carried out during the course of this study and to John Keil, who determined some of the physical properties reported in this paper.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

The Vapor Phase Photolysis of Trifluoroacetone at Wave Length 3130 Å.[1]

BY ROBERT A. SIEGER AND JACK G. CALVERT[2]

RECEIVED JUNE 5, 1954

A kinetic study is made of the photolysis of CF_3COCH_3 vapor at various temperatures, concentrations, and light intensities to determine the relative reactivity of CF_3 and CH_3 toward H-abstraction reactions. The gaseous products are: CO, CH_4, CF_3H, C_2H_6, CF_3CH_3 and C_2F_6. In experiments at low $[CF_3COCH_3]$ and high I_a the methanes and ethanes are formed only in the reactions: $CH_3 + CF_3COCH_3 \rightarrow CH_4 + CF_3COCH_2$ (1); $2CH_3 \rightarrow C_2H_6$ (2); $CF_3 + CF_3COCH_3 \rightarrow CF_3H + CF_3COCH_2$ (3); $2CF_3 \rightarrow C_2F_6$ (4). The activation energy differences are: $E_1 - E_2/2 = 8.9$; $E_3 - E_4/2 = 6.6$ kcal./mole; the Arrhenius P factors are: $P_1/P_2^{1/2} = 5 \times 10^{-4}$, $P_3/P_4^{1/2} = 1 \times 10^{-4}$. The quantum yields of CO, CH_4 and C_2H_6 are greater than 1.0 at high temperatures and increase markedly with temperature increase. The quantum yields of CF_3H, C_2F_6 and CF_3CH_3 are less than 1.0 at all temperatures and decrease at high temperatures. In explanation of these unusual results a chain mechanism is proposed which involves C_2H_6 formation in a reaction other than (2) at high temperatures. This may be a rare example of a methyl-abstraction reaction. The results provide evidence for a rarely postulated, gas phase, radical addition to a carbonyl double bond. It is suggested that CF_3 radicals generate CH_3 radicals at high temperatures by the reactions: $CF_3 + CF_3COCH_3 \rightleftarrows (CF_3)_2COCH_3$, and $(CF_3)_2COCH_3 \rightarrow CH_3 + CF_3COCF_3$.

In view of the results of the many detailed studies of acetone photolysis[3] it seemed probable that trifluoroacetone would undergo photodecomposition forming in part methyl and trifluoromethyl radicals. The present study was initiated in an attempt to gain information concerning the relative reactivity of the CH_3 and CF_3 radicals and to determine the effect of fluorine atom substitution in the acetone molecule on the mechanism of acetone photodecomposition.

Experimental

Apparatus.—The all-glass photolysis system consisted of a quartz photolysis cell (50 mm. long, 30 mm. diam.), a glass circulating pump, trap and mercury manometer. This system was isolated from stopcocks by mercury valves. The cell was suspended in an aluminum block furnace (regulated to ±1°). Radiation from a Hanovia type A(S-500) burner (run on a regulated 3.00 amp. a.c. current) was filtered to isolate wave length 3130 Å.[4] The light beam was well collimated by a series of lenses and stops so that a fairly homogeneous beam of radiation filled the cell volume (35.3 cc.) almost completely. The geometrical arrangement of all components in the light train remained fixed during the entire study. A photomultiplier-amplifier system was used to measure the fractions of light absorbed. Absolute intensities were estimated by chemical actinometry at five regularly spaced intervals during the course of the photochemical runs. Estimates of the total quanta entering the cell per sec. $\times 10^{-15}$ were: 1.14, 0.93 (uranyl oxalate actinometry[5]), 1.06, 1.19, 1.14 ($K_3Fe(C_2O_4)_3$ actinometry[6]). No aging of the light source was apparent, so an average value of 1.09×10^{15} q./sec. was used as the incident light intensity in quantum yield calculations for all runs. Calibrated uniform density filters were placed in the light path to obtain lower incident intensities in some experiments.

Materials.—Carefully fractionated CF_3COCH_3 was purchased from the Caribou Chemical Co. (b.p. 21-22° (750 mm.)) and further purified by fractionation at reduced pressure in a high vacuum system. The mass spectrum of the purified sample was consistent with that expected for pure CF_3COCH_3; approx. mol. wt. (Dumas method), 114 g./mole; approx. v.p. in mm., 6 (−65°), 18 (−51°), 98 (−23°), 200 (−9°), 385 (5°), 537 (12°). High purity reference samples of the gases CF_3H, C_2F_6, CH_3CF_3 and CF_4 were provided by the Organic Chemicals Department of E. I. du Pont de Nemours & Co. Additional samples of these gases were supplied by the Minnesota Mining and Manufacturing Co. and Professor J. D. Park, University of Colorado. C_2H_6 and CH_4 reference gases were Phillips Research Grade. CO was prepared by the action of H_2SO_4 on NaO_2CH and purified in the conventional manner.

