, light intensity and concentration. The ratio of

$$k_3/k_2 = R_{C_8H_{18}}/R_{C_4H_8}$$

and has an average value of 2.39 for Runs 3, 4, 7, and 8. Table 27 shows the tabulated values for the ratio of H abstraction to combination, that is $k_4'/k_3^{1/2}$ as a function of temperature and

ketone concentration. The ratio

$$\frac{k_4'}{k_3} I^{1/2} = \frac{R_{C_4H_{10}} - R_{C_4H_8}}{R_{C_8H_{18}}^{1/2} [R_2CO]}$$

where, $R_{C_4H_8} = R_{C_8H_{18}} (T > 110^\circ C.) \times \frac{R_{C_4H_8}}{R_{C_8H_{18}}} (T \leq 110^\circ C.)$

and, $\frac{R_{C_8H_{18}}}{R_{C_4H_8}} (T \leq 110^\circ C.) = 2.39.$

A plot of $\log_{10}(k_4'/k_3)^{1/2}$ versus $1/T$ is shown in Figure 22, and the straight line shown is a result of a least squares treatment of the data. The calculation gave a value for

$$k_4'/k_3^{1/2} = 2.64 \times 10^4 e^{-7.6/RT}.$$

Table 28 shows the tabulated results for the rates of C_3H_6 , CH_4 , and CO as a function of temperature and light intensity.

Table 20. Diethyl Ketone Photolysis with Full Arc; Product Rates and the Ratio of the Rate of Disproportionation to Combination.

Run No.	Run time sec.	I_0	Pmm.	Temp. °C.	[R ₂ CO] moles/ c.c. X 10 ⁶	Product Rates, moles/c.c. sec. X 10 ¹²			k_2/k_3
						R _{C₂H₄}	R _{C₂H₆}	R _{C₄H₁₀}	
3	600	100	56.0	108.2	2.35	3.27	11.8	25.5	.128
4	1200	100	56.0	109.3	2.34	3.05	10.9	21.4	.143

Table 21. Di-tert.-butyl Ketone Photolysis with Full Arc; Product Rates.

Run No.	Run time sec.	I_0	Pmm.	Temp. °C.	[R ₂ CO] moles/ c.c. X 10 ⁶	Product Rates, moles/c.c. sec. X 10 ¹²			
						R _{CO}	R- <u>iso</u> -C ₄ H ₁₀	R- <u>iso</u> -C ₄ H ₈	R-C ₈ H ₁₈
1	600	100	22.0	117.0	0.905	22.5	12.2	14.0	2.57
2	600	56	23.5	114.9	0.971	12.2	7.89	8.92	1.96
3	1320	39	23.5	117.6	0.963	8.04	5.44	5.74	1.23
4	600	100	10.0	118.1	0.410	10.5	6.86	8.23	1.70
5	660	100	40.5	119.0	1.65	25.2	16.9	19.3	3.36
6	900	100	28.9	250.7	0.884	16.3	12.0	13.7	3.30
7	900	100	26.3	178.0	0.935	19.8	13.0	15.0	3.16
8	1200	0	----	322.2	0.897	----	0.49	4.04	----
9 ^a	1292	100	33.2	321.8	0.895	16.0	11.0	10.8	2.00
10	1300	100	23.2	102.0	0.985	23.6	14.0	15.3	3.50
11 ^b	600	100	23.2	104.8	0.983	----	0.0	27.1(?)	0.0
12 ^c	600	100	23.8	106.9	1.00	----	0.0	22.1(?)	0.0

a. Rates corrected for thermal decomposition; results can be considered only approximate.

b. P_{NO} = 29.3 mm.

c. P_{NO} = 10.5 mm.

Table 22. Ratio of the Rate of Combination to Disproportionation for Di-tert.-butyl Ketone.

Run No.	Temp. °C.	I_0	$[R_2CO]$ moles/ c.c. sec. $\times 10^6$	k_3/k_2
10	102	100	0.99	0.24
1	117	100	0.91	0.20
2	115	56	0.97	0.23
3	118	39	0.96	0.22
4	118	100	0.41	0.23
5	119	100	1.65	0.19
7	178	100	0.94	0.23
6	251	100	0.88	0.26
9	322	100	0.90	0.18

Table 23. Rate of Product Formation as a Function of Pressure for Di-tert.-butyl Ketone. (Full Arc, Approx., 110°C.).

