THE VAPOR PHASE PHOTOLYSIS OF
TRIFLUOROACETONE AT WAVE
LENGTH 3130 Å.

A Thesis

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I. INTRODUCTION

Within the last 25 years, more than 100 papers have combined to describe the photolysis of acetone in exhaustive detail. The majority of the material in these papers could be grouped under two main topics: first, the proposal and proof of the mechanism of decomposition, and second, the study of properties and reactivities of the methyl, CH_3 , and the acetyl, COCH_3 , radicals.

From experiments at temperatures between 0° and 125°C . and at acetone pressures in the range 110 - 150 mm., Noyes and Dorfman¹ proposed the following reaction scheme to account quantitatively for the products formed.

Later an additional reaction which becomes important above 250°C . was suggested² to explain ketene formation at high temperatures.

Trotman-Dickenson and Steacie³ investigated the photolysis at acetone pressures from 3.9 to 100 mm., and at temperatures between 100 and 300°C. At these temperatures the acetyl radical is very short lived. Thus, reactions (a) and (b) become

and reactions (c), (e), and (i) are unimportant. In these experiments the rates of formation of CO, CH₄, and C₂H₆ were in agreement with the scheme of Noyes and Dorfman. More than 100 other investigations have made important contributions to the proof of this mechanism. This is evident in the extensive reviews of the progress^{4,5}.

In more recent years a systematic study of the reactions of methyl radicals was begun by Steacie and coworkers^{3,6,7,8} using acetone as the methyl radical source.

In view of these studies it seemed likely that CF₃COCH₃ would furnish the radical CF₃. Reactions of this radical are becoming increasingly important.

It is the object of this work, then, to study thoroughly the photodecomposition of CF₃COCH₃ in an attempt to establish the mechanism, and to evaluate the relative reactivities of methyl and trifluoromethyl radicals.

II. EXPERIMENTATION

A. Experimental Apparatus

The various systems which constitute the experimental apparatus will be considered separately. These systems are, in the order of their description: the photolysis system, the temperature control system, the optical system, the product removal system, and the high vacuum system.

1. The Photolysis System. Refer now to Figures 1 and 1A. The photolysis system consists of an all glass circulating pump C, a trap D, a quartz cell E, and 8 mm. Pyrex connecting tubing with a total volume of these parts estimated to be 280 cc. The glass circulating pump consists of a cylinder 27 cm. long made of 22 mm. Pyrex tubing with a close fitting Pyrex glass piston sealed about a soft iron bar. At each end the cylinder is tapered to the size of the connecting tubing, and at the bottom of the cylinder is a ground glass valve. The piston is lifted by the activation of a solenoid which is placed around the cylinder. Intermittent current is supplied to the solenoid by an electronic timer⁹, which in turn is connected through a Powerstat to the 110 v. line. The cylinder is operated in a vertical position; thus, when the solenoid is actuated, the piston is lifted suddenly, and the resulting pressure differential causes the gas to lift the glass valve and enter the cylinder. When the

FIGURE 1. PHOTOLYSIS AND GAS HANDLING SYSTEMS

Figure 1A. The Photochemical Apparatus

piston reaches the desired height, controlled by proper placement of the solenoid, the current is cut off. As the valve drops into its seat, the piston falls slowly while the trapped gas diffuses up between the piston and cylinder walls. The trap D (17 cm. long) is made of 25 mm. Pyrex tubing. The cell E, is an all quartz cylinder 5 cm. in length and 3 cm. in diameter with planar quartz windows fused in each end.

2. The Temperature Control System. The reaction temperature is controlled by enclosing the cell in an oven, which consists of two identical halves for easy removal and inspection of the cell. The inner portion of the oven is an aluminum cylinder having an inner diameter of 4.4 cm., and an outer diameter of 9.5 cm. Around the cylinder is wrapped a mica sheet for electrical insulation; around the mica is wrapped resistance wire. The wire is covered with a thick layer of asbestos which is surrounded by a sheet-metal jacket. The extreme outside diameter of the oven is 14.6 cm., and the overall length of both halves combined is 21.6 cm. Thus, a space of more than 8 cm. from the end of the cell to the near end of the oven insures a minimum temperature fluctuation which could be caused by diffusion of heat to the two quartz windows L, at each end of the oven.

A Sorenson a. c. Voltage Regulator, Model 1000-S

provides a stabilized 110 a.c. voltage to a powerstat. The stabilized voltage to the oven can be selected in the range 0-110 v. Oven temperatures can be controlled to within $\pm 1^\circ$ as long as serious room drafts are avoided.

3. The Optical System. The optical system is designed to provide a uniform radiation of $3130 \text{ \AA}$. through the length of the cell. The source used is a Hanovia S-500 type A burner, approximately 10 cm. in length and about 2 cm. in diameter. It is mounted in a brass cylinder with $1/4$ in. copper tubing wrapped and soldered to the outside through which water circulates to provide the means of cooling. A stable 250 v. potential is provided for the arc circuit by connecting the 110 v. line through the Sorenson a.c. Voltage Regulator to a Model 20651 transformer. Then the output of the arc is controlled with a series 50-ohm, 500 w., Ohmite variable resistor. Included in the arc circuit are an a.c. voltmeter and an a.c. ammeter. In all runs in this work the current through the arc is adjusted to 3.0 amp. by means of the resistor. A potential of 150 v. appears across the arc.

The radiations from the arc are passed through a series of filters designed by Hunt and Davis¹⁰ to isolate $3130 \text{ \AA}$. with less than 0.01% extraneous light. The radiation from the arc F (Figure 1) is collimated with a quartz lens G (3 and $3/4$ in. focal length), and passed

through an arrangement of liquid filters contained in a 3-compartment quartz cell H. The cell is 50 mm. in diameter; its two larger compartments are each 50 mm. long and contain NiCl_2 and K_2CrO_4 solutions, respectively. The smaller one is 10 mm. in length and is filled with potassium acid phthalate solution. Included in the filter system is a glass filter I (Corning Red Purple Corex No. 9863), which is 3 mm. thick. From this the $3130 \text{ \AA}$. radiation passes through a quartz lens J (3 and $3/4$ in. focal length), a stop K (25 mm. diameter) which decreases the beam cross-section to approximately the area of the cell, a quartz window L, the reaction cell E, and a second quartz window L. The per cent of light transmitted is measured with a No. 10-210 Aminco Photomultiplier Microphotometer (labeled O). To obtain conditions providing linear response, the intensity is reduced using a Corex Red Purple Glass No. 9863 (labeled N) at the front of the photomultiplier tube housing, and by placing a cell M containing K_2CrO_4 in front of the glass filter.

4. The Product Removal System. Preliminary investigations indicate the following products are noncondensable at dry ice temperature: CO , CH_4 , C_2H_6 , C_2F_6 , CF_3CH_3 , and CF_3H . In addition, the starting material, CF_3COCH_3 , has an appreciable vapor pressure at that temperature. The immediate problem, then, is to effect a complete

removal of all products from the photolysis system, and, avoid any appreciable concentrations of CF_3COCH_3 .

CO and CH_4 could be separated quite easily. At the completion of a photolysis run, liquid nitrogen is placed around trap D (Figure 1) for no less than 30 min. Then, with mercury cut-off valves P and Q closed, R is lowered allowing CO and CH_4 to diffuse to the Toepler pump S. After allowing several minutes for equilibration, a positive nitrogen pressure is applied through stopcock 5, causing the mercury to rise until it traps the CO and CH_4 in the pump. Further increase in pressure forces the gases through the capillary to the mercury reservoir T, where they are collected in small glass thimbles by displacement of mercury. The pumping is continued, each time with equilibration, until collapsing of the bubble in the capillary indicates that CO and CH_4 are completely removed.

Separation of the remaining four products proved quite difficult. Several techniques were attempted and discarded. These involved the removal of the ketone by hydration, by dissolving in concentrated H_2SO_4 , and by reaction with 2,4-dinitrophenylhydrazine in 2 N. HCl in a train using carrier gas.

The method finally developed involves a low temperature distillation. Trap D, is maintained in the range -100 to -110°C . by a system described by Ward¹¹, and then

the products removed as in the CO and CH₄ fraction. The temperature control system includes a copper cylinder which fits around trap D, and contains Skelly Solve "F" which provides better contact for heat transfer. Around the cylinder is placed an unsilvered Dewar, and about this a larger silvered Dewar containing liquid nitrogen. Thus, the trap temperature, which is measured by a thermocouple inside the copper cylinder, can be controlled by adjusting the level of the liquid nitrogen in the outer Dewar. In all runs in this work, this second fraction is removed by making 35 pumps with the Toepler, with trap D in the temperature range -100 to -110°C.