Product Analysis.—A maximum of 2% photodecomposition of the original ketone was allowed in all runs. CO and CH_4 products were removed following photolysis using a Toepler pump with the other products and excess ketone condensed at liquid N_2 temperature. A second fraction of the products was removed from the ketone excess using a modified Ward still[7] maintained at −110 to −100°. The analysis scheme was checked with known mixtures; almost complete recovery of CH_4, CO, C_2F_6, C_2H_6, CF_3H and about 90% recovery of CF_3CH_3 could be effected from the excess ketone. (CF_3CH_3 is the product with the lowest vapor pressure.) CO was analyzed by chemical means[8] using a Blacet–Leighton gas analysis system. The ethanes and methanes were determined using a General Electric analytical mass spectrometer.

Results

Products.—CO, CH_4, C_2H_6, CH_3CF_3 and C_2F_6 were identified as the major gaseous products. Proved absent were the possible products CH_3F, CF_4, HF, SiF_4 and F_2. An unsuccessful attempt was made to identify other products from the mass spectrum of the condensable fraction containing excess ketone.

Molar Extinction Coefficients.—At a fixed temperature the absorption of 3130 Å. radiation by CF_3COCH_3 vapor followed Beer's law within the experimental error of the determinations over the range of concentrations, 17.3 to 0.84×10^{18} molec./cc. The coefficient showed an almost linear increase with increase in temperature. Representative values of ϵ for CF_3COCH_3 vapor at 3130 Å. are: 3.6 (25°) and 6.4 (350°), where $\log_{10}(I_0/I) =$

---

[1] Taken from the thesis of R. A. Sieger submitted for the Master of Science degree, The Ohio State University, 1954. Presented in part before the Division of Physical and Inorganic Chemistry of the American Chemical Society, New York, September, 1954.

[2] Author to whom communications should be addressed.

[3] For reviews of work see: (a) W. Davis, Jr., *Chem. Revs.*, **40**, 201 (1947); (b) W. A. Noyes, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **16**, 788 (1948).

[4] R. E. Hunt and W. Davis, Jr., THIS JOURNAL, **69**, 1415 (1947).

[5] W. G. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930); G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).

[6] C. A. Parker, *Proc. Roy. Soc.* (*London*), **A220**, 104 (1953).

[7] E. C. Ward, *Ind. Eng. Chem., Anal. Ed.*, **10**, 169 (1938).

[8] F. E. Blacet, G. D. MacDonald and P. A. Leighton, *ibid.*, **5**, 272 (1933).

TABLE I

QUANTUM YIELDS OF PRODUCTS AT 117° AS A FUNCTION OF I_a AND $[CF_3COCH_3]$

Run	Ia, q./cc.-sec. × 10^{-13}	$[CF_3COCH_3]$, molec./cc. × 10^{-18}	Quantum yields CO	CH_4	CF_3H	C_2H_6	C_2F_6	CF_3CH_3
1	1.54	8.20	0.52	0.138	0.258	0.072	0.0075	0.027
2	0.864	8.24	.54	.172	.312	.097	.0052	.025
3	.592	8.20	.56	.174	.323	.116	.0062	.019
4	.251	8.21	.58	.208	.294	.100	.0051	.010
5	2.37	17.3	.38	.116	.189	.062	.0039	.0093
6	1.53	8.20	.51	.153	.250	.086	.0061	.028
7	0.711	3.12	.65	.099	.291	.132	.020	.068
8	.210	0.841	.77	.069	.305	.180	.055	.099
9	.711	3.12 $[CO_2]$ = 10.0	.63	.078	(CO_2 excess prevented analysis for these products)			

ϵcl; c is concentration in moles/l., l is the path length in cm.

