JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

(Registered in U. S. Patent Office) (© Copyright, 1956, by the American Chemical Society)

VOLUME 78 JUNE 8, 1956 NUMBER 11

PHYSICAL AND INORGANIC CHEMISTRY

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

The Vapor Phase Photolysis of Trifluoroacetophenone and Mixtures of Trifluoroacetophenone and Trifluoroacetone[1]

BY ROBERT M. SMITH AND JACK G. CALVERT[2]

RECEIVED JANUARY 13, 1956

The gas phase photolysis of $C_6H_5COCF_3$ is studied at various temperatures, concentrations, and intensities of 3660 Å., 3130 Å., and full mercury arc light. The major gaseous products are CO, CF_3H and C_2F_6. $(C_6H_5CO)_2$ and C_6H_6 are identified in the condensable products. A chemically unreactive, clear polymer film formed on the reaction cell window during the photolysis. In experiments at high absorbed light intensities, CF_3H and C_2F_6 are formed primarily in the homogeneous reactions: $CF_3 + C_6H_5COCF_3 \rightarrow CF_3H + C_6H_4COCF_3$ (a), and $2CF_3 \rightarrow C_2F_6$ (b). The activation energy difference $E_a - E_b/2 = 7.2 \pm 0.5$ kcal./mole; the ratio of collision theory P-factors $P_a/P_b{}^{1/2}$ is in the range 10^{-4}–10^{-6}. A large fraction of the CF_3 radicals formed photochemically do not appear in the gaseous reaction products. It is proposed that these add to the aromatic nucleus of the parent ketone and initiate polymer formation. In the photolyses of mixtures of $C_6H_5COCF_3$ and CH_3COCF_3, the high temperature chain reaction of CH_3COCF_3 involving CO and CH_3-containing species is confirmed. The expected product CF_3COCF_3 could not be detected in the reaction products of CH_3COCF_3 photolyses. Thus, the previously proposed reaction sequence: $CF_3 + CH_3COCF_3 \rightleftarrows CH_3CO(CF_3)_2$, $CH_3CO(CF_3)_2 \rightarrow CH_3 + CF_3COCF_3$, appears to be unimportant. The generation of CH_3 from CF_3 radicals probably occurs by some other undefined heterogeneous path.

This work was initiated to study the photolysis of pure $C_6H_5COCF_3$ and to determine its efficiency as a CF_3 radical source in the near ultraviolet. In view of the high extinction coefficient for $C_6H_5COCF_3$ at 3660 Å., it was supposed that selective photodecomposition of $C_6H_5COCF_3$ in CH_3COCF_3 mixtures could be effected at this wave length. If CF_3 radicals could be produced in this manner, their interaction with CH_3COCF_3 molecules could be determined to test the suggested mechanism of CH_3COCF_3 chain decomposition[3]

$$CF_3 + CH_3COCF_3 \rightleftarrows CH_3CO(CF_3)_2 \quad (1)$$

$$CH_3CO(CF_3)_2 \longrightarrow CH_3 + CF_3COCF_3 \quad (2)$$

$$CH_3 + CH_3COCF_3 \longrightarrow C_2H_6 + CF_3CO \quad (3)$$

$$CH_3 + CH_3COCF_3 \longrightarrow CH_4 + CH_2COCF_3 \quad (4)$$

$$CF_3 + CH_3COCF_3 \longrightarrow CF_3H + CH_2COCF_3 \quad (5)$$

$$CF_3CO \longrightarrow CF_3 + CO \quad (6)$$

$$CH_2COCF_3 \longrightarrow CH_2CO + CF_3 \quad (7)$$

The identification of CH_4, C_2H_6, CF_3CH_3 and/or CF_3COCF_3 products from these photolyses would provide evidence for the suggested scheme.

Experimental

Apparatus.—The all-glass photolysis system consisted of a quartz photolysis cell (15.0 cm. long, 3.0 cm. diam), a glass circulating pump, trap, two high vacuum stopcocks lubricated with high temperature silicone grease, and a sickle gage. These parts were suspended in a large air thermostat which was maintained at 100 ± 1° by a system of heaters, Fenwall regulator and circulating fan. Radiation from a Hanovia type A (S-500) burner (run on a regulated 3.00 amp. d.c. current) was filtered to isolate wave lengths 3660[4] and 3130 Å.,[5] and was also used unfiltered in some experiments. The light beam was always well collimated by a series of lenses and stops so that a fairly homogeneous beam of radiation filled the cell volume (106 cc.) almost completely. A photomultiplier-amplifier was used to measure fractions of light absorbed at wave lengths 3660 and 3130 Å. Absorptions of full arc radiation were estimated from these values together with Fig. 1 and the manufacturer's data for the relative intensities of the wave lengths in the arc spectrum. Relative absorption by $C_6H_5COCF_3$ and CH_3COCF_3 at similar concentrations can be compared from the CH_3COCF_3 and $C_6H_5COCF_3$ (B) curves. Curve A was determined at a much lower concentration to show best the nature of the absorption band. Absolute intensities were estimated by $K_3Fe(C_2O_4)_3$ actinometry[6] at intervals during the course of the photochemical runs. The total quanta entering the cell/cc.-sec. × 10^{-12} were: 3660 Å., 20.4; 3130 Å., 4.39 (av. 6 detns.); full arc, 66.1. The full arc value was calculated using a weighed