5. The High Vacuum System. The high vacuum system includes the following components connected in series: a Welch Duo-Seal Oil Pump Model 1400-B, a 3-stage mercury diffusion pump, a removable trap with 20 mm. connecting tubing, a 20 mm. hollow bore vacuum stopcock, a main high vacuum line made of 25 mm. tubing, and a McLeod gauge. The latter has a gas trap volume of 500 cc., a 1.0 mm. diameter capillary, and is calibrated according to the method described by Dushman¹². With the system described it is possible to evacuate to about 1×10^{-6} mm.

6. The Sample Carrier. The sample carrier is designed to transfer the products from the glass thimbles, in which they are collected and stored over mercury, to the mass

FIGURE 2. SAMPLE CARRIER

spectrometer for analysis. The sample carrier (Figure 2) consists of a standard taper joint which fits the introduction system of the mass spectrometer, a vacuum stopcock 6, a glass trap which contains the sample, and a side arm made of capillary tubing equipped with a non-vacuum type stopcock 7. The volume of the carrier is approximately 25 cc.

In use the sample carrier is both simple and efficient. With stopcock 7 closed, it is partially evacuated through stopcock 6. Then, with 6 closed, the capillary tip is placed under mercury, and 7 opened until mercury is drawn in to fill the entire capillary. Closing 7, the carrier is completely evacuated through 6, and then 6 is also closed. Then, the capillary tip is dipped under the mercury and brought up inside the thimble which contains the sample. With the tip touching the top of the thimble, stopcock 7 is opened. Immediately, the entire sample is drawn into the carrier and followed over more slowly by the mercury. When the mercury fills the capillary, stopcock 7 is closed. The sample is then in the carrier ready to be introduced into the mass spectrometer.

B. Experimental Procedure

1. Chemicals and Reagents.

a. CF_3COCH_3 is a product of the Caribou Chemical Company of Columbus, Ohio ($b.p. = 21-22^\circ\text{C.}$). Mass

spectrometric analysis indicates some impurity present which is not identified, but it is believed to have a slightly higher vapor pressure than CF_3COCH_3 in the region -100 to -120°C . This fact appeared when several techniques of product separation attempted caused a concentration of the impurity.

The following procedure eliminates the impurity. From 30-40 cc. are distilled into the system to storage bulb A (Figure 1) through an introduction system not shown. Then bulb A is cooled to dry ice - acetone temperature, and then pumped directly by the high vacuum system until only 50-70% of the original sample remains. Periodically, samples are taken with the Toepler pump and placed in the mass spectrometer to follow the purification. In these analyses several mass peaks, which could not arise from CF_3COCH_3 , decrease to very small values while others disappear entirely, thus indicating removal of the impurity. The remaining peaks are at masses expected from the CF_3COCH_3 fragments.

Molecular weight determinations and vapor pressure measurements are made using the purified CF_3COCH_3 . Five molecular weight determinations gave an average value of 116.6. The vapor pressure change with temperature is summarized by six representative points taken from the smooth curve of $\log P_{\text{mm}}$ against $1/T$. (5° , 385 mm.), (-10° , 194 mm.), (-23° , 98 mm.), (-35° , 49 mm.), (-51° ,

18 mm.), (-64° , 6.3 mm.).

b. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Potassium acid phthalate, and K_2CrO_4 , all used in the filter cell solutions, are Mallinckrodt Analytical Reagents.

c. Na_2SO_4 (anhydrous) used in the thermocouple calibration is Baker's Analyzed Reagent.

d. Skelly Solve "F", used in the temperature control of trap D, is a product of the Skelly Oil Company, and has a boiling range of $35-55^{\circ}\text{C}$.

e. Ag_2O , used for the CO determination, is prepared according to the method described by Blacet and coworkers¹³.

f. A 0.1000 N. KMnO_4 solution, used for titration in the uranyl oxalate actinometer, is furnished by the Ohio State University Laboratory Supply Stores, and is standardized against $\text{Na}_2\text{C}_2\text{O}_4$ according to the procedure of the National Bureau of Standards.

g. The uranyl oxalate actinometer solution, prepared by the Ohio State University Laboratory Supply Stores, is 0.002 m. in uranium nitrate, and 0.00985 m. in oxalic acid. Both chemicals are Bakers and Adamson Reagent Grade.

h. $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$, used in actinometer

determinations, is obtained by water recrystallization of a sample of the salt provided by Professor H. H. Sisler of this department.

2. Analytical Methods. The products are obtained in two different fractions with no product appearing in both fractions. Unnecessary complications are avoided by separate analysis of each fraction. All gas volumes mentioned in the analysis are measured with a Model 5937-A Blacet-Leighton Apparatus for Micro Gas Analysis.

a. Liquid Nitrogen Fraction. The liquid nitrogen fraction contains only CO and CH₄. CO is determined by reaction on a Ag₂O bead according to the method of Blacet and coworkers¹³ ($2 \text{ Ag}_2\text{O} + \text{CO} \longrightarrow \text{Ag}_2\text{CO}_3 + 2 \text{ Ag}$). The volume difference found by measuring the fraction before and after CO removal is a direct measurement of CO.

CH₄ is analyzed in a General Electric Analytical Mass Spectrometer. The peak heights obtained at masses 16, 15, 14, and 13 from the run sample, and from a known CH₄ sample of approximately the same size, are measured the same day. From the ratio of the 16 peaks, and the quantity of CH₄ in the known, the amount of CH₄ in the unknown is calculated. CH₄ samples are analyzed in the order: a known CH₄ sample, from 1-8 unknown CH₄ samples, followed by another known CH₄ sample. The average intensity of the 16 mass peaks from the two knowns is used in the unknown

analysis calculation.

b. The Second Fraction. The second fraction contains C_2F_6 , CF_3CH_3 , CF_3H , C_2H_6 , and some CF_3COCH_3 (usually less than 50%). The analysis is made in the mass spectrometer by a method very similar to the CH_4 determination. In this case, the known sample used for peak height comparison is a mixture of C_2F_6 , CF_3CH_3 , CF_3H , and C_2H_6 in about the same relative quantities as obtained in the runs. Each product gives a characteristic mass peak, and no two overlap. The peaks used are: 119 peak for C_2F_6 ($C_2F_5^+$ ion), the 65 peak for CF_3CH_3 ($CF_2CH_3^+$ ion), the 51 peak for CF_3H (CF_2H^+ ion), and the 30 peak for C_2H_6 ($C_2H_6^+$ ion).

The presence of CF_3COCH_3 makes necessary very small corrections on the 65 and 30 mass peaks, and a relatively larger correction on the 51 peak. The magnitude of these corrections is found by analyzing a known sample of CF_3COCH_3 on the same day as the unknowns are analyzed. From the ratio of the 43 peaks in the known CF_3COCH_3 and in the second fraction sample, and from the 65, 51, and 30 peaks in the known CF_3COCH_3 , the respective corrections are calculated.

3. Thermocouples and Their Calibration. Three thermocouples are included with the apparatus. Two are placed inside the oven to measure the run temperature at

Table 1. Thermocouple Calibrations.

<u>Calibration Point</u>	<u>Experimental</u>	<u>Theoretical</u>	<u>Correction</u>
H ₂ O freezing (0°C.)	0.00	0.00	0.00
Na ₂ SO ₄ ·10H ₂ O (32.4°)	1.63	1.71	+0.08
H ₂ O boiling (97.8°)	5.17	5.28	+0.11
Lead melting (327.4°)	17.82	18.08	+0.26

both the front and rear of the photolysis cell. The third is used to measure the temperature of the trap during the removal and collection of the second fraction. The thermocouples are of iron-constantan in circuit with a Rubicon portable potentiometer and a Rubicon spotlight galvanometer. Four points are used in the calibration: the melting point of water, the transition point of sodium sulfate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{SO}_4 + 10 \text{H}_2\text{O}$), the boiling point of water, and the melting point of pure lead. The results are listed in Table 1. An approximate correction of +0.10 millivolts is applied to all potentiometer readings.

4. Actinometer Determinations. Two methods of actinometry are employed; the conventional uranyl oxalate type, and a method using potassium ferrioxalate¹⁴. These require exposure times of 8-12 hrs. and 20-40 min., respectively.