Effect of Variables on the Quantum Yields of Products.—The data at different temperatures are summarized in Fig. 1 ($[CF_3COCH_3]$ is approximately constant at 8.2×10^{18} molec./cc.; I_0 is constant at 1.09×10^{15} q./sec.). Φ_{CO} values of Herr and Noyes[9a] from CH_3COCH_3 photolysis (at 110 mm.) are shown also for comparison. Other experiments[9b] have shown that Φ_{CO} remains near unity up to 400° (shown by the dotted line in Fig. 1). A slow thermal reaction in the run at 350° necessitated a small correction to the total rate of product formation. (This correction amounted to the following % of the total rate of each product: C_2H_6, 9%; CO, 4%; CF_3H, 3%; CH_4, 0.4%; C_2H_4 was a major product of the thermal reaction; none was formed photochemically.) There was negligible thermal reaction in the runs at all the lower temperatures. The absolute and the relative values of the quantum yields are probably accurate to about ±15% and ±5%, respectively, for all products other than C_2F_6 and CF_3CH_3. The very small yield of C_2F_6 limited greatly the accuracy of its determination. C_2F_6 yields are too small to be represented with the data in Fig. 1. Representative values of $\Phi_{C_2F_6}$ at various temperatures are: 0.0003 (26°), 0.0010 (79°), 0.0040 (113°), 0.0041 (136°), 0.0050 (153°), 0.0025 (205°), 0.0018 (254°), 0.0003 (299°), 0.0006 (351°). $\Phi_{CF_3CH_3}$ values are probably consistently low by 10% (incomplete removal. Φ's of products as a function of $[CF_3COCH_3]$ and I_a at 117° are given in Table I. Run 9 was identical to run 7 in every respect except that CO_2 was added to a concentration of 10.0×10^{18} molec./cc.

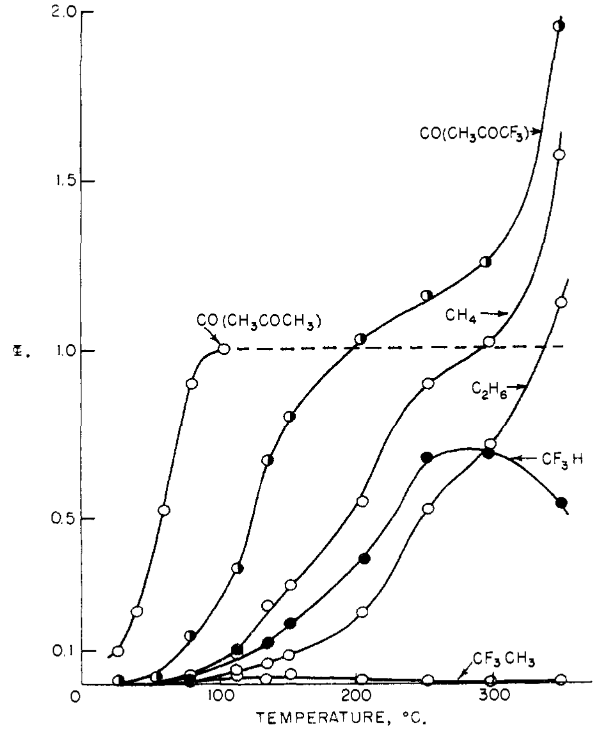

Fig. 1.—The quantum yields of products of CF_3COCH_3 photolysis as a function of temperature: $[CF_3COCH_3]$, about 8.2×10^{18} molec./cc.; I_0, about 1.09×10^{15} q./sec. The CO yields from CH_3COCH_3 are from Herr and Noyes.[9a]

Discussion

The Relative Reactivity of CH_3 and CF_3 in H-Abstraction Reactions.—By analogy with CH_4 and C_2H_6 forming reactions demonstrated in CH_3COCH_3 photolysis[3] one might suggest the following reactions for the formation of the methanes and the ethanes in CF_3COCH_3 photolysis

$$CH_3 + CF_3COCH_3 \longrightarrow CH_4 + CF_3COCH_2 \quad (1)$$

$$2CH_3 \longrightarrow C_2H_6 \quad (2)$$

$$CF_3 + CF_3COCH_3 \longrightarrow CF_3H + CF_3COCH_2 \quad (3)$$

$$2CF_3 \longrightarrow C_2F_6 \quad (4)$$

$$CF_3 + CH_3 \longrightarrow CF_3CH_3 \quad (5)$$

A simple test of the mechanism is applied to the data by the method of Dorfman and Noyes.[10] Assuming the mechanism 1–4 the relations *a* and *b* can be derived. In Fig. 2 the functions $\Phi_{CH_4}/\Phi_{C_2H_6}{}^{1/2}$ and $\Phi_{CF_3H}/\Phi_{C_2F_6}{}^{1/2}$ are plotted *vs.* $[CF_3COCH_3]/I_a{}^{1/2}$ using the data from runs at 117° (Table I). At values of $[CF_3COCH_3]/I_a{}^{1/2} < 3 \times 10^{12}$ molec. (sec./cc.-q.)$^{1/2}$ the data show the linear relationship between the variables expected from the relations *a* and *b*. At high concentrations and/or low light intensities, deviations from the