Pmm.	Rate of Product Formation, moles/c.c. sec. $\times 10^{12}$			
	CO	<u>iso</u> -C ₄ H ₁₀	<u>iso</u> -C ₄ H ₈	C ₈ H ₁₈
10.0	10.5	6.9	8.2	1.7
22.0	22.5	12.2	14.0	2.6
40.5	25.2	16.9	19.3	3.4
23.2	23.6	14.0	15.3	3.50
23.2				
29.3*	- - - - -	-0.0	27.1	0.0
23.8				
10.5*	- - - - -	-0.0	22.1	0.0

Table 24. Rates of Product Formation as a Function of Light Intensity for Di-tert.-butyl Ketone Constant. (Temp., 117°C.).

I ₀	Rate of Product Formation, moles/c.c. sec. X 10 ¹²			
	CO	<u>iso</u> -C ₄ H ₁₀	<u>iso</u> -C ₄ H ₈	C ₈ H ₁₈
100	22.5	12.2	14.0	2.57
56	12.2	7.89	8.92	1.96
39	8.04	5.44	5.74	1.23

Table 25. Di-iso-butyl Ketone Photolysis with Full Arc; Product Rates.

Run No.	I ₀	Pmm.	Temp. °C.	Time, [R ₂ CO], moles/ sec. c.c. X 10 ⁶	[R ₂ CO], moles/ c.c. X 10 ⁶	Product Rates, moles/ c.c. sec. X 10 ¹²					
						R _{CO}	R _{CH₄}	R _{C₃H₆}	R _{-iso-C₄H₈}	R _{-iso-C₄H₁₀}	R _{C₈H₁₈}
(1)	100	18.0	102.2	600	0.796	---	---	4.05	---	1.24	---
(2)	100	40.3	102.7	900	1.72	---	---	8.84	---	2.04	---
3	100	23.8	108.2	3570	1.00	3.20	0.074	5.32	0.170	0.961	0.417
4	39	23.8	108.9	9000	1.00	1.10	0.021	2.33	0.080	0.589	0.163
5	100	26.9	155.9	4500	1.00	3.57	0.070	5.94	8.52	2.34	0.426
6	100	29.8	193.9	4500	1.02	5.59	0.050	7.14	3.40	5.16	0.519
7	100	40.6	102.0	4500	1.74	3.94	0.065	8.52	0.304	2.12	0.812
8	100	21.9	78.0	4500	1.00	2.92	0.024	6.30	0.198	0.470	0.479

Table 26. The Ratio of Combination to Disproportionation for Di-iso-butyl Ketone.

Run No.	Temp. °C.	I_o	$[R_2CO]$ moles/ c.c. $\times 10^6$	k_3/k_2
8	78.0	100	1.00	2.42
7	102.0	100	1.74	2.67
1	102.2	100	0.80	0.87
2	102.7	100	1.72	1.45
3	108.2	100	1.00	2.45
4	108.9	39	1.00	2.03
5	155.9	100	1.01	0.48
6	193.9	100	1.02	0.15

Table 27. The Ratio of H Abstraction to Combination for Di-iso-butyl Ketone.

Run No.	Temp. °C.	$[R_2CO]$ moles/ c.c. $\times 10^6$	$\frac{k_4^{1/2}}{k_3}$
3	108.2	1.00	1.22
4	108.9	1.00	1.29
5	155.9	1.01	3.34
6	193.9	1.02	6.73
7	102.0	1.74	1.14
8	78.0	1.00	0.39

Table 28. The Rates of Product Formation for C_3H_6 , CH_4 , and CO as a Function of Temperature and Light Intensity from Di-iso-butyl Ketone.