The actinometry runs are carried out in the

Table 2. Summary of Actinometer Data.

<u>Date</u>	<u>Type of Actinometer</u>	<u>Intensity, q./sec.</u>
Nov. 16, 1953	Uranyl oxalate	1.14×10^{15}
Feb. 15, 1954	Uranyl oxalate	0.93×10^{15}
Feb. 24, 1954	$K_3Fe(C_2O_4)_3 \cdot 3H_2O$	1.06×10^{15}
Mar. 5, 1954	$K_3Fe(C_2O_4)_3 \cdot 3H_2O$	1.19×10^{15}
Mar. 15, 1954	$K_3Fe(C_2O_4)_3 \cdot 3H_2O$	1.14×10^{15}

mean intensity = 1.09×10^{15} q./sec.

conventional manner. The rear half of the oven is removed, and the actinometer cell is placed so as to catch all the light coming through the cell. With the quartz window L removed, the 3130 Å. radiations which emerge from the filter system must pass through 3 quartz windows (front and rear of cell, actinometer cell window) before being absorbed by the actinometer solution. During the actual runs the light passes through only 2 quartz windows (window L at front of oven, front of reaction cell). Since the intensity inside the reaction cell E is the quantity to be measured, a correction factor²⁴ of +4% (water-quartz-air interface) is applied in the calculations to compensate for reflection losses by the extra quartz window. The results are listed in Table 2. The mean value of intensity (1.09×10^{15} q./sec.) is used as the lamp intensity I_0 , in all calculations.

III. TABULATION OF DATA

The data from the photochemical runs are compiled in Tables 3-11. Each table will be described in detail, and sample calculations shown.

A. Absorbed Light Intensity

An absorption coefficient is calculated for each run. When a plot is made of absorption coefficients against temperature (Figure 3), the points exhibit a good deal of scatter from the expected straight line. This scatter is believed to be due to instrumental errors, introduced by the photomultiplier microphotometer. In order to avoid such errors, the absorption coefficients are taken from the smoothed curve at the individual run temperatures. Then, using the CF_3COCH_3 pressure and the run temperature, the fraction of light absorbed is calculated.

In Table 3, column 1 gives the run number, column 2 the per cent of light absorbed found experimentally, column 3 the temperature at the start of the run when the light absorption is measured, column 4 the mean run temperature, column 5 the CF_3COCH_3 pressure in mm., column 6 the calculated fraction of light absorbed, column 7 the fraction of light transmitted by standard quartz filters placed in the light path to vary the intensity of the incident light, and column 8 the intensity of the light absorbed in q./cc.-sec.

FIGURE 3. ABSORPTION COEFFICIENT, α , ($I/I_0 = e^{-\alpha cl}$) VS. TEMPERATURE

Table 3. Intensity of Absorbed Light.

Run no.	% Absorption (Experimental)	Start of run, temp., °C.	Mean run temp., °C.	CF ₃ COCH ₃ pressure, mm.	Calc'd fraction I ₀ absorbed	Standard filters % trans.	I _a q./cc.-sec. x 10 ⁻¹³
5	42.3	24.7	25.5	250	0.428		1.32
6	47.5	113.7	113.0	330	0.497		1.54
7	58.0	254.6	254.1	447	0.581		1.79
8	52.2	152.7	152.7	362	0.521		1.61
9	63.0	351.6	351.1	528	0.633		1.95
11	48.9	79.1	78.7	307	0.480		1.48
12	49.0	133.4	135.7	342	0.504		1.56
14	53.8	203.2	205.4	398	0.547		1.69
15	60.5	298.9	298.7	477	0.601		1.86
16	45.5	50.7	49.8	273	0.449		1.39
17	50.5	116.6	116.8	331	0.497		1.54
18	47.0	116.6	117.5	332	0.498	16.3	0.251
19	54.0	116.6	117.3	333	0.500	56.0	0.864
20	54.8	116.6	118.9	333	0.500	38.5	0.592
21	51.4	116.6	115.5	330	0.496		1.53
22	76.2	116.6	117.9	699	0.766		2.37
23	8.0	116.6	117.3	34	0.068		0.210
24	25.0	116.6	116.8	126	0.230		0.711
25	21.0	116.6	117.2	126 *	0.230		0.711
26	42.7	51.1	53.7	273	0.448		1.38

* 406 mm. CO₂ added.

Sample calculations are shown from the data in run no. 6. The experimentally determined absorption coefficient is calculated using the combined laws of Beer and Lambert, $I/I_0 = e^{-\alpha cl}$, from which $\alpha = (RT \ln I_0/I)/lP$. Here, I_0/I is 1/fraction of light transmitted, l is the path length in cm., and $P/RT = c$, the molar concentration where T is the temperature at the start of the run when the transmission is measured. Using data from run 6:

$$\alpha = \frac{\ln (1/0.525) \times 0.08207 \times 387 \times 760}{5 \times 330} = 9.4_3$$

This value is plotted in Figure 3.

The mean temperature of the run is 113.0°C. Thus, the absorption coefficient read from the smooth curve (Figure 3) is 10.0. This value is used to calculate the fraction of light transmitted I/I_0 , again using the combined absorption laws. T now is the mean run temperature.

$$\ln I/I_0 = -\alpha lP/RT$$

$$\ln I/I_0 = - \frac{10.0 \times 5 \times 330}{0.08207 \times 386.2 \times 760}$$

and

$$I/I_0 = 0.50_3$$

The calculated fraction of I_0 absorbed is $1 - I/I_0$, or 0.497. (0.47₅ is measured experimentally in this run.)

Using the mean incident intensity, 1.09×10^{15} q./sec., and the photolysis cell volume, 35.3 cc., one calculates the light absorbed, I_a .

$$I_a = \frac{1.09 \times 10^{15} \times 0.497}{35.3} = 1.54 \times 10^{13} \text{ q./cc.-sec.}$$

B. Product Analysis

Data pertaining to the determination of the products are listed in Tables 4, 5, and 6. In Table 4, column 1 is the run number, column 2 the total run time measured in minutes, column 3 the volume in μ l. of CO at S.T.P. produced in each run. Column 4 gives the height of the 16 mass peak from the CH_4 produced in each run, column 5 the series in which the CH_4 sample is analyzed. The a series contains only CH_4 . All CH_4 samples indicated by 1a are analyzed on the same day with a known sample run at the beginning and at the end of the series in order to determine the sensitivity of the mass spectrometer. Columns 6, 7, 8, and 9 give the height of the peaks used in measuring the amounts of C_2F_6 , CF_3CH_3 , CF_3H , and C_2H_6 , respectively. Column 10 gives the series in which the second fraction of each run is analyzed. All second fraction samples designated 1b are analyzed the same day. Known samples are run at the beginning and at the end of each series to determine the mass spectrometer sensitivity. Those samples marked 2b are analyzed on another day by the

Table 4. Experimental data.

Peak heights from mass spectrometric analysis of products.
(Corrected for presence of CF_3COCH_3)

Run No.	Time of run, min.	CO , ml. S.T.P.	CH_4	CH_4 Analysis Series	C_2F_6	CF_3CH_3	CF_3H	C_2H_6	Sec. Fract. Analysis Series
5	240	1.4	12.0	1a	0.9	1.4	5.2	7.6	1b
6	210	89.2	1142	1a	11.2	43.8	262	116	1b
7	90	147	5725	1a	2.5	6.9	855	778	1b
8	120	122	2250	1a	8.3	25.5	271	156	1b
9	60	187	7222	1a	0.6	1.7	512	1350	2b
10	60	8.0	33.8	2a	-	-	18.1	126	2b
11	240	39.8	534	2a	2.7	9.3	67.2	31.2	3b
12	180	149	3214	2a	9.0	26.8	267	164	3b
13	60	No Products							
14	75	103	3315	2a	2.5	9.1	356	245	3b
15	45	82.4	4103	2a	0.2	2.1	431	533	3b
16	240	7.3	Sample lost in handling						
17	95	59.5	1005	3a	9.1	27.2	404	58.3	4b
18	465	53.2	1203	3a	5.0	8.3	353	61.9	4b
19	150	55.2	1104	3a	5.6	21.6	41.6	67.1	4b
20	180	47.2	917	3a	5.5	14.1	355	65.8	4b
21	90	55.7	564	4a	7.0	25.8	356	63.3	4b
22	60	42.8	443	4a	4.6	9.1	280	47.4	4b
23	488	61.9	173	5a	47.5	66.8	320	95.5	4b
24	180	65.7	311	5a	20.8	58.2	386	89.9	4b
25	180	63.0	907	6a	Analysis impossible, CO_2 present				
26	404	10.7	113	6a	3.1	5.6	140	73.0	5b
28	196.5		352	7a	3.7		74.2	126	6b
29	311.5		136	8a				56.1	7b
30	55.55		4410	9a				705	8b
31	68.5		2828	10a				382	9b

same procedure.