$$\Phi_{CH_4}/\Phi_{C_2H_6}{}^{1/2} = k_1[CF_3COCH_3]/k_2{}^{1/2}I_a{}^{1/2} \quad (a)$$

$$\Phi_{CF_3H}/\Phi_{C_2F_6}{}^{1/2} = k_3[CF_3COCH_3]/k_4{}^{1/2}I_a{}^{1/2} \quad (b)$$

---

[9] (a) D. S. Herr and W. A. Noyes, Jr., THIS JOURNAL, **62**, 2052 (1940); (b) E. I. Akeroyd and R. G. W. Norrish, *J. Chem. Soc.*, 890 (1936); H. S. Taylor and C. Rosenblum, *J. Chem. Phys.*, **6**, 119 (1932); J. A. Leermakers, THIS JOURNAL, **56**, 1899 (1934); C. A. Winkler, *Trans. Faraday Soc.*, **31**, 761 (1935).

[10] L. M. Dorfman and W. A. Noyes, Jr., *J. Chem. Phys.*, **16**, 557 (1948).

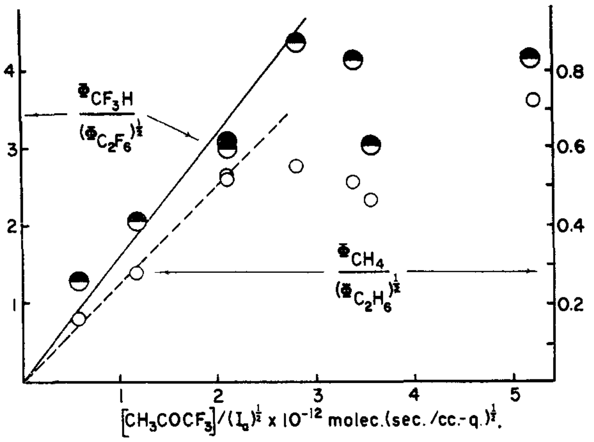

Fig. 2.—Quantum yield functions *vs.* $[CF_3COCH_3]/I_a^{1/2}$; temperature, 117°. The open and half-darkened circles refer to the CH_4–C_2H_6 and CF_3H–C_2F_6 functions, respectively.

simple linear relation are apparent. Acetone results show no such marked deviation over a wide range of variables.[10,11] Following the system used in the acetone studies activation energy differences were evaluated; the experimental conditions were chosen so that kinetics consistent with reactions 1–4 were obtained. In Fig. 3 a plot of the logarithm of the rate functions $R_{CH_4}/R_{C_2H_6}{}^{1/2}[CF_3COCH_3]$ and $R_{CF_3H}/R_{C_2F_6}{}^{1/2}[CF_3COCH_3]$ *vs.* $1/T$ is given. A typical linear plot of the CF_3H–C_2F_6 function is obtained for the entire temperature range, but a sharp break-off is seen in the plot of the CH_4–C_2H_6 function. At high temperatures (as well as high $[CF_3COCH_3]$ and low I_a) a reaction in addition to 2 which forms C_2H_6 becomes important (discussed with the high temperature reactions). A correction to the C_2H_6 rate data for the four low temperature runs was made to eliminate the high temperature C_2H_6 forming reaction. (This correction to the rate function in the runs at different temperatures amounted to 20% (113°), 3% (69°), 1% (46°) and 0.6% (25°). A least squares treatment of the corrected rate data gave $E_1 - E_2/2 = 8.9$ and $E_3 - E_4/2 = 6.6$ kcal./mole. The Arrhenius P factors were calculated to be $P_1/P_2{}^{1/2} = 5 \times 10^{-4}$ and $P_3/P_4{}^{1/2} = 1 \times 10^{-4}$ (assuming $\sigma_{CH_3} = \sigma_{CF_3} = 3.5$ Å. and $\sigma_{CF_3COCH_3} = 5.5$ Å.). Compare these estimates with results from acetone studies. $E_1' - E_2/2 = 9.7$[12] (9.6[11]) kcal./mole and $P_1'/P_2{}^{1/2} = 10 \times 10^{-4}$ (where E_1' and P_1' refer to the reaction: $CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3$ (1')). It is interesting but probably fortuitous that $P_1/P_2{}^{1/2}$ is one-half $P_1'/P_2{}^{1/2}$, a result consistent with the simple collision picture of the two reactions 1 and 1'. Certainly the similarity of the two results from the different systems adds credence to the kinetic interpretation given. It is probable that E_2 and E_4 are both near zero, and thus $E_1 - E_3$ is about 2.3 kcal./mole. The high reactivity of CF_3 for H-abstraction compared to CH_3 may reflect a higher strength of CF_3–H bond compared to the CH_3–H bond. There appear to be no bond strength data available to test this suggestion.