Run No.	I_0	Temp. °C.	$[R_2CO]$ moles/ c.c. $\times 10^6$	Product Rates, moles/ $\times 10^{12}/I_0$	c.c. sec.	
				$R_{C_3H_6}/I_0$	R_{CH_4}/I_0	R_{CO}/I_0
3	100	108.2	1.00	5.32	0.070	3.20
4	39	108.9	1.00	6.05	0.055	2.86
8	100	78.0	1.00	6.30	0.024	2.92
5	100	155.9	1.00	5.94	0.070	3.57
6	100	193.9	1.02	7.14	0.050	5.59

4. Di-sec.-butyl Ketone Photolysis.

The product rates are tabulated in Table 29, and in Table 30 the ratio k_3/k_2 for the combination to disproportionation reactions, where

$$k_3/k_2 = \frac{R_{C_8H_{18}}}{\sum R_{C_4H_8}}.$$

The ratio of $R_{2-C_4H_8}/R_{1-C_4H_8}$ and the ratio $R_{cis-2-C_4H_8}/R_{trans-2-C_4H_8}$ are also tabulated in Table 30 and the average values are 0.70 and 0.40, respectively.

5. 2-Methylbutanal Photolysis.

The product rates for this compound are also given in Table 29 and the rate of combination to disproportionation is given in Table 30.

6. Estimated Quantum Efficiencies for all Products.

The quantum efficiencies for the products formed from the respective ketones studied are tabulated in Table 32. These Φ 's are shown as a function of temperature, pressure and light intensity.

Table 29. Di-sec.-butyl Ketone and 2-Methylbutanal Photolysis Full Arc;
Product Rates.

Run No.	I ₀	Pmm.	Temp. °C.	Time, sec.	[R ₂ CO], moles/c.c. X 10 ⁶	Product Rates, moles/ c.c. sec. X 10 ¹²						
						n-C ₄ H ₁₀	1-C ₄ H ₈	cis-2-C ₄ H ₈	trans-2-C ₄ H ₈	C ₂ H ₄	C ₈ H ₁₈	C ₆ H ₁₄
1	100	21.8	98.1	4500	0.940	2.57	1.24	0.200	0.597	3.74	0.911	*
2	39	23.3	105.1	7200	0.987	1.25	0.615	0.106	0.313	1.77	0.413	*
3	100	37.4	101.3	4500	1.60	3.55	1.72	0.614	1.16	5.12	1.62	*
1 ^a	100	49.4	102.0	1800	2.11	12.4	0.655	0.230	0.431	---	0.552	-

* C₆H₁₄ or 3-methyl pentane detected but not measured quantitatively.

1^a is the 2-methylbutanal photolysis run.

Table 30. A Comparison of Product Rate Ratios for Di-sec.-butyl
Ketone and 2-Methylbutanal.

Temp. °C.	I ₀	[R ₂ CO] moles/c.c. X 10 ⁶	R _{C₂H₁₈} / Σ R _{C₄H₈}		Σ R _{2-C₄H₈} / R _{1-C₄H₈}		R _{cis-2-C₄H₈} / R _{trans-2-C₄H₈}		Rates in moles/c.c.sec. X 10 ¹²	
			Σ R _{2-C₄H₈}		Σ R _{2-C₄H₈}		Σ R _{2-C₄H₈}		Σ R _{C₄H₈}	
89	100	0.94	0.447	0.643	0.335	0.797	2.037			
105	39.2	0.99	0.399	0.681	0.338	0.419	1.034			
101	100	1.60	0.464	1.03	0.529	1.77	3.49			
102*	100	2.11	0.42	1.01	0.533	0.661	1.316			

* is the 2-methylbutanal run.

Table 31. Estimated Overall Φ 's of Products.

(Di-tert.-butyl Ketone)									
Run No.	Temp. °C.	Pmm.	I ₀	Product Φ's					
				CO	iso-C ₄ H ₁₀	iso-C ₄ H ₈	C ₈ H ₁₈		
4	118	10.0	100	0.85	0.56	0.67	0.14		
1	117	22.0	100	1.10	0.60	0.68	0.12		
5	119	40.5	100	0.95	0.64	0.73	0.13		
10	102	23.2	100	1.10	0.65	0.71	0.12		
2	115	23.5	56	1.03	0.67	0.76	0.17		
3	118	23.5	39	0.98	0.67	0.70	0.15		
6	251	28.9	100	0.80	0.59	0.67	0.16		

(Di-iso-butyl Ketone)									
Run No.	Temp. °C.	Pmm.	I ₀	Product Φ's					
				CO	C ₃ H ₆	iso-C ₄ H ₁₀	iso-C ₄ H ₈	C ₈ H ₁₈	CH ₄
3	108	23.8	100	0.18	0.31	0.055	0.010	0.024	0.004
4	109	23.8	39	0.17	0.35	0.089	0.012	0.025	0.003
7	102	40.6	100	0.16	0.35	0.088	0.013	0.034	0.003
6	194	29.8	100	0.32	0.41	0.295	0.019	0.030	0.003