Runs 1-4, which are not included, are preliminary experiments made before a quantitative analytical technique had been developed.

Run 10 is a thermal run carried out at the same conditions of temperature, CF_3COCH_3 pressure, time, etc. as those in run 9. Small amounts of CF_3H , C_2H_6 , CH_4 , and CO are found, and the corrections applied to run 9.

Run 13 is a thermal run carried out at 310°C . Negligible amounts of products are found after a contact time of one hour.

In runs 5-15 the temperature is varied in the range $25-355^\circ\text{C}$.; the CF_3COCH_3 concentration is maintained in the range $8.03-8.42 \times 10^{18}$ molecules/cc.; the incident intensity is constant, and as a result of changes in absorption coefficient, the absorbed intensity varies between $1.32-1.95 \times 10^{13}$ q./cc.-sec.

The products of run 16 were lost in handling.

In runs 17-20 the absorbed intensity is varied from $0.25-1.5 \times 10^{13}$ q./cc.-sec.; the CF_3COCH_3 concentration is maintained at 8.2×10^{18} molecules/cc.; and the temperature is maintained in the range $117-119^\circ\text{C}$.

In runs 21-24 the CF_3COCH_3 concentration is varied between $0.841-17.3 \times 10^{18}$ molecules/cc.; with the incident intensity constant, the absorbed intensity varies with the concentration between $0.210-2.37 \times 10^{13}$ q./cc.-sec.; the

temperature is maintained in the range 117-118°C.

In run 25, 406 mm. of CO_2 are added to the CF_3COCH_3 in the photolysis system. With CO_2 present the second fraction cannot be separated, and only CO and CH_4 are analyzed.

Run 26 is an experiment carried out to give additional information at low temperature (49°C.). The results are considered outside the limit of experimental error, and are discarded.

Runs 28 and 29 are experiments carried out to give additional points for determining activation energy of H atom abstraction by methyl radicals. Only CH_4 and C_2H_6 are measured.

Run 27 was lost in handling.

Runs 30 and 31 are carried out at about 265°C. with the CF_3COCH_3 concentration in run 30 about double that in run 31. These data are to be a test of the mechanism proposed for the H atom abstraction by methyl radicals in the high temperature range. Only CH_4 and C_2H_6 are measured.

In Table 5 the sensitivity of the mass spectrometer, which is determined from the known samples, is listed for each product in each analysis series. Column 1 lists the analysis series, column 2 the CH_4 sensitivity in molecules per unit peak height, columns 3, 4, 5, and 6 the sensitivities of C_2F_6 , CF_3CH_3 , CF_3H , and C_2H_6 , respectively, in the same units.

Table 5. Mass Spectrometer Sensitivity.

Analysis series	Known sample sensitivities in molecules/unit peak height $\times 10^{-15}$				
	CH_4	C_2F_6	CF_3CH_3	CF_3H	C_2H_6
1a	0.537				
1b		2.45	3.82	2.71	2.30
2a	0.441				
2b		2.59	3.91	2.73	2.29
3a	0.428				
3b		2.72	4.11	2.84	2.35
4a	0.790				
4b		2.54	3.22	2.12	4.10
5a	0.866				
5b		0.941	1.30	0.904	1.12
6a	0.233				
6b		0.892	- - -	1.13	1.16
7a	0.292				
7b		- - -	- - -	- - -	1.09
8a	0.224				
8b		- - -	- - -	- - -	1.05
9a	0.234				
9b		- - -	- - -	- - -	
10a	0.241				0.997

Sample calculations are shown for the analysis series designated, 4b. Known I for this series contains 3.69×10^{-6} moles of gas, while known II for this series contains 3.72×10^{-6} moles. The peak heights of known I are multiplied by the ratio $3.72/3.69$ to correct for the difference in amount, and then averaged with known II as shown.

<u>Component</u>	<u>Known I peak ht.</u>	<u>Corrected known I peak ht.</u>	<u>Known II peak ht.</u>	<u>Average peak ht.</u>
C_2F_6	34.8	35.1	38.9	37.0
CF_3CH_3	40.9	41.2	43.8	42.5
CF_3H	605	610	647	628
C_2H_6	161	162	169	164

The known gas mixture, made with the gas buret, consists of 59.5% CF_3H , 30.2% C_2H_6 , 6.1% CF_3CH_3 , and 4.2% C_2F_6 . Therefore, 3.72×10^{-6} moles of the mixture contain the following amounts of each component.

$$3.72 \times 10^{-6} \text{ moles}$$

$$\times 59.5\% = 2.21 \times 10^{-6} \text{ moles } CF_3H$$

$$\times 30.2\% = 1.12 \times 10^{-6} \text{ moles } C_2H_6$$

$$\times 6.1\% = 0.227 \times 10^{-6} \text{ moles } CF_3CH_3$$

$$\times 4.2\% = 0.156 \times 10^{-6} \text{ moles } C_2F_6$$

The sensitivity is calculated from the equation,

$$\text{Sensitivity} = \frac{\text{Moles of component in known} \times \text{Avogadro's No.}}{\text{Peak height of component}}.$$

Then the CF_3H sensitivity is

$$\frac{2.21 \times 10^{-6} \times 6.023 \times 10^{23}}{628} =$$

$$2.12 \times 10^{15} \text{ molecules/unit peak height.}$$

By the same method the C_2H_6 sensitivity is 4.10×10^{15} ; CF_3CH_3 is 3.22×10^{15} ; and C_2F_6 is 2.54×10^{15} . The sensitivity for the a series is calculated in the same manner. In this case the knowns contain only CH_4 .

In Table 6 column 1 gives the run number, column 2 the mean run temperature, column 3 the CF_3COCH_3 concentration in molecules/cc. Columns 4-9 give the rate of formation of C_2F_6 , CF_3CH_3 , CF_3H , C_2H_6 , CH_4 , and CO , respectively. The rates are tabulated in molecules/cc.-sec., and all rates mentioned hereafter will be in those units.

Sample calculations are shown for run 6. The CF_3COCH_3 concentration is calculated using the perfect gas law. Pressures are listed in Table 3.

$$[\text{CF}_3\text{COCH}_3] = P/RT \times \text{Avogadro's No.}$$

$$[\text{CF}_3\text{COCH}_3] = \frac{330 \times 6.023 \times 10^{23}}{760 \times 82.07 \times 386.2} =$$

$$8.25 \times 10^{18} \text{ molecules/cc.}$$

Table 6. Rate of Formation of Products.

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Run no.	Mean run temp., °C.	$\frac{[\text{CF}_3\text{COCH}_3]}{\text{molecules/cc.} \times 10^{-16}}$	Rate of product formation in molecules/cc.-sec. $\times 10^{-10}$					
			CF_3H	C_2H_6	CH_4	CO		
5	25.5	8.08	0.433	1.05	2.77	3.43	1.27	7.54
6	113.0	8.25	6.15	37.7	160	60.1	138	538
7	254.1	8.19	3.23	13.8	1213	938	1612	2080
8	152.7	8.21	7.99	38.5	289	141	476	1290
9*	351.1	8.17	1.12	5.07	1055	2212	3060	3800
11	78.7	8.42	1.44	7.51	37.7	14.4	46.2	212
12	135.7	8.08	6.40	28.9	199	101	371	1050
14	205.4	8.03	4.28	23.5	637	363	921	1740
15	298.7	8.05	00.569	9.04	1283	1315	1895	2320
17	116.8	8.20	11.5	41.9	397	111	213	796
18	117.5	8.21	1.29	2.58	73.9	25.1	52.1	145
19	117.3	8.24	4.48	21.5	270	84.1	149	467
20	118.9	8.20	3.65	11.5	191	68.8	103	334
21	115.5	8.20	9.32	43.1	382	132	234	785
22	117.9	17.3	9.21	22.0	448	147	275	904
23	117.3	0.841	11.6	20.7	64.0	37.7	14.5	161
24	116.8	3.12	13.9	48.7	207	94.1	70.5	465
25	117.2	3.12					55.5	445
26	53.7	8.06	0.340	0.853	14.8	9.49	3.09	33.7
28	68.9	8.52	0.793		20.1	35.1	24.6	
29	45.6	8.27				9.30	4.63	
30	264.5	3.63				612	888	
31	263.1	1.80				269	462	

* Corrections made on CF_3H , C_2H_6 , CH_4 , and CO rates for thermal contributions, determined from run 10, which was a thermal run at the same conditions as run 9.