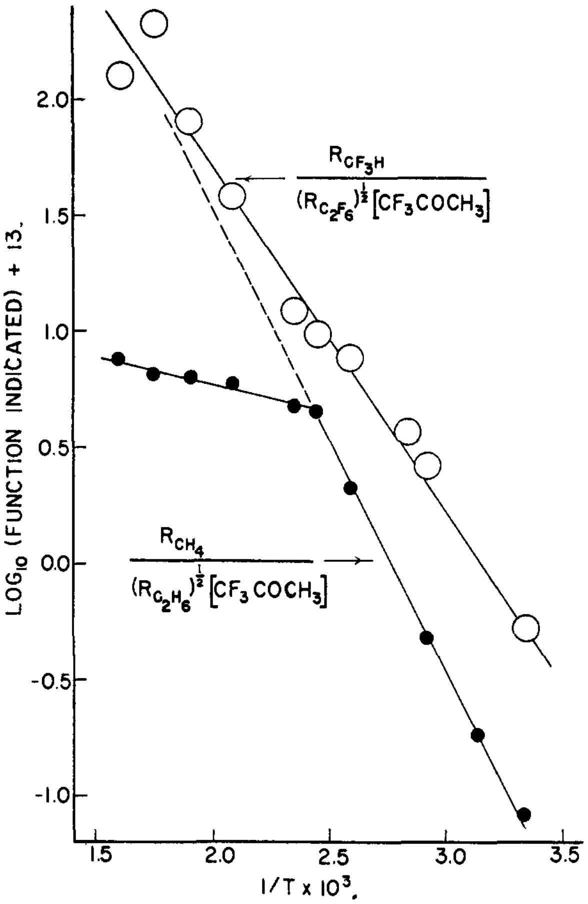

Fig. 3.—Arrhenius plot of rate functions: $[CF_3COCH_3]$, about 8.2×10^{18} molec./cc.; I_0, about 1.09×10^{15} q./sec. Darkened and open circles refer to CH_4–C_2H_6 and CF_3H–C_2F_6 rate functions, respectively.

As an alternative explanation of the activation energy data one may suggest that configurational differences between CF_3 and CH_3 might result in $E_4 > 0$.[13] It seems highly unlikely that E_4 is as great as 4.6 kcal./mole in any case, and thus E_1 is probably greater than E_3.

In light of the possible differences between E_2 and E_4 it is interesting to compare the yields of the ethanes formed. If $E_2 = E_4 = E_6$, $P_2 = P_4 = P_6$, and the ethanes are formed only in reactions 2, 4 and 6, then the ratio $\Phi_{CF_3CH_3}/\Phi_{C_2F_6}{}^{1/2}\Phi_{C_2H_6}{}^{1/2}$ should equal 2.29 (assuming $\sigma_{CF_3} = \sigma_{CH_3} = 3.5$ Å.). Experimental values of this ratio are: 1.8 (79°); 2.2 (113°); 1.3, 1.4, 1.0, 1.4 (117°); and 1.6 (136°). A correction was made to the C_2H_6 rate data at the temperature 113° and above to eliminate C_2H_6 formation by reactions other than 2. The inaccuracy of the CF_3-CH_3 analysis (probably low by 10%) and the small yields of C_2F_6 and resultant inaccuracy in $\Phi_{C_2F_6}$ estimates make these results of questionable value. However it appears likely that $E_6 - E_4/2 - E_2/2$ is not far from zero and $P_6/P_4{}^{1/2}P_2{}^{1/2}$ is about

---

[11] A. J. C. Nicholson, THIS JOURNAL, **73**, 3981 (1951).