---

[1] Taken from the Thesis of R. M. Smith submitted in partial fulfillment of the requirements for the Ph.D. degree, The Ohio State University, 1955. Presented before the Division of Physical and Inorganic Chemistry, 129th National Meeting of the American Chemical Society, Dallas, Texas, April, 1956.

[2] Author to whom communications should be addressed.

[3] R. A. Sieger and J. G. Calvert, THIS JOURNAL, **76**, 5197 (1954).

[4] W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, p. 69.

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

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

average quantum yield of 1.15 for the ferrioxalate decomposition. (Approximately half of the absorbed radiation was below 3000 Å.) The results of photolyses of mixtures of $C_6H_5COCF_3$ and CH_3COCF_3 with 3130 Å. were compared with results of separate photolyses of the individual components at the same conditions of concentration, temperature and absorbed light intensity. Uniform density filters reduced the incident intensity used for the pure CH_3COCF_3 photolyses so that the intensity of light absorbed by CH_3COCF_3 was approximately the same as in mixture photolyses with which comparison was made.

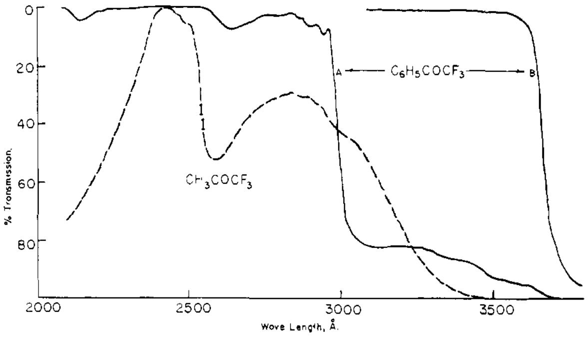

Fig. 1.—The ultraviolet absorption spectra of $C_6H_5COCF_3$ and CH_3COCF_3: $C_6H_5COCF_3$(A), vapor at 3 mm. (1.5×10^{-4} *M*), 25°, 10 cm. path length; $C_6H_5COCF_3$ (B), 1.0×10^{-2} *M* in CCl_4 solution, 25°, 5 cm. path length; CH_3COCF_3, vapor at 206 mm. (1.1×10^{-2} *M*), 30°, 5 cm. path length.

Materials.—$C_6H_5COCF_3$ and CH_3COCF_3 were purchased from the Caribou Chemical Co. and purified by fractionation at reduced pressures in a high vacuum system. High purity samples of CF_3H, C_2F_6 and CF_3CH_3 were provided by the Organic Chemicals Department of E. I. du Pont de Nemours and Co. C_2H_6 and CH_4 reference gases were Phillips Research Grade. A sample of CF_3COCF_3 was furnished by Dr. Robert R. Brown of The Ohio State University.

Product Analysis.—CO and CH_4 were removed following photolysis using a Toepler pump with the other products condensed at N_2(l) temperature. CF_3H and C_2F_6 (together with a small amount of CO_2 and C_6H_6) were removed at Dry Ice temperature after photolyses of $C_6H_5COCF_3$. Following photolyses of pure CH_3COCF_3 and mixtures of the two ketones, the second fraction containing CF_3H, C_2F_6, CH_3CF_3 and some CH_3COCF_3 was removed at −110 to −100° using a modified Ward still.[7] There was essentially complete recovery of all products except CF_3CH_3 which was about 10% low.[3] CO was analyzed by reaction with Ag_2O using a Blacet-Leighton gas analysis system.[8] In several experiments portions of the low temperature fraction were examined mass spectrometrically for SiF_4 before the Ag_2O treatment. CF_3H, C_2F_6, CF_3CH_3, CH_4 and C_2H_6 were determined using a General Electric analytical mass spectrometer. Very minor amounts of CO_2 and C_6H_6 were detected mass spectrometrically. $(C_6H_5CO)_2$ was identified in the condensable fraction from its absorption spectrum in CCl_4 solution (max. at 370 mμ).[9] A small deposit of a clear, solid film of a very insoluble and unreactive material (suggestive of a fluorinated polymer) built up on the photolysis cell front window during the photochemical runs. The solid absorbed strongly in the ultraviolet and was removed regularly to avoid serious lowering of the incident intensity. Of the common solvents employed only hot fuming HNO_3 was successful in removing the polymer. Even in this case *no* apparent chemical reaction with the polymer was involved, but a prolonged treatment promoted the detachment of the solid film from the quartz wall. The amounts of material formed were too small to enable analysis. No indications of SiF_4 and CF_4 were found mass spectrometrically in any of the experiments. The infrared spectrum of the condensable fraction, containing a great excess of ketone, was determined on a Perkin-Elmer double beam instrument with pure $C_6H_5COCF_3$ in the reference beam. The spectrum was complex and showed absorption peaks not characteristic of $C_6H_5COCF_3$ at the following wave lengths in microns: 2.85, 3.30, 6.02, 6.75, 7.09, 7.70, 8.0?, 9.1?, 9.3?, 9.75, 9.93, 11.1?, 11.7, 13.5, 14.4. (The questioned numbers are of doubtful significance.) No satisfactory correlation with possible simple products such as $C_6H_5CF_3$, $(C_6H_5)_2$ or $C_6H_5COC_6H_5$, and observed products $(C_6H_5CO)_2$ and C_6H_6 was evident.