The rates of C_2F_6 , CF_3CH_3 , CF_3H , C_2H_6 , and CH_4 are calculated from the data in Tables 4 and 5. Calculation of the rate of C_2F_6 production in run 6 is shown.

$$\text{Rate} = \frac{C_2F_6 \text{ peak ht.} \times C_2F_6 \text{ sensitivity}}{\text{cell vol.} \times \text{run time}}$$

$$R_{C_2F_6} = \frac{11.2 \times 2.45 \times 10^{15}}{35.3 \times 1.26 \times 10^4} =$$

$$6.15 \times 10^{10} \text{ molecules/cc.-sec.}$$

The amount of CO produced is measured directly in $\mu\text{l.}$ and converted to standard conditions. The rate then is

$$R_{CO} = \frac{CO, \text{ ml. at S.T.P.} \times \text{Avogadro's No.}}{22,414 \times \text{cell vol.} \times \text{run time}}.$$

Thus, for run 6:

$$R_{CO} = \frac{89.2 \times 10^{-3} \times 6.023 \times 10^{23}}{22,414 \times 35.3 \times 1.26 \times 10^4} =$$

$$538 \times 10^{10} \text{ molecules/cc.-sec.}$$

C. Rate Calculations

Several functions involving rates are calculated. The calculated data in Table 7 are used to determine activation energies for H atom abstraction by CF_3 radicals. The data pertaining to H atom abstraction by CH_3 radicals requires correcting (Table 9) before an activation energy is determined. In Table 7 column 1 gives the run number,

Table 7. Calculated Rate Data.

Run no.	1/T°K. x 10 ³	13 + log R _{CF₃H}	13 + log R _{CH₄}
		$\frac{1}{2} \frac{R_{CF_3H}}{R_{C_2F_6}} [CF_3COCH_3]$	$\frac{1}{2} \frac{R_{CH_4}}{R_{C_2H_6}} [CF_3COCH_3]$
5	3.35	-0.283	-1.071
6	2.59	0.893	0.334
7	1.90	1.915	0.808
8	2.35	1.093	0.688
9	1.60	2.100	0.880
11	2.84	0.572	0.161 *
12	2.45	0.989	0.662
14	2.09	1.584	0.778
15	1.75	2.324	0.812
28	2.92	0.423	-0.313
29	3.14	- - -	-0.735

* Discarded (outside limit of experimental error).

column 2 1/temp.°K., column 3 the logarithm of the rate function $R_{CF_3H}/R_{C_2F_6}^{1/2} [CF_3COCH_3]$, column 4 the logarithm of the function $R_{CH_4}/R_{C_2H_6}^{1/2} [CF_3COCH_3]$.

Sample calculations are shown for run 6. The function 1/T°K. is 1/386.2 = 2.59 x 10⁻³ degrees⁻¹. Substitution of the data in the rate function in column 3 gives

$$\log \frac{160 \times 10^{10}}{(6.15 \times 10^{10})^{1/2} (8.25 \times 10^{18})} = 0.893 - 13 .$$

For the rate function in the 4th column, substitution gives

$$\log \frac{138 \times 10^{10}}{(60.1 \times 10^{10})^{1/2} (8.25 \times 10^{18})} = 0.334 - 13 .$$

In Table 8, the rate data of the high temperature runs is calculated to clarify the mechanism for production of

Table 8. Calculated Rate Data.

Run no.	$1/T^{\circ}K. \times 10^3$	$R_{C_2H_6}$ from chain $\times 10^{-10}$	$\log \frac{R_{CH_4}}{R_{C_2H_6}(\text{chain})}$	$\log \frac{R_{CH_4}}{R_{C_2H_6}^{1/2}(\text{chain})} - 5$
8	2.35	74	0.808	1.743
14	2.09	338	0.435	1.700
7	1.90	925	0.241	1.724
15	1.75	1310	0.161	1.719
9	1.60	2208	0.143	1.814
30	1.86	598	0.170	
31	1.86	253	0.260	

Table 9. Calculated Rate Data.

Run no.	$1/T^{\circ}K. \times 10^3$	$\log \frac{R_{CH_4}}{R_{C_2H_6}(\text{chain})}^*$	$R_{C_2H_6}$ corrected for chain contribution $\times 10^{-10}$	$\log \frac{R_{CH_4}}{R_{C_2H_6}^{1/2} [CF_3COCH_3]}$	$\log \frac{R_{CH_4}}{R_{C_2H_6}^{1/2} [CF_3COCH_3]} - 5$
6	2.59	1.01	46.6	245	2.389
28	2.92	1.37	34.0	49.5	1.695
29	3.14	1.61	9.18	18.5	1.267
5	3.35	1.84	3.41	8.49	0.929

* From extrapolation of curve in Figure 12.

ethane by a chain process which predominates above 140°C. Column 1 is the run number, column 2 1/temp.°K., column 3 the rate of ethane produced by the chain alone, column 4 is the rate function $\log (R_{CH_4}/R_{C_2H_6}(\text{chain}))$, and column 5 is the rate function $\log (R_{CH_4}/R_{C_2H_6}^{1/2}(\text{chain}))$.

Calculations are shown for run 14. In order to calculate the ethane rate by the chain process, it is necessary to correct the data for the ethane produced by methyl recombination. See Figure 8. At the temperatures included on curve 2, ethane is formed mainly by methyl recombination, while at the higher temperatures corresponding to curve 3, ethane is formed mainly by a chain process. Curve 2 is extrapolated to the high temperatures. At the temperature corresponding to run 14 the logarithm function = 1.36 - 13. From this the rate of ethane formation by methyl recombination at the high temperatures can be calculated. It is assumed that CH_4 is formed only by H atom abstraction by methyl radicals. Thus,

$$\log \frac{R_{CH_4}}{R_{C_2H_6}^{1/2} [CF_3COCH_3]} = 1.36 - 13$$

and substitution gives

$$\frac{921 \times 10^{10}}{R_{C_2H_6}^{1/2} \times 8.03 \times 10^{18}} = 23 \times 10^{-13},$$

and

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$$R_{C_2H_6} = 25 \times 10^{10}$$

for methyl combination alone. The rate for the chain process alone is the difference between the total rate and the rate by methyl recombination. Thus,

$$363 \times 10^{10} - 25 \times 10^{10} = 338 \times 10^{10}$$

for the chain process alone. Substituting in the rate function $\log (R_{CH_4}/R_{C_2H_6}(\text{chain}))$, gives

$$\log \frac{921 \times 10^{10}}{338 \times 10^{10}} = 0.435.$$

For the rate function $\log (R_{CH_4}/R_{C_2H_6}^{1/2}(\text{chain}))$,

$$\log \frac{921 \times 10^{10}}{(338 \times 10^{10})^{1/2}} = 1.700 + 5$$

In Table 9 the ethane formation in the low temperature range 25-120°C. (where methyl recombination is most important) is corrected for contribution from the chain process. Column 1 gives the run number, column 2 1/temp.°K, column 3 the value of the function $\log (R_{CH_4}/R_{C_2H_6}(\text{chain}))$, which is read from an extrapolation of the curve in Figure 12, column 4 the rate of ethane from methyl recombination alone, column 5 the rate function $R_{CH_4}/R_{C_2H_6}^{1/2} [CF_3COCH_3]$, column 6 the logarithm of the rate function in column 5.

Calculations are shown for run 6. The value of the

function $\log (R_{CH_4}/R_{C_2H_6(chain)})$, read from extrapolation of curve 2 in Figure 8, is 1.01. Thus,

$$\frac{138 \times 10^{10}}{R_{C_2H_6(chain)}} = 10.2 ,$$

and

$$R_{C_2H_6(chain)} = 13.5 \times 10^{10} .$$

The ethane rate from methyl recombination is the difference between the total rate and the rate from the chain process. Thus,

$$60.1 \times 10^{10} - 13.5 \times 10^{10} = 46.6 \times 10^{10}$$

for the rate of ethane production by methyl recombination alone. Substitution in the rate function in column 5 gives

$$\frac{138 \times 10^{10}}{(46.6 \times 10^{10})^{1/2} (8.25 \times 10^{18})} = 245 \times 10^{-15} ,$$

and its logarithm is 2.389.