[12] A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **18**, 1097 (1950).

[13] Calculations of T. Itoh, K. Ohno and M. Kotani, *J. Phys. Soc. Japan*, **8**, 41 (1953), show that the most stable CH_3 configuration may be near tetrahedral. Qualitatively a more nearly planar configuration of CF_3 might be expected as a result of the F atom electronegativity. The adjustment of two such CF_3 radicals to the near tetrahedral arrangement in C_2F_6 (J. L. Brandt and R. L. Livingston, THIS JOURNAL, **76**, 2096 (1954)) might result in $E_4 > 0$.

unity. The simplest condition for the E and P functions to be 0 and 1, respectively, is for $E_6 = E_4 = E_2$ and for $P_6 = P_4 = P_2$, but obviously other values would fit the data as well. All of the results seem most consistent with the interpretation that CF_3 has a high H-abstraction reactivity compared to CH_3.

It is apparent from the lack of CF_4 and CH_3F in the products that F-abstraction reactions of CF_3 and CH_3 are unimportant up to 350°.

High-Temperature Reactions.—There are several striking differences between the high temperature photolyses of CF_3COCH_3 and CH_3COCH_3. (1) CO is formed in a chain process in the high temperature photolysis of CF_3COCH_3; acetone shows no CO chain up to 400°. (Compare Φ_{CO} from the acetones in Fig. 1.) (2) A chain forming CH_3-containing molecules is present at high temperatures in the CF_3COCH_3 system as seen from the quantum yield summations given in Fig. 4. ($\Sigma\Phi_{CH_3} = \Phi_{CH_4} + 2\Phi_{C_2H_6} + \Phi_{CF_3CH_3}$; $\Sigma\Phi_{CF_3} = \Phi_{CF_3H} + 2\Phi_{C_2F_6} + \Phi_{CF_3CH_3}$.) Acetone shows no such marked chain for CH_3-containing species. (3) Fig. 3 shows a sharp break in the CH_4–C_2H_6 rate function for CF_3COCH_3 photolyses at temperatures above 150°. Acetone data show no break up to 400°. (4) The data in Fig. 2 show marked deviations from the linear dependence of the variables expected from the simple reaction sequence 1–4. Some of these unusual results can be explained in terms of a reaction forming C_2H_6 (in addition to 2) which becomes important at high temperatures, high $[CF_3COCH_3]$ and low I_a. To determine the kinetics of this ethane forming reaction three experiments at 265° were made at varied $[CF_3COCH_3]$. The values of $R_{CH_4}/R_{C_2H_6}$ (corrected for minor contribution to $R_{C_2H_6}$ from 2) at various pressures were: 1.64 (444 mm.), 1.45 (202 mm.), 1.83 (100 mm.). The relative constancy of the ratio with variation in $[CF_3COCH_3]$ shows that C_2H_6 and CH_4 rates are proportional to the same power of $[CF_3COCH_3]$. If one assumes that CH_4 is formed only by reaction 1 then C_2H_6 formation by 6 or 7 and 8 is consistent with these results.

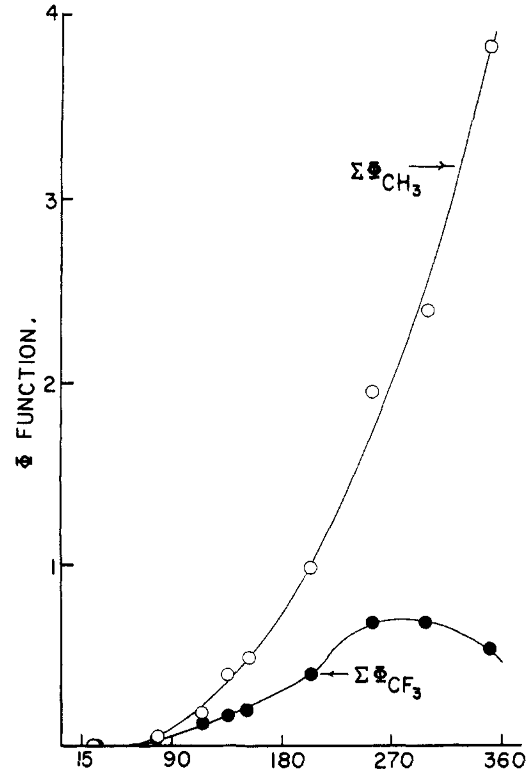

Fig. 4.—Summations of quantum yields of gaseous products of CF_3COCH_3 photolysis as a function of temperature; $\Sigma\Phi_{CH_3} = \Phi_{CH_4} + 2\Phi_{C_2H_6} + \Phi_{CF_3CH_3}$; $\Sigma\Phi_{CF_3} = \Phi_{CF_3H} + 2\Phi_{C_2F_6} + \Phi_{CF_3CH_3}$.