Results

Molar Absorbancy Indices.—At a given temperature $C_6H_5COCF_3$ and CH_3COCF_3 vapor followed Beer's law within the experimental error over forty-fold and tenfold pressure ranges, respectively. Representative values of a_M are: $C_6H_5COCF_3$ at 3130 Å., 73.8 (245.1°); at 3660 Å., 6.17 (214.6°), 11.4 (279.9°). CH_3COCF_3 at 3130 Å., 5.91 (245.1°), 6.08 (348.2°). $\log_{10}(I_0/I) = a_M bc$; *b* is the path length in cm.; *c* is the molar concn.

Effect of Variables in the Photolysis of $C_6H_5COCF_3$.—Quantum yields of products in 3660 and 3130 Å. experiments are given in Table I. The results of runs 6–42 are shown in graphical form only. In order to obtain reasonable quantities of C_2F_6 the high intensity of the full arc was utilized in these experiments. The variation of product rates of formation with absorbed light intensity, concentration of ketone and temperature are summarized in Figs. 2, 3 and 5, respectively. A slow but measurable thermal reaction necessitated a small correction to the rates in the highest temperature run (338.9°). The correction amounted to the following per cent. of the total rate of each product: CO, 0.2; CF_3H, 0.4; C_2F_6, 2.6.

TABLE I

QUANTUM YIELDS OF PRODUCTS IN THE PHOTOLYSIS OF $C_6H_5COCF_3$

Run no.	Wave length, Å.	$I_a \times 10^{-12}$, q./cc.-sec.	Temp., °C.	$[C_6H_5COCF_3]$, molec./cc. $\times 10^{-18}$	Quantum yields CO	CF$_3$H	C$_2$F$_6$
1	3660	8.16	214.6	1.45	0.0004[a]	0.003_4	0.0004_2
2	3660	11.3	279.9	1.24	.0001[a]	$.007_2$	$.0001_4$
4	3130	8.07	304.3	1.09	$.17_7$	$.05_9$	$.0005_1$
5	3130	8.01	157.6	1.28	$.002_2$	$.0009_4$	$.0000_1$[a]

[a] Corresponds to the limit of detection.

Photolysis of Mixtures of $C_6H_5COCF_3$ and CH_3COCF_3.—The rates of product formation in the mixture photolyses are given in Table II. The intensity of light absorbed by component (a) in the mixture was calculated using $I_0(1 - I/I_0)(a_a c_a)/(a_a c_a + a_b c_b)$. The rate and quantum yield sums shown in the last columns were calculated from the equations

$$\Sigma R_{CH_3} = R_{CH_4} + 2R_{C_2H_6} + R_{CF_3CH_3}$$
$$\Sigma R_{CF_3} = R_{CF_3H} + 2R_{C_2F_6} + R_{CF_3CH_3}$$

or the similar equations involving quantum yields. Two confirmatory experiments were made on the photolysis of pure CH_3COCF_3 under conditions favoring the chain decomposition. The results of these experiments are given in Table III. CF_3COCF_3 could not be detected mass spectrometrically in the products of runs 46 and 54 although known mixture analysis proved the high sensitivity

---

(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).

(9) N. J. Leonard, R. T. Rapala, H. J. Herzog and E. R. Blout, THIS JOURNAL, **71**, 2997 (1949).