D. Quantum Yields

Quantum yields are calculated for the six products. In Table 10 column 1 is the run number; columns 2-7 give the quantum yields of CO, CH₄, C₂F₆, CF₃CH₃, CF₃H, and C₂H₆, respectively.

Quantum yields are calculated from the equation

Table 10. Quantum Yields.

Run no.	Quantum yields of gaseous products				
	$\frac{\text{CO}}{\text{CH}_4}$	$\frac{\text{CH}_4}{\text{C}_2\text{F}_6}$	$\frac{\text{CF}_3\text{CH}_3}{\text{CF}_3\text{H}}$	$\frac{\text{C}_2\text{H}_6}{\text{C}_2\text{H}_4}$	
5	0.00570	0.00096	0.00080	0.0024	0.0026
6	.346	.090	.024	.104	.039
7	1.16	.901	.0077	.678	.524
8	.801	.296	.624	.180	.088
9	1.95	1.57	.0026	.541	1.13
11	.143	.031	.0051	.025	.0097
12	.673	.238	.019	.128	.065
14	1.03	.545	.014	.377	.215
15	1.25	1.02	.0049	.690	.707
16	.028				
17	.517	.138	.027	.258	.072
18	.578	.208	.010	.294	.100
19	.540	.172	.025	.312	.097
20	.564	.174	.019	.323	.116
21	.513	.153	.028	.250	.086
22	.381	.116	.0093	.189	.062
23	.767	.069	.099	.305	.180
24	.654	.099	.068	.291	.132
25	.626	.078			
26	.024	.0022	.00062	.011	.0069

$$\Phi = \frac{\text{No. molecules of a product formed/cc.-sec.}}{\text{No. quanta absorbed/cc.-sec.}}$$

The quantum yield of CO in run 6 is given by

$$\Phi_{\text{CO}} = \frac{538 \times 10^{10}}{1.54 \times 10^{13}} = 0.349$$

In Table 11 are tabulated several functions involving quantum yields. These functions are plotted in figures appearing in the discussion section. Column 1 gives the run number, column 2 the summation of all quantum yields involving methyl radicals, column 3 a similar summation for all compounds containing trifluoromethyl radicals CF_3 . Column 4 gives the function $\Phi_{\text{CF}_3\text{H}}/\Phi_{\text{C}_2\text{F}_6}^{1/2}$, column 5 the function $\Phi_{\text{CH}_4}/\Phi_{\text{C}_2\text{H}_6}^{1/2}$, column 6 the function $[\text{CF}_3\text{COCH}_3]/I_a^{1/2}$.

The summation of quantum yields involving methyl radicals is calculated from the equation

$$\Sigma \Phi_{\text{CH}_3} = \Phi_{\text{CH}_4} + \Phi_{\text{CF}_3\text{CH}_3} + 2\Phi_{\text{C}_2\text{H}_6}$$

Thus, for run 6,

$$\Sigma \Phi_{\text{CH}_3} = 0.090 + 0.024 + 2 \times 0.039 = 0.192$$

The summation involving CF_3 radicals is calculated in a similar way. The functions tabulated in columns 4, 5, and 6 are self-explanatory.

Table 11. Quantum Yield Functions.

Run no.	$\sum \Phi_{CH_3}$	$\sum \Phi_{CF_3}$	$\frac{\Phi_{CF_3H}}{\Phi_{C_2F_6}^{1/2}}$	$\frac{\Phi_{CH_4}}{\Phi_{C_2H_6}^{1/2}}$	$\frac{[\Phi_{CF_3COCH_3}]}{I_3^{1/2}}$
5	0.0070	0.00356			2.09
6	.192	.136		0.515	5.20
7	1.96	.689		.658	2.80
8	.496	.214		.553	3.37
9	3.84	.545		.510	2.10
11	.0555	.0320		.522	3.55
12	.387	.155	2.98	.466	0.580
14	.989	.396	4.12	.163	1.17
15	2.44	.696	4.33	.273	
17			4.10		
18			3.20		
19			3.03		
20			1.30		
21			2.06		
22					
23					
24					

IV. DISCUSSION

The proposed reaction mechanism will be stated. Then the experimental data will be discussed with regard to the mechanism.

A. Proposed Reaction Mechanism

It is probable that an activated ketone molecule is formed on absorption of 3130 Å. radiation.

The excited molecule can then decompose by one of the following processes.

Or, deactivation may occur by collision with other molecules.

The experimental evidence gives no support for primary process (iv). The amount of CF_3CH_3 produced is very small in nearly all the experiments. In the regions where the photodecomposition follows the mechanism given below, the CF_3CH_3 produced can be accounted for by radical recombination. At temperatures up to 100°C. the quantum yields of the products (Figure 10) are quite low (less than 0.25 for CO and 0.07 for all others). This may be due to collisional deactivation of excited molecules. More evidence for collisional deactivation appears from the

general increase in quantum yields (Figure 5) as the CF_3COCH_3 concentration is decreased, and the decrease in the CO and CH_4 yields in run 25 with added CO_2 . (Compare with data of run 24 without CO_2) The evidence here is not sufficient to choose between primary processes (ii) and (iii). At all temperatures above 80°C . the number of CH_3 radicals appearing in gaseous products is at least twice as large as the corresponding number of CF_3 radicals (Figure 11). This suggests that the molecule splits into CH_3 and COCF_3 radicals; that is, process (ii) predominates over process (iii).

The primary photodecomposition is followed by the reactions:

Reactions 2-10 are supported by the experimental evidence obtained. For completeness, the following additional reactions are included. By analogy with acetone photolysis they are believed likely to occur, but no attempt has been

made to obtain supporting evidence.

B. Discussion of Experimental Data

The discussion of experimental data will be divided into two parts: the relative reactivities of the CH_3 and CF_3 radicals, and the photolysis mechanism at high temperatures (above $140^\circ\text{C}.$).

1. The Relative Reactivities of the CH_3 and CF_3

Radicals. In order to determine the relative reactivities the effects of several variables are studied: the variation of the CF_3COCH_3 concentration and the absorbed intensity I_a , the effect of temperature variation, and the variation of the rates of formation of CF_3CH_3 , C_2F_6 , and C_2H_6 .

a. Variation of CH_3COCF_3 Concentration and I_a .

The results of the six-fold intensity variation on quantum yields are presented graphically in Figure 4. In another series of experiments (Figure 5) the CF_3COCH_3 concentration is varied over the range $0.8\text{--}17.3 \times 10^{18}$ molecules/cc. However, due to the increase in absorption, the intensity varies at the same time over the range $2\text{--}24 \times 10^{12}$ q./cc.-sec. Thus, the effect of concentration alone cannot be ascertained from this data. The suggested mechanism is in qualitative agreement with the variation in the product yields with CF_3COCH_3 concentration and I_a . In an effort to determine the combined effect of concentration and intensity, and to make a quantitative test of the suggested mechanism, plots are made of $\Phi_{\text{CH}_4}/\Phi_{\text{C}_2\text{H}_6}^{1/2}$ and $\Phi_{\text{CF}_3\text{H}}/\Phi_{\text{C}_2\text{F}_6}^{1/2}$ against $[\text{CF}_3\text{COCH}_3]/I_a^{1/2}$ (Figures 6 and 7). It is found that below $[\text{CF}_3\text{COCH}_3]/I_a^{1/2}$ values of about 3×10^{12} the data follows a straight line through the origin. The straight line through the origin would be predicted from the simple mechanism given here. However, above $[\text{CF}_3\text{COCH}_3]/I_a^{1/2}$ value 3×10^{12} , which region corresponds to low intensities or high concentrations, the simple mechanism breaks down. At present, no quantitative explanation can be offered for this behavior. (A qualitative explanation can be had in the C_2H_6 forming reactions (9) and (10), discussed later.) The slopes obtained from the straight lines are of importance. If all C_2H_6 and CH_4 are formed by reactions

FIGURE 4. EFFECT OF $I_{ABS.}$ ON QUANTUM YIELDS AT 117°C. AND $[CF_3COCH_3] = 8.2 \times 10^{18}$ MOLECULES/CC.