$$CH_3 + CF_3COCH_3 \longrightarrow C_2H_6 + CF_3CO \quad (6)$$

$$CH_3 + CF_3COCH_3 \rightleftharpoons CF_3CO(CH_3)_2 \quad (7)$$

$$CF_3CO(CH_3)_2 \longrightarrow C_2H_6 + CF_3CO \quad (8)$$

Evidence for reactions of the type of 6 is rare indeed, and that which exists is not compelling. Trotman-Dickenson[14] cites only two known examples of a reaction in which a CH_3 radical abstracts a radical from a molecule. Recent data from $(CH_3)_2Hg$ photolyses indicate that one of the stated examples, $CH_3 + (CH_3)_2Hg \rightarrow C_2H_6 + CH_3Hg$, is unimportant up to 200°.[15] The other example is that proposed by Blacet and Bell[16] in explanation of the results from biacetyl photolysis at high temperatures: $CH_3 + (CH_3CO)_2 \rightarrow CH_3COCH_3 + CH_3 + CO$. An alternative explanation of the biacetyl results may be given in terms of the reaction sequence: $CH_3 + (CH_3CO)_2 \rightleftharpoons (CH_3)_2COCOCH_3$; $(CH_3)_2COCOCH_3 \rightarrow CH_3COCH_3 + CH_3CO$. (Similar reactions of radical addition to a carbonyl double bond are consistent with the results of the present study.) It appears that there are few, if any, known reactions similar to 6. One might expect the analogous reaction, $CF_3 + CF_3COCH_3 \rightarrow CF_3CH_3 + COCF_3$, in this system if 6 were important. In Fig. 1 it is seen that $\Phi_{CF_3CH_3}$ decreases at high temperatures in contrast to the increase for $\Phi_{C_2H_6}$. Reactions 7 and 8 provide an alternative scheme for C_2H_6 formation at high temperatures. Reaction 7 is analogous to that suggested by Rust, Seubold and Vaughan[17] in explanation of 4-heptanol formation in the peroxide initiated thermal decomposition of gaseous n-butyraldehyde. However reaction 8 is unattractive because it involves a hitherto unobserved and unexpected radical rearrangement. Definite conclusions regarding these reaction paths must await further studies of this and related systems. The temperature dependence of $R_{CH_4}/R_{C_2H_6}$ from runs at temperatures above 150° leads to $E_1 - E_6$ or $E_1 - \Delta H_7 - E_8$ (depending on the mechanism choice) $= -5 \pm 1$ kcal./mole. (In obtaining this estimate minor corrections to measured $R_{C_2H_6}$ data were made to eliminate C_2H_6 formation from 2.)

If 1, 2 and 6 (or 7 and 8) describe CH_4 and C_2H_6 formation completely then the quantum yield data from all the runs should be described by the relation c.

[14] A. F. Trotman-Dickenson, *Quart. Rev.* (*London*), **7**, 198 (1953).

[15] R. A. Holroyd and W. A. Noyes, Jr., THIS JOURNAL, **76**, 1583 (1954); R. E. Rebbert and E. W. R. Steacie, *Can. J. Chem.*, **31**, 631 (1953).

[16] F. E. Blacet and W. E. Bell, *Discs. Faraday Soc.*, **14**, 70 (1953).

[17] F. F. Rust, F. H. Seubold and W. E. Vaughan, THIS JOURNAL, **70**, 4253 (1948).

$$\Phi_{C_2H_6}/\Phi^2_{CH_4} = (k_2 I_a/k_1^2[CF_3COCH_3]^2) + k_6/k_1\Phi_{CH_4} \quad (c)$$

At low temperatures, high I_a, or low $[CF_3COCH_3]$ the first term of *c* predominates, and *c* reduces to *a*. At 117° the second term becomes important for values of $[CF_3COCH_3]/I_a^{1/2} > 3 \times 10^{12}$ molec. (sec./cc.-q.)$^{1/2}$ (see Fig. 2). The two terms are of about equal size at 150° for the experimental conditions used in obtaining the data plotted in Fig. 3; a transition in the kinetics is evident from the break in the CH_4–C_2H_6 rate function plot. At 265° the second term predominates. Although relation *c* gives a satisfactory description of most of the data, it fails to explain the results from experiments at 117° and at very high $[CF_3COCH_3]$ or low I_a. Under these conditions it appears that heterogeneous reactions forming C_2H_6 and C_2F_6 become important.