TABLE II

RATES OF PRODUCT FORMATION IN THE PHOTOLYSIS OF PURE CH_3COCF_3 AND $C_6H_5COCF_3$ AND THEIR MIXTURES AT 3130 Å.
(I_0 = 4.39 × 10^{12} Q./CC.-SEC.; TEMP., 245°)

Run	(Pressure, mm.) (a) CH_3COCF_3	(b) $C_6H_5COCF_3$	I_a × 10^{-12}, q./cc.-sec.	Measured rates, molec./cc.-sec. × 10^{-10} CO	CH_4	C_2H_6	CF_3H	C_2F_6	CF_3CH_3	ΣR_{CH_3}	ΣR_{CF_3}	$\Sigma\Phi_{CH_3}$	$\Sigma\Phi_{CF_3}$
43[a]	38.2	0.0	(a) 0.351	48.6	36.2	16.5	25.1	0.223	0.250	69.5	25.8	1.98	0.73
45	0.0	33.2	(b) 4.07	158	0.0	0.0	21.0	.410	0.0	0.0	21 8	0.0	.054
44	38.2	33.2	(a) 0.349										
			(b) 3.79	324	26.1	20.5	76.2	.598	1.82	68.9	79.2	..	..
Rate sums runs 43 and 45:				207	36.2	16.5	46.1	.633	0.250	69.5	47.6	..	..
46[a]	82.0	0.0	(a) 0.665	117	35.7	43.3	56.7	.176	.410	123	57.5	1.85	.86
47	82.0	29.8	(a) 0.746										
			(b) 3.39	420	39.5	50.7	116	.317	.433	141	117	..	..
Rate sums runs 45 and 46:				275	35.7	43.3	77.7	.586	.410	123	79.3	..	..
49[a]	60.0	0.0	(a) 0.520	85.6	36.5	28.6	43.6	1.10	2.02	95.7	47.8	1.84	.92
51	60.0	31.6	(a) 0.549										
			(b) 3.59	319	30.9	33.4	96.0	1.36	0.856	98.6	99.6	..	..
Rate sums runs 45 and 49:				244	36.5	28.6	64.6	1.51	2.02	95.7	69.6	..	..

[a] I_0 was lowered in these runs by using uniform density filters so that the intensity of light absorbed by CH_3COCF_3 was essentially the same in the CH_3COCF_3–$C_6H_5COCF_3$ mixture runs which followed.

TABLE III

QUANTUM YIELDS OF PRODUCTS IN THE PHOTOLYSIS OF CH_3COCF_3 AT 3130 Å.

Run	Pressure CH_3COCF_3, mm.	Temp., °C.	I_a × 10^{-12}, q./cc.-sec.	Quantum yields of products CO	CH_4	C_2H_6	CF_3H	C_2F_6	CF_3CH_3	ΣCH_3	ΣCF_3
53	228.4	245	3.34	1.11	0.811	0.159	0.560	0.0013	0.0035	1.13	0.57
54	534.6	346	4.15	7.42	8.82	11.3	1.37	.000	.220	31.6	1.59

of the analytical method. Thermal corrections were necessary for run 54; the correction was the following % of the total rate: CO, 3.5; CH_4, 3.0; C_2H_6, 30.4; CF_3H, 6.7; C_2F_6, 100; CF_3CH_3, 6.6.

Discussion

The Mechanism of Trifluoroacetophenone Photolysis; CF_3H and C_2F_6 Formation.—The data suggest that CF_3H and C_2F_6 are formed in the reactions

$$CF_3 + C_6H_5COCF_3 \longrightarrow CF_3H + C_6H_4COCF_3 \quad (8)$$

$$2CF_3 \longrightarrow C_2F_6 \quad (9)$$

$$CF_3\ (+\ \text{wall}) \longrightarrow {}^1/_2C_2F_6\ (+\ \text{wall}) \quad (10)$$

In Fig. 2 it is seen that the rate of C_2F_6 formation is directly proportional to the absorbed light intensity, $R_{C_2F_6} = kI_a$. If 9 is the dominant mode of C_2F_6 formation $R_{C_2F_6}$ will be given by

$$R_{C_2F_6} = k_9[CF_3]^2 = kI_a \quad (11)$$

If 10 alone leads to C_2F_6 then

$$R_{C_2F_6} = k_{10}[CF_3] = kI_a \quad (12)$$

The rate of CF_3H formation

$$R_{CF_3H} = [CF_3][C_6H_5COCF_3]k_8 \quad (13)$$

is approximately proportional to $I_a^{1/2}$ at the high light intensities and tends toward a direct proportionality to I_a at the lowest intensities. These results point to the dominance of C_2F_6 formation by 9 at the high intensities (combine 11 and 13) and by 10 at the low intensities (combine 12 and 13). In the experiments with varied temperature and concentration the intensities were maintained in the high range where 9 predominates.

In Fig. 4 the rate function $R_{CF_3H}/R_{C_2F_6}{}^{1/2}$ is seen to have a linear dependence on the concentration of $C_6H_5COCF_3$, a result consistent with CF_3H and C_2F_6 formation in reactions 8 and 9. From these