FIGURE 5. EFFECT OF $[\text{CF}_3\text{COCH}_3]$ ON QUANTUM YIELDS AT 117°C .

FIGURE 6. EFFECT OF $[CF_3COCH_3]$ and I_0 on $\frac{k_{CH_4}}{k_{C_2H_6}^{1/2}}$

FIGURE 7. EFFECT OF $[CF_3COCH_3]$ AND I_a ON $\frac{k_{CF_3H}}{k_{C_2F_6}^{1/2}}$

(2) and (3), respectively, one can write

$$R_{C_2H_6} = k_2 [CH_3]^2 \quad (23)$$

and

$$R_{CH_4} = k_3 [CH_3] [CF_3COCH_3], \quad (24)$$

where $R_{C_2H_6}$ and R_{CH_4} are rates of formation of ethane and methane, and k_2 and k_3 are rate constants for reactions (2) and (3). Taking the square root of equation (23), and dividing into (24) gives

$$\frac{R_{CH_4}^{1/2}}{R_{C_2H_6}^{1/2}} = \frac{k_3}{k_2} [CF_3COCH_3] \quad (25)$$

Now the rates can be replaced by quantum yields (since

$$\Phi_X = R_X/I_a).$$

$$\frac{\Phi_{CH_4}^{1/2}}{\Phi_{C_2H_6}^{1/2}} = \frac{R_{CH_4}/I_a^{1/2}}{R_{C_2H_6}/I_a^{1/2}} \quad (26)$$

Then

$$\frac{\Phi_{CH_4}^{1/2}}{\Phi_{C_2H_6}^{1/2}} = \frac{k_3}{k_2} \frac{[CF_3COCH_3]}{I_a^{1/2}} \quad (27)$$

Thus, the slope of the line from the plot of $\Phi_{CH_4}^{1/2}/\Phi_{C_2H_6}^{1/2}$ versus $[CF_3COCH_3]/I_a^{1/2}$ gives the ratio of the rate constants, $k_3/k_4^{1/2}$. The value obtained from Figure 6 gives $k_3/k_4^{1/2} = 2.5 \times 10^{-13}$. The value of $k_5/k_4^{1/2}$, determined by the same procedure, is 1.6×10^{-12} (Figure 7).

b. Temperature Variation. A series of experiments is made in which the temperature is varied over the range 25-355°C. The conditions are such that the ratio $[\text{CF}_3\text{COCH}_3]/I_a^{1/2}$ is always below the value 2.5×10^{12} . In this region, as was previously shown, the kinetics follow the postulated mechanism.

One of the primary aims of this work is to estimate the activation energies for the two abstraction reactions (4) and (6), or at the least, to find some basis for comparing them. If one replaces the rate constants in equation (25) with $PZ e^{-E/RT}$ from the Arrhenius equation, it follows that

$$\log \frac{R_{\text{CH}_4}}{R_{\text{C}_2\text{H}_6}^{1/2} [\text{CF}_3\text{COCH}_3]} = \frac{1}{2.3} \log \frac{P_3 Z_3}{(P_2 Z_2)^{1/2}} - \frac{E_3 - E_2/2}{2.3 RT} \quad (28)$$

Thus, if a plot is made of the term on the left side of equation (28) against $1/T$, the activation energy difference $E_3 - E_2/2$, can be calculated from the resulting slope. By a similar procedure one can get $E_5 - E_4/2$. The plot of $\log (R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2} [\text{CF}_3\text{COCH}_3])$ versus $1/T$ (curves 2 and 3, Figure 8) shows a sharp break at about 140°C. From Figures (10) and (11) it becomes evident that a chain reaction, which will be discussed later, is taking place in the region corresponding to curve 3 in Figure 8. When the data of curve 2 is corrected for chain contribution (Table 9, Figure 9), the activation energy difference

FIGURE 8. TEMPERATURE DEPENDENCE OF RATE FUNCTIONS

FIGURE 9. CORRECTED RATE FUNCTION FROM EXPERIMENTS AT LOW TEMPERATURES USED TO DETERMINE E_{ACT} . FOR H ABSTRACTION BY CH_3 RADICALS.

$E_3 - E_2/2$ is found to be 8.9 kcal./mole by the least squares method. This compares with the value, 9.7 kcal./mole, which Trotman-Dickenson and Steacie³ obtain for H atom abstraction from ordinary acetone. Numerous other compounds have been used by Steacie and coworkers^{6,7,8} in studying the H atom abstraction by methyl radicals. Most values for the activation energy difference fall between 7 and 10 kcal./mole.

From curve 1 of Figure 8, the activation energy difference $E_5 - E_4/2$ is found by the method of least squares to be 6.6 kcal./mole.

The ratios of the collision theory steric factors are found by the least squares treatment of the rate data in which correction has been made for the temperature dependence of the Z factors. The assumed collision diameters³ are: $\sigma_{CH_3} = \sigma_{CF_3} = 3.5\text{\AA.}$; $\sigma_{CF_3COCH_3} = 5.5\text{\AA.}$. Then $P_3/P_2^{1/2} = 5.1 \times 10^{-4}$, and $P_5/P_4^{1/2} = 1.1 \times 10^{-4}$.

The activation energy difference, $E_5 - E_4/2 = 6.6$ kcal./mole, is low compared with the energy difference of $E_3 - E_2/2 = 8.9$ kcal./mole. This difference could be the result of a lower activation energy for abstraction reaction (5) compared to abstraction by methyl radicals (3). Or, the CF_3 radical recombination may have a higher activation energy than the CH_3 radical recombination. The lower activation energy for abstraction by CF_3 radicals would result if the $CF_3 - H$ bond were stronger than the

CH₃ - - H bond. At present, there is no evidence to support this. Neither is there much real evidence for the higher activation energy for CF₃ recombination. On the basis of mathematical calculations, Itoh and coworkers¹⁵ propose that the methyl radical does not have a planar structure, but is near tetrahedral. Now the structure of the trifluoromethyl radical might be somewhat more planar due to the greater repulsive forces of the highly electronegative fluorine atoms. If this is true, then an appreciable energy may be necessary to reorient the fluorine atoms upon reaction of two CF₃ radicals to form the near tetrahedral configuration shown present in C₂F₆¹⁶. However, it is unlikely that E₄ is as great as 4.6 kcal./mole. Thus, it is more probable that E₃ is greater than E₅, and the CF₃ radical is more reactive than the CH₃ radical toward H atom abstraction.

c. Variation of the Rates of Formation of CF₃CH₃, C₂F₆, and C₂H₆.

If one assumes that the C₂H₆, C₂F₆, and CF₃CH₃ are formed only by reactions 2, 4, and 6, respectively, one can write

$$R_{C_2H_6} = k_2 [CH_3]^2 \quad (23)$$

$$R_{C_2F_6} = k_4 [CF_3]^2 \quad (29)$$

$$R_{CF_3CH_3} = k_6 [CF_3][CH_3] \quad (30)$$

Solving for $[CH_3]$ and $[CF_3]$ in equations (23) and (29), and substituting in (30) gives

$$\frac{R_{CF_3CH_3}}{R_{C_2H_6}^{1/2} R_{C_2F_6}^{1/2}} = \frac{k_6}{k_2^{1/2} k_4^{1/2}} \quad (31)$$

Since $\Phi_x = R_x/I_a$,

$$\frac{k_6}{k_2^{1/2} k_4^{1/2}} = \frac{\Phi_{CF_3CH_3}}{\Phi_{C_2H_6}^{1/2} \Phi_{C_2F_6}^{1/2}} \quad (32)$$

If one assumes further that $E_6 - E_2/2 - E_4/2 = 0$, and that the ratio of the steric factors $P_6/P_2^{1/2} P_4^{1/2} = 1$, then the ratio of quantum yields in (32) should depend only on collision numbers for reactions (2), (4), and (6).

Theoretically then,

$$\frac{\Phi_{CF_3CH_3}}{\Phi_{C_2F_6}^{1/2} \Phi_{C_2H_6}^{1/2}} = 2.29 \quad (33)$$

assuming collision diameters as before. In Table 12 are listed the values obtained for the quantum yield function of equation (33). Only those experiments in the range of conditions where the ethane formation by (2) predominates are included. A correction is applied to remove ethane formation by reactions (9) and (10). The results do not show any wide deviations which might be expected if the assumptions were incorrect. The consistently low results

Table 12. Calculated Data.