An additional sequence of reactions must be suggested to account for the chain forming CH_3-containing molecules ($4CH_3$/quantum at 350°; see Fig. 4) and the marked deficiency in CF_3-containing species in the gaseous products; $\Sigma\Phi_{CF_3}$ reaches a maximum of 0.6 at about 280° and decreases with further temperature increase. The reactions 6 or 7 and 8 together with 9–12 are consistent with these results. Reactions 9 and 10 generate CH_3 radicals from CF_3.

$$CF_3 + CF_3COCH_3 \rightleftharpoons (CF_3)_2COCH_3 \quad (9)$$

$$(CF_3)_2COCH_3 \longrightarrow CH_3 + CF_3COCF_3 \quad (10)$$

$$CF_3CO \longrightarrow CF_3 + CO \quad (11)$$

$$CH_2COCF_3 \longrightarrow CH_2CO + CF_3 \quad (12)$$

Reactions 11 and 12 are proposed to complete the chain sequence. The reverse reactions in 7 and 9 and the reaction 10 are analogous to the *t*-butoxy radical decomposition. Reaction 10 might be favored over the reverse of 9 (because of bond strength differences). To date analytical difficulties have prevented analysis for CF_3COCF_3 and CH_2CO which are expected major products of the high temperature photolysis and the suggested reaction scheme. However the results presented give strong indirect evidence for the rarely postulated gas phase reaction of free radical addition to a carbonyl bond. The reaction sequence 1–12 describes well the results of CF_3COCH_3 photolysis, but definite conclusions regarding many points in the mechanism must await further experimentation. We are seeking additional information concerning the possible reactions 7, 8, 9 and 10 through the thermal and photochemical generation of CH_3 and CF_3 radicals in the presence of CF_3COCH_3 and CH_3COCH_3.

Primary Processes.—The light-activated state of CF_3COCH_3 formed at 3130 Å. appears to have a greater stability than that formed from CH_3COCH_3 at this wave length. This is evident in the very low quantum yields of products at low temperature (see Fig. 1), the increase in quantum yields at low concentrations (compare Φ_{CO} in runs 5–8 in Table I) and the decrease in Φ_{CO} and Φ_{CH_4} when CO_2 gas is added (compare runs 7 and 9 in Table I). Collisional deactivation (reaction 13) is probably important following activation at low temperatures and high concentrations.

$$CF_3COCH_3 + h\nu \longrightarrow CF_3COCH_3^* \quad (I)$$

$$CF_3COCH_3^* + M \longrightarrow CF_3COCH_3 + M' \quad (13)$$

Three possible primary decomposition modes which might be expected in this molecule are

$$CF_3COCH_3^* \longrightarrow CF_3CO + CH_3 \quad (II)$$

$$\longrightarrow CF_3 + CH_3CO \quad (III)$$

$$\longrightarrow CF_3CH_3 + CO \quad (IV)$$

Reaction IV must be unimportant since the magnitudes of the different ethane yields are in reasonable agreement with that expected from purely random recombination of CH_3 and CF_3 radicals. Process II might be expected to predominate over III on the basis of probable bond strength differences. Analysis was not accomplished for $(CF_3CO)_2$, $(CH_3CO)_2$ and other such products which might be helpful in deciding this question. However at every temperature the quantum yield summation, $\Sigma\Phi_{CH_3}$, is at least twice the magnitude of $\Sigma\Phi_{CF_3}$ (see Fig. 4), a result which is consistent with the predominant occurrence of II.

Acknowledgment.—The authors wish to thank The Ohio State University Development Fund which provided one of us (R.A.S.) with a research fellowship. Grateful acknowledgment is made to Professor Albert L. Henne and his co-workers for their coöperation in the pursuance of this study, the Organic Chemicals Department of E. I. du Pont de Nemours & Co., the Minnesota Mining and Manufacturing Co., and Professor J. D. Park for samples of fluorocarbons which they provided.

COLUMBUS, OHIO