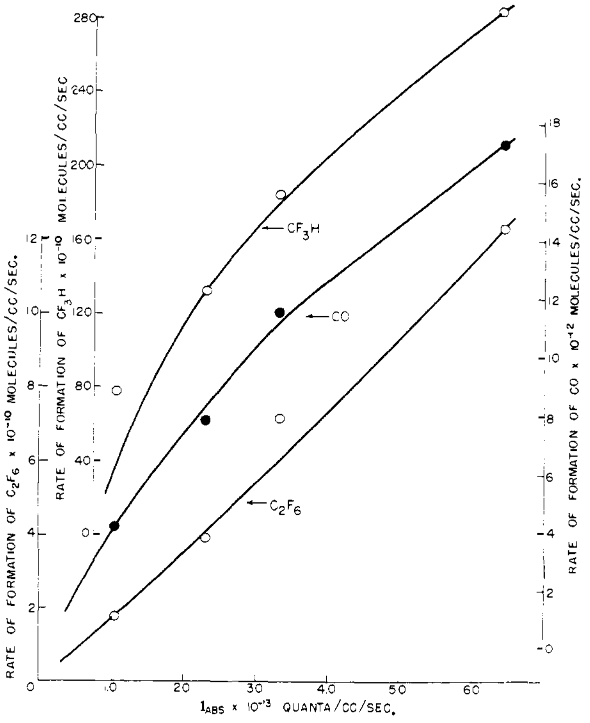

Fig. 2.—The effect of absorbed light intensity on the rates of formation of gaseous products in the photolysis of $C_6H_5COCF_3$ vapor using the full mercury arc: temperature, 289°; $[C_6H_5COCF_3]$, 1.46 × 10^{18} molec./cc.

data the ratio of the rate constants $k_8/k_9{}^{1/2}$ is estimated to be 5.6 × 10^{-12} (cc./molec.-sec.)$^{1/2}$ at the temperature 289°. Comparable values from other systems at this temperature are $k_5/k_9{}^{1/2}$, 6.4 × 10^{-10}; $k_4/k_{14}{}^{1/2}$ 8.7 × 10^{-12}, $2CH_3 \rightarrow C_2H_6$ (14)[3];

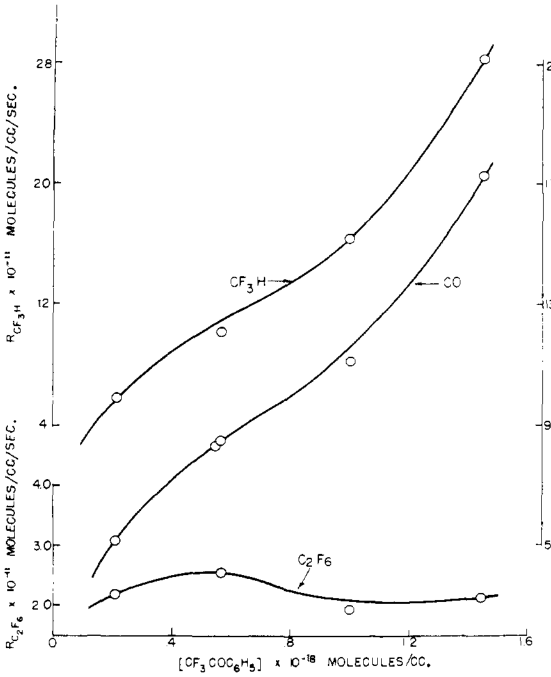

Fig. 3.—The effect of $[C_6H_5COCF_3]$ on the rates of formation of gaseous products in the photolysis of $C_6H_5COCF_3$ using the full mercury arc: temperature, 289°; I_a, 41.6 × 10^{12} to 59.5 × 10^{12} q./cc.-sec. from the lowest to the highest concentration, respectively.

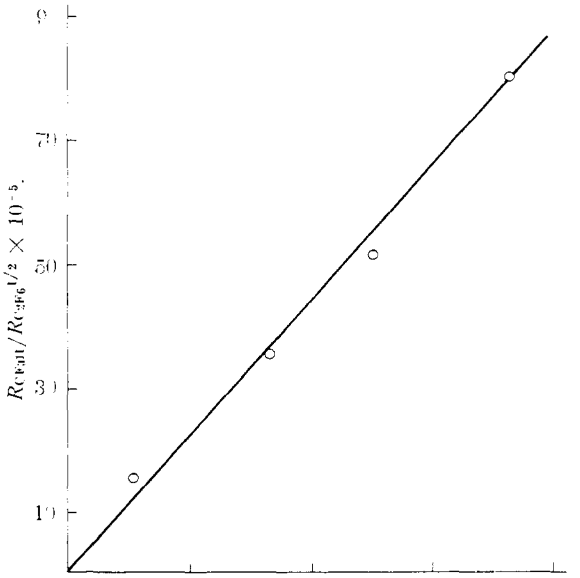

Fig. 4.—The effect of $[C_6H_5COCF_3]$ on the rate function $R_{CF_3H}/R_{C_2F_6}^{1/2}$: photolysis of $C_6H_5COCF_3$ with full mercury arc; temperature, 289°.