(Di-sec.-butyl Ketone)									
Run No.	Temp. °C.	Pmm.	I ₀	Product Φ's					
				n-C ₄ H ₁₀	1-C ₄ H ₈	cis-2-C ₄ H ₈	trans-2-C ₄ H ₈	C ₂ H ₄	C ₈ H ₁₈
1	98.1	21.8	100	0.18	0.087	0.014	0.042	0.26	0.064
2	105.1	23.3	39	0.22	0.11	0.019	0.056	0.31	0.073
3	101.3	37.4	100	0.19	0.090	0.032	0.060	0.27	0.085

C. Discussion of Results

The results obtained from the diethyl ketone studies, namely that $k_2/k_3 = 0.135$, are in good agreement with the work recently done⁶ which yielded a value of 0.12. This seemed to be reasonable proof that our apparatus and techniques were operating satisfactorily. The butyl radical studies were then undertaken.

1. A Proposed Mechanism for Di-tert.-butyl Ketone Photolysis.

The following reaction mechanism is proposed for the photodecomposition of di-tert.-butyl ketone. It is suggested that the primary process is

The instability of the RCO radical, at temperatures above 100°C., is such that decomposition into R and CO follows process (Ib) almost without exception. Hence, at the temperatures used in these studies the primary split into free radicals may be described by reaction (Ia) alone. This convention has been followed throughout the discussion. The radicals formed presumably take part in secondary reactions:

Undoubtedly, there are other secondary reactions occurring; however, these must be of minor importance as other products were not determined. The unimportance of the hydrogen abstraction reaction of

tert.-butyl radicals, reaction (4), is demonstrated by the near

constancy of the butane to butene ratio with increasing temperature shown in Table 21 and Figure 19. This rather surprising stability of the tert.-butyl radical probably reflects the strength of the primary C-H bond in the parent ketone and the weakness of the tertiary C-H bond in the product iso-butane.

Reaction path (Ia), appears to be valid as rates of product formation are relatively constant with increasing temperature. See Figure 19. Whereas, if reaction path (Ib)

were important, it would show an increase in rates of product formation with temperature for all components because of the instability of the radical $\text{COC}(\text{CH}_3)_3$ with increasing temperature. The absence of C_3H_6 and C_2H_4 definitely rules out reaction path (Ic).

Further proof that the decomposition proceeded by a free radical mechanism was obtained from the NO inhibition runs, Table 23. The reactions proposed for the inhibition runs are:

In the presence of NO, the normal products, iso- C_4H_{10} , C_8H_{18} , were

FIGURE 19 DITERT.-BUTYL KETONE PHOTOLYSIS PRODUCTS.
RATE OF FORMATION VS. TEMPERATURE

absent and the gas chromatography apparatus showed only one peak with an elution time comparable to iso-C₄H₈. Possibly the (CH₃)₃CNO molecule decomposed homogeneously or on the column packing, reaction (9), to yield iso-C₄H₈ and HNO. One alternative possibility is direct H-abstraction from (CH₃)₃C by NO; the reaction (8) above. It was also observed that the R_{iso-C₄H₈} was approximately twice as great as in the uninhibited runs. This is consistent with the suggested mechanism since every tert.-butyl radical reacts to form iso-C₄H₈ in the runs with added NO, and only one-half of the butyl radicals form this product in reaction (2) of the normal runs.

2. A Proposed Mechanism for Di-iso-butyl Ketone Photolysis.

The following reaction mechanism is proposed for the photodecomposition of di-iso-butyl ketone. The possibly primary processes are

The radicals formed presumably take part in secondary reactions:

Again the other secondary reactions occurring must be of minor importance since sizable quantities of other products were not

detected. It should be noted in Table 25 and Figure 20 that the rate of product formation for CO, iso-C₄H₈ and iso-C₄H₁₀ increases with temperature hence indicating a chain mechanism for these products at temperatures greater than 100°C.