Run no.	Temp. °C.	$\frac{I_{CH_3CF_3}}{I_{C_2H_6}^{1/2} I_{C_2F_6}^{1/2}}$
5	25.5	0.9
6	113.0	2.2
11	78.7	1.8
12	135.7	1.6
17	117	1.3
21	117	1.4
23	117	1.0
24	117	1.4

may be due to experimental errors in the determination of CF_3CH_3 ; this compound is the most difficult of the products to separate by the distillation technique. Analysis of known mixtures showed that only about a 90% recovery of CF_3CH_3 was possible.

2. Mechanism at High Temperatures. It is seen from Figure 8 that the simple mechanism which applies at low temperatures (below 140°C.) is no longer valid at the higher temperatures. The break in the curve could be due to either a sharp decrease in the CH_4 rate, or to an even greater increase in the C_2H_6 rate. Since the quantum yields (Figure 10) of both CH_4 and C_2H_6 are increasing regularly, it follows that C_2H_6 is being formed by a reaction other than methyl recombination. It is seen from Figures 10 and 11 that there is a chain reaction, which produces CO , CH_4 , and C_2H_6 , and, at the same time, the CF_3 radical concentration is lowered by some process.

FIGURE 10. EFFECT OF TEMPERATURE ON QUANTUM YIELD
AT $[\text{CF}_3\text{COCH}_3] = 8.2 \times 10^{18}$ MOLECULES/CC.

FIGURE II. VARIATION OF $\Sigma\Phi_{CH_3}$ AND $\Sigma\Phi_{CF_3}$ WITH TEMPERATURE

Reactions 7-10 are postulated to account for this behavior. The extra methyl radicals produced by (7) and (8) account for the increases in the CH_4 and C_2H_6 yields, and at the same time, CF_3 radicals are removed. Additional C_2H_6 is produced by (9) and (10), and at the higher temperatures, almost all C_2H_6 is produced in this way. Breakdown of the CF_3CO radicals produced in (10) account for the CO in the chain.

The chain mechanism shown here is in direct contrast with the case of acetone, where no CO forming chain is found. The data of Herr and Noyes¹⁷ show that the quantum yield of CO in acetone decomposition rises rapidly from 0.1 at 25°C. to about 1.0 at 107°C. (Figure 10). Other experimenters^{18,19,20,21,22} have shown that, within the limit of experimental error, the CO yield remains 1.0 up to 400°C.

There is evidence to support the proposal of radical-molecule addition in (7) and (9). Rust and coworkers²³ found di-n-propylcarbinol as one of the products in the thermal decomposition of n-butyraldehyde sensitized by di-t-butyl peroxide. Their mechanism included the addition reaction

which is the same type as (7) and (9).

A plot of $\log (R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6})$, where the ethane is produced only by (9) and (10), against $1/T$ (Table 8,

FIGURE 12. RATE FUNCTION $\text{LOG} \frac{R_{\text{CH}_4}}{(R_{\text{C}_2\text{H}_6})_{\text{CHAIN}}}$ VS. TEMPERATURE
AT HIGH TEMPERATURES

Figure 12) shows straight line characteristics. That this is consistent with the mechanism is made evident by the following. If one assumes that at high temperatures all the CH_4 is produced by (3), and all the C_2H_6 is produced by (9) and (10), then one can write

$$R_{\text{CH}_4} = k_3 [\text{CH}_3] [\text{CF}_3\text{COCH}_3] \quad (24)$$

$$R_{\text{C}_2\text{H}_6} = k_{10} [\text{CF}_3\text{CO}(\text{CH}_3)_2] \quad (35)$$

Now reaction (9) is an equilibrium expression. Thus, it follows that

$$[\text{CF}_3\text{CO}(\text{CH}_3)_2] = K_9 [\text{CH}_3] [\text{CF}_3\text{COCH}_3] \quad (36)$$

and substitution of (36) in (35) gives

$$R_{\text{C}_2\text{H}_6} = k_{10} K_9 [\text{CH}_3] [\text{CF}_3\text{COCH}_3] \quad (37)$$

Dividing (24) by (37) gives

$$\frac{R_{\text{CH}_4}}{R_{\text{C}_2\text{H}_6}} = \frac{k_3}{k_{10} K_9} \quad (38)$$

Thus, the straight line is expected in Figure 12, and the activation energy, 5 ± 1 kcal./mole, calculated from the slope corresponds to

$$E_{\text{Act.}} = E_3 - (\Delta H_9 + E_{10}) \quad (39)$$

(The most inaccurate highest temperature run is omitted)

Equation (38) should be independent of CF_3COCH_3 concentration. Two experiments (runs 30, 31) are carried out at about 264°C . to test this. The two hexagonal points in Figure 12 are the results of these experiments.

($[\text{CF}_3\text{COCH}_3]$ was varied from 8.2 to 1.8×10^{18} molecules/cc.) If all C_2H_6 formed is the result of reaction (2), then a linear plot of the function $\log (R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2})$ versus $1/T$ is expected. The scattered results in Figure 13 show the incorrectness of this mechanism.

An alternative explanation of C_2H_6 formation, also consistent with the observed kinetics, would involve the direct abstraction of a methyl radical by a methyl radical.

Even in more favorable compounds, such as mercury dimethyl, there is no evidence for the analogous reaction occurring. Then too, if (40) were important one might expect abstraction by CF_3 radicals as well, and CF_3CH_3 would be formed in the chain process. However, the CF_3CH_3 yield is very low at all times, and, in fact, decreases at the higher temperatures, thus precluding the possibility of chain formation.

FIGURE 13. RATE FUNCTION $\text{LOG} \frac{R_{\text{CH}_4}}{(R_{\text{C}_2\text{H}_6}^{1/2})_{\text{CHAIN}}}$ VS. TEMPERATURE AT HIGH TEMPERATURES.

V. SUGGESTIONS FOR FURTHER WORK

Much additional experimental evidence is needed to check the postulated mechanism. The nature of the break in the primary process might be determined by experiments with free radical traps, such as iodine or nitric oxide, present. The possibility that the primary process involves an activated molecule could be checked further by experiments at low temperature with an added inert gas present. The effect of collisional deactivation would be enhanced, and quantum yields would be expected to decrease. The chain mechanism should be closely checked for further supporting evidence. If one could detect the presence of hexafluoroacetone in high temperature experiments, reactions (7) and (8) would be substantiated. In addition, experiments are now in progress in which mixtures of CF_3COCH_3 and trifluoroacetophenone are photolyzed in a region where only the trifluoroacetophenone absorbs. The decomposition of trifluoroacetophenone is expected to furnish CF_3 radicals. If CH_4 and C_2H_6 can be detected there will be further evidence for reactions (7) and (8). More information concerning reactions (9) and (10) might be gained if one could obtain the compound $\text{CF}_3(\text{CH}_3)_2\text{COOC}(\text{CH}_3)_2\text{CF}_3$, which is analogous to di-t-butyl peroxide. Upon decomposition one would expect the radical $\text{CF}_3(\text{CH}_3)_2\text{CO}$, which is the intermediate postulated in reactions (9) and (10). If one obtained ethane as a

product by a first order process, reaction (10) would be substantiated. Another interesting study would be the thermal decomposition of trifluoroacetone. At temperatures above 350°C., large amounts of ethylene are produced (run 10).

VI. SUMMARY

The results of the photodecomposition of CF_3COCH_3 by 3130 Å. radiation are listed.

The mechanism postulated for the formation of the ethanes and methanes (2) - (6) is valid when the ratio $[\text{CF}_3\text{COCH}_3]/I_a^{1/2}$, is less than 3×10^{12} .

The activation energy differences $E_3 - E_2/2$, and $E_5 - E_4/2$ are 8.9 and 6.6 kcal./mole, respectively. Since it is very unlikely that E_4 is as large as 4.6 kcal./mole, then E_3 is greater than E_5 , and the CF_3 radical is more reactive than the CH_3 radical toward H atom abstraction.

Above 140°C. CO, CH_4 , and C_2H_6 are formed in a chain process. In this region, C_2H_6 is not formed by methyl recombination alone, but by reactions (9) and (10),

or by a previously unobserved CH_3 abstraction reaction (40).

The value of the function, $E_3 - \Delta H_9 - E_{10}$, is 5 ± 1 kcal./mole. There is evidence for the reaction of radical

addition to a carbonyl double bond in (7) and (9).

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