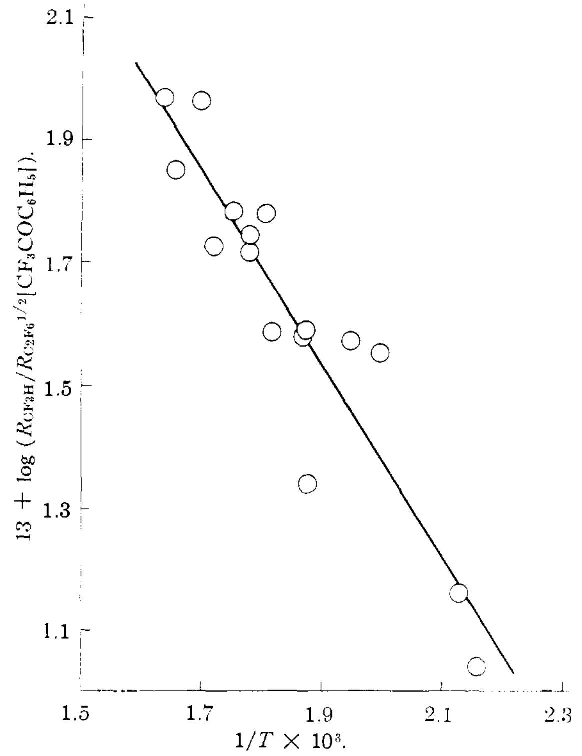

Fig. 5.—The Arrhenius plot of the rate function, $R_{CF_3H}/R_{C_2F_6}^{1/2}[C_6H_5COCF_3]$: photolyses of $C_6H_5COCF_3$ with full mercury arc.

$k_{15}/k_{14}^{1/2}$, 1.4 × 10^{-12}, $CH_3 + C_6H_6 \rightarrow CH_4 + C_6H_5$ (15).[10] The function $R_{CF_3H}/R_{C_2F_6}^{1/2}$ $[C_6H_5COCF_3]$, equal to $k_8/k_9^{1/2}$ in terms of the suggested mechanism, is plotted *versus* $1/T$ in Fig. 5. The rather large scatter is primarily the result of the inaccuracy in the analysis of small quantities of C_2F_6, but it may reflect as well a small variable con-

TABLE IV

COMPARISON OF THE ACTIVATION ENERGY FOR H-ABSTRACTION BY CH_3 AND CF_3

Reaction	$E_a - E_c/2$, kcal./mole	ΔE, kcal./mole
$CF_3 + C_6H_5COCF_3 \rightarrow CF_3H + C_6H_4COCF_3$	7.2	2.0
$CH_3 + C_6H_6 \rightarrow CH_4 + C_6H_5$[10]	9.2	
$CF_3 + CH_3COCF_3 \rightarrow CF_3H + CH_2COCF_3$[3]	6.6	2.3
$CH_3 + CH_3COCF_3 \rightarrow CH_4 + CH_2COCF_3$[3]	8.9	
$CF_3 + CH_4 \rightarrow CF_3H + CH_3$[16,11]	9.5–10.3	2.6–4.5
$CH_3 + CH_4 \rightarrow CH_4 + CH_3$[17,12]	12.9–14.0	
$CF_3 + C_2H_6 \rightarrow CF_3H + C_2H_5$[11]	7.5	2.9
$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$[13]	10.4	
$CF_3 + n\text{-}C_4H_{10} \rightarrow CF_3H + C_4H_9$[16]	5.5	2.8
$CH_3 + n\text{-}C_4H_{10} \rightarrow CH_4 + C_4H_9$[13]	8.3	
$CF_3 + CF_3CHO \rightarrow CF_3H + CF_3CO$[14]	6.2–6.5	0.3–1.3
$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$[15]	7.5–6.8	

---

(10) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

(11) P. B. Ayscough, J. C. Polanyi and E. W. R. Steacie, *Can. J. Chem.*, **33**, 743 (1955).

(12) J. R. McNesby and A. S. Gordon, THIS JOURNAL, **76**, 4196 (1954).

(13) A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951).

(14) R. E. Dodd, University of Durham, private communication.

(15) (a) D. H. Volman and R. K. Brinton, *J. Chem. Phys.*, **20**, 1764 (1952); (b) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 31 (1955).

(16) G. O. Pritchard, H. O. Pritchard and A. F. Trotman-Dickenson, *Chemistry and Industry*, 564 (1955).

(17) F. S. Dainton and D. E. McElcheran, *Trans. Faraday Soc.*, **51**, 657 (1955).