There is abundant evidence in the product distribution and rates which favors path (Ia). The presence of C₃H₆ supports the idea that the intramolecular process (Ic) is also important. The small quantity of CH₄ in the products may reflect the occurrence of (Id). Further evidence is shown in Table 28, where the effects of temperature and light intensity on product rates are recorded, and the constancy of the values for C₃H₆ and CH₄ is noted.

3. A Proposed Mechanism for Di-sec.-butyl Ketone Photolysis.

The proposed reaction mechanism for the photodecomposition of di-sec.-butyl ketone has as possible primary processes:

The sec.-butyl radicals formed apparently enter into the secondary reactions:

Secondary reactions occurring, in addition to the above, are those

FIGURE 20 DIISOBUTYL KETONE MAJOR PHOTOLYSIS PRODUCTS. RATE OF FORMATION VS. TEMPERATURE

FIGURE 21 DIISOBUTYL KETONE MINOR PHOTOLYSIS PRODUCTS. RATE OF FORMATION VS. TEMPERATURE.

to produce 3-methyl-pentane, ethane and methane; none of these are tabulated in Table 29, as only a qualitative analysis was made for the presence of each.

The evidence for products derived from the interaction of sec.-butyl radicals suggests reaction (Ia). Reaction path (Ic), seems likely because of the presence of large quantities of C_2H_4 in the reaction products. The production of C_2H_5 radicals appears as a possibility due to the presence of both ethane and 3-methyl-pentane in the reaction products. The formation of methane in the products presumably follows reaction (Id').

The reaction mechanism for the photodecomposition of 2-methylbutanal will not be discussed in detail as it has been previously published by Gruver and Calvert¹⁷.

4. The Primary Quantum Efficiencies for Di-butyl Ketones.

No direct measure of quantum efficiencies could be made in the present studies. The desired maximum light intensities which favor high radical concentrations and radical-radical interactions are obtained through the use of the full spectrum of the mercury arc. Approximate values of the average quantum efficiency of the various processes over the wavelengths used are derived assuming $\Phi_{CO} = 1.0$ for di-tert.-butyl ketone photolyses at temperatures over 100°C. This appears to be justified in view of the results of Whiteway and Masson¹⁰ from di-iso-propyl ketone photolyses. This value and the relative rates of products formed are used to obtain the

estimates for each ketone. At the temperatures where RCO decomposition is complete and there is no appreciable formation of CO in chain reactions (near 100°C.), only reaction (Ia) need be considered for CO formation and RCO is then a measure of the rate of this primary reaction. The efficiencies of primary processes (Ic) are estimated from the rate of C₂H₄ or C₃H₆ formation and that of (Id) from the rate of CH₄ formation.

It is seen that the primary efficiency of radical formation in the di-iso-butyl and di-sec.-butyl ketones is much less than that in the di-tert.-butyl ketone; in these cases the intramolecular processes forming olefin play a very prominent part.

5. Disproportionation, Combination and Hydrogen Abstraction Reactions.

A follow-up on the secondary reactions of the tert.-butyl radical indicates that there are no chain mechanisms operating. This is evidenced by the relative temperature independence of the product rates and also the constancy of the rate of combination to disproportionation with temperature, pressure and light intensity; k_3/k_2

has an average value of 0.22. In Table 31, the estimated quantum efficiencies also indicate that the products formed are not temperature, pressure or light intensity dependent.

Iso-butyl radicals present a somewhat more complex series of secondary reactions as shown by the variety of products in Table 25. The data indicate a considerable temperature dependence for the rate of formation of iso-butane and iso-butene. The quantum efficiency also reflects this same trend. It should be noted that the rate of formation for octane is temperature independent. Examination of the ratio of octane to iso-butene rates reveal a large decrease for temperatures greater than 110°C. This same effect is observed when the ratio of hydrogen abstraction to combination ($k_4/k_3^{1/2}$) is studied as a function of temperature. Therefore, only the k_3/k_2 values = 2.39 for $T < 110^\circ\text{C}$., are a true measure of the disproportionation to combinations; these are averaged to obtain a representative value for this radical. This average value is then used to correct the iso-butane rates for the hydrogen abstraction reaction as described in section B-3. A linear least squares treatment of the data shown in Figure 22 yields the relation:

$$k_4/k_3^{1/2} = 2.64 \times 10^4 e^{-7.6/RT} (\text{c.c./mole sec.})^{1/2}.$$

An estimate made by Trotman-Dickenson and Steacie¹ for the reaction

is $k_{11}/k_{12}^{1/2} = 1.5 \times 10^4 e^{-7.6/RT} (\text{c.c./mole sec.})^{1/2}$

FIGURE 22 LOG OF RATE FUNCTION VS. TEMPERATURE FOR DI-ISO-BUTYL KETONE

The agreement between these two experimental data is surprisingly close. Since both reactions (4) and (11) involve the formation of a primary C-H bond and the breaking of a tertiary C-H bond, and since k_3 is probably near equal to k_{12} , this result is not totally unexpected.

The secondary reactions for the sec.-butyl radical are even more numerous than those for the iso-butyl radicals. It should be noted in Table 29 that the products contain three different butene molecules; of these, cis-2-C₄H₈ and trans-2-C₄H₈ show a ratio average of 0.4 which is in agreement with thermodynamic equilibrium composition. The ratio of the rate of combination to disproportionation is relatively constant and invariant with pressure and light intensity; $k_3/(k_2 + k_2') = 0.44$ for an average value. Because of the complexity of the products of the di-sec.-butyl ketone photolysis, it was deemed desirable to use 2-methylbutanal as an independent source of sec.-butyl radicals. It is estimated for this compound that the ratio $k_3/(k_2 + k_2') = 0.42$. In view of the good agreement with the results from the ketone, we can assume that there are no complicating reactions leading to butenes and octane in the ketone experiments. It should also be noted that the quantum yields for the products from di-sec.-butyl ketone show a very small or negligible pressure and light intensity effect. This is consistent with the suggestion that butenes and octane are formed only in reactions (2) and (3), respectively.

6. Summary.

A compilation of the previous data in terms of the ratio of disproportionation to combination, i.e., k_2/k_3 , can be made as follows:

Radical	k_2/k_3	$k_2/k_3(.418)$	No. H abstractable
<u>tert.</u> -C ₄ H ₉	4.59	11.0	9
<u>iso</u> -C ₄ H ₉	0.418	1.0	1
<u>sec.</u> -C ₄ H ₉	2.27	5.4	5

Column 3 is obtained by normalizing column 2, i.e., taking $k_2/k_3 = 0.418$ and dividing this number into the same ratio for the tert.- and sec.-butyl radicals. This is made with the assumption that the activation energy of the combination reaction (3) is equal in all cases, thus, the normalized value is a relative measure of the disproportionation reaction constant (k_2). The correlation between this experimental value and the number of abstractable hydrogen atoms to form an olefin for each of the butyl radicals is excellent. It appears that the dominant factor which determines the rate of the disproportionation reaction of butyl radicals is the probability of formation of the transition state. This probability is directly related to the number of abstractable hydrogens which can be removed from the radical to form a stable olefin. There is a further check on this simple picture. In the

reaction between sec.-butyl radicals, the ratio of the average rate formation of 2-butene to 1-butene in the most reliable runs is 0.66; the ratio of the number of abstractable H-atoms which can lead to 2-butene and 1-butene from sec.-butyl radicals is 0.67. We anticipated some qualitative correlation but the near quantitative relation was totally unexpected. These results provide excellent evidence for the near equality of the rates of combination of the different butyl radicals. This conclusion is somewhat surprising in the light of the suggestion of Trotman-Dickenson, et al.,²² that the combination of tert.-butyl radicals should have

22. Trotman-Dickenson, A. F., "Gas Kinetics," Academic Press, Inc. (1955).

an activation energy of several kcal./mole while the activation energy for the other butyl radical combination is expected to be near zero.

From these results we can predict with confidence that the ratio of k_2/k_3 for n-butyl radicals should be near 0.92.

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AUTOBIOGRAPHY

I, John Walter Kraus, was born in Columbus, Ohio, February 9, 1924. I received my secondary school education in the public schools of Columbus, Ohio, and my undergraduate training at Ohio State University, which granted me the Bachelor of Science degree in 1949, and the Master of Science degree in 1952. After one year in industry, I returned to Ohio State University, where I consulted in mass spectrometric problems and maintained the Department of Chemistry Mass Spectrometer. I held this position for three years while completing the requirements for the degree Doctor of Philosophy.