tribution from some heterogeneous reaction such as 10. The least squares line through all the points gives $E_8 - E_9/2 = 7.2 \pm 0.5$ kcal./mole. The ratio of collision theory P-factors $P_8/P_9^{1/2}$ is in the range 10^{-4} to 10^{-6}, assuming the collision diameters for CF_3 and $C_6H_5COCF_3$ to be 4.0 and 6.3 Å., respectively. The range of values is a consequence of the uncertainty in the effective reaction volume (about 90% of the incident light was absorbed in these runs). Summarized in Table IV are the activation energy differences $E_a - E_c/2$, activation energy for H-abstraction minus one-half that for the combination reaction of CH_3 or CF_3, and ΔE, equal to the difference between the activation energies for H-abstraction by CH_3 and CF_3 minus $E_{14}/2$ plus $E_9/2$, for a series of related reactions of CH_3 and CF_3. It is unlikely that the possible configurational rearrangement[3] or dipole–dipole interaction[11] of combining CF_3 radicals would lead to an energy barrier as great as 4.0 kcal./mole for reaction 9, and it is probable that E_{14} is near zero. Therefore the present results and all available data show that the activation energy for similar H-abstraction reaction is lower for CF_3 than for CH_3 radicals. The exact magnitude of the activation energy differences must await further study of the CF_3 combination reaction. The difference in activation energy is probably not a consequence of a difference in the C–H bond dissociation energies of CH_4 and CF_3H; D_{CF_3-H} appears to be approximately equal to D_{CH_3-H}.[18] It may reflect the higher electron affinity of the CF_3 radical.[19]

Addition of CF_3 to $C_6H_5COCF_3$.—One of the most striking features of $C_6H_5COCF_3$ photolysis is the large unbalance between CO and CF_3-containing compounds found in the gaseous products. See Figs. 2 and 3. At 197° the ratio $R_{CO}/(R_{CF_3H} + 2R_{C_2F_6}) = 26.1$. This ratio decreases regularly with increase in temperature; at 339° it is 2.8. It is apparent that the major reaction of CF_3 radicals in this system is not 9 or 10 but some reaction of low activation energy forming condensable products. Ayscough, Polanyi and Steacie[11] proposed that CF_3 radicals react with a quartz cell to form CO_2 and SiF_4 under certain conditions. This reaction is not important in this system since no SiF_4 could be detected in the present work. (A trace of CO_2 of unknown origin was found in some of the runs.) A chemically inert, clear film of polymeric material formed on the cell walls during photolysis. The small quantity of the solid precluded the possibility of chemical analysis, but the extremely inert character of the deposit is suggestive of a fluorinated polymer. It may be suggested that the polymer formation and the large unbalance in CF_3-containing gaseous compounds are related, and that polymer formation may be initiated by the addition of CF_3 radicals to the aromatic nucleus of $C_6H_5COCF_3$

$$CF_3 + C_6H_5COCF_3 \longrightarrow CF_3C_6H_5COCF_3 \longrightarrow \text{polymer} \quad (16)$$

It has been demonstrated by Szwarc and co-workers[20] that CH_3 radical addition to various aromatic systems occurs in isoöctane solutions. The expected higher electron affinity of the CF_3 radical would favor a more pronounced interaction of CF_3 with aromatic systems than that found for CH_3. Presumably 16 results in the transformation of the the benzene nucleus to a substituted cyclohexadiene free radical which leads to polymer in further undefined reactions. Reasonable speculation concerning the mechanism of polymerization is impossible at present.

Other Secondary Reactions.—Indirect evidence for the presence of CF_3CO radicals is obtained in consideration of the effect of ketone concentration on the rates of product formation from runs at 289°, Fig. 3. R_{CF_3H} and R_{CO} increase markedly as the concentration of ketone increases. However, the ratio $R_{CO}/(R_{CF_3H} + 2R_{C_2F_6})$ remains essentially constant: 5.95, 5.88, 6.00 and 5.60 for $[C_6H_5COCF_3]$ of 0.212, 0.564, 1.00 and 1.45×10^{18} molec./cc., respectively. This ratio is also relatively insensitive to changes in I_a (data from Fig. 2): 5.60, 6.06, 5.62 and 5.13 at I_a values of 59.5, 33.3, 23.2 and 10.1×10^{12} q./cc.-sec., respectively. These facts are consistent with the proposed reaction sequence and the additional reactions 17 and 18.

$$CF_3CO \longrightarrow CF_3 + CO \quad (17)$$

$$CF_3CO\ (+\ \text{wall}) \longrightarrow \text{non-volatile product}\ (+\ \text{wall}) \quad (18)$$

In terms of this mechanism the increase in R_{CF_3H} and R_{CO} with increase in the concentration of $C_6H_5COCF_3$ reflects the increasing importance of 17. High concentrations would favor 17 since diffusion to the wall during the lifetime of the radical is less likely under these conditions. Presumably the CF_3 radical formed in 17 would react primarily by 8 and 16 (to a minor extent by 9). Since the rates of both 8 and 16 are proportional to $[CF_3][C_6H_5COCF_3]$, the ratio of the rates of these reactions would remain constant with change in $[C_6H_5COCF_3]$, and the ratio of $R_{CO}/(R_{CF_3H} + 2R_{C_2F_6})$ would be unchanged as observed. (Essential to these arguments is the assumption that the extent of reaction 20 is not a function of ketone concentration, or that 20 is a negligible source of CO at 289°.)

The observed products $(C_6H_5CO)_2$ and C_6H_6 can be accounted for by conventional reactions

$$2C_6H_5CO \longrightarrow (C_6H_5CO)_2 \quad (19)$$

$$C_6H_5CO \longrightarrow C_6H_5 + CO \quad (20)$$

$$C_6H_5 + C_6H_5COCF_3 \longrightarrow C_6H_6 + C_6H_4COCF_3 \quad (21)$$

The steady-state concentration of C_6H_5 in this system is apparently very low since no $(C_6H_5)_2$, $C_6H_5COC_6H_5$ or $CF_3C_6H_5$ would be found in the condensable products. $(C_6H_5CO)_2$ was present in the products in easily detectable quantities following photolysis at 275°. The high thermal stability of the benzoyl radical, to which this points, is in marked contrast to the demonstrated thermal instability of the acetyl radical in pure acetone vapor at temperatures above 100°[21]; this difference is consistent

---

[18] G. O. Pritchard, H. O. Pritchard, H. I. Schiff and A. F. Trotman-Dickenson, *Chemistry and Industry*, 896 (1955).

[19] H. O. Pritchard, J. B. Pyke and A. F. Trotman-Dickenson, THIS JOURNAL, **77**, 2629 (1955).

[20] M. Levy and M. Szwarc, *J. Chem. Phys.*, **22**, 1621 (1954); M. Levy, M. Steinberg and M. Szwarc, THIS JOURNAL, **76**, 3439 (1954); M. Szwarc, *J. Chem. Phys.*, **23**, 204 (1955); M. Levy and M. Szwarc, THIS JOURNAL, **77**, 1949 (1955).

[21] D. S. Herr and W. A. Noyes, Jr., *ibid.*, **62**, 2052 (1940).

with the expected resonance stabilization of the benzoyl radical.

The Primary Process in $C_6H_5COCF_3$ Photolysis.—The results are consistent with the occurrence of two primary processes

$$C_6H_5COCF_3 + h\nu \longrightarrow \begin{cases} \longrightarrow C_6H_5CO + CF_3 & (I) \\ \longrightarrow C_6H_5 + COCF_3 & (II) \end{cases}$$

The identification of bibenzoyl in the reaction products gives strong evidence for I. This process is analogous to that suggested for acetophenone photodecomposition.[22] Process II is indicated by the evidence cited for the presence of CF_3CO radicals in this system. The relative importance of these cannot be estimated from the present data. Trifluorotoluene could not be detected in the condensable products. Thus a third possible primary process leading to $CF_3C_6H_5$ and CO in a concerted mechanism must be unimportant.

No single mechanism seems completely satisfying in the explanation of the low quantum yields. $C_6H_6COCF_3$ vapor absorbs strongly at 3660 Å. (curve B of Fig. 1), but the efficiency of gaseous product formation is extremely low. The data of Table I shows that little CO and other gaseous products are formed even at 280° ($\Phi_{CO} < 0.0001$). Low quantum yields are also found at 3130 Å.; even in photolyses at 304°, less than 20% of the absorbing molecules decompose to give gaseous molecules. It would be rather surprising if reaction 16, its analog involving CF_3CO, and recombination reactions are fast enough to exclude essentially all of reactions 8, 9 and 17. An alternative proposal of an excited molecule mechanism has certain inconsistencies. One might expect that fluorescence would play some part in the deactivation process. In qualitative experiments there was no visible fluorescence when pure $C_6H_5COCF_3$ vapor at 3 mm. and 25° was irradiated with 3660—3000 Å. light. Furthermore there is no indication of collisional deactivation in the observed effect of increased ketone pressure on the rate of product formation. The choice of detailed mechanism of the primary process must await further study.

The Photolysis of Mixtures of $C_6H_5COCF_3$ and CH_3COCF_3.—The original plan of selective photolysis of $C_6H_5COCF_3$ in mixtures with CH_3COCF_3 by irradiation with 3660 Å. light was discarded because of the apparent low efficiency of CF_3 radical formation at this wave length. Both ketones absorb 3130 Å. light, but the absorbancy indices are greatly different. (Compare the spectra of CH_3COCF_3 and $C_6H_5COCF_3$, curve B, in Fig. 1.) In view of this, mixture photolyses were made at 3130 Å. in an attempt to test the suggested CH_3COCF_3 photolysis mechanism (reactions 1–7). Runs were made with the pure components alone and then in combination. The incident light intensity was lowered with filters in the pure CH_3COCF_3 runs so that approximately equal numbers of quanta were absorbed by the CH_3COCF_3 when alone or in the mixture photolyses (see Table II). Thus the rate of CH_3 radical formation as a result of light absorption should be about the same in both runs. The ratio of the rate constants k_5/k_8 at 245° is estimated to be 126.[3] If this is used as an estimate of the relative rates of the corresponding CH_3 reactions no significant increase in R_{CH_3} should be found in mixture photolyses as a consequence of reaction 22

$$CH_3 + C_6H_5COCF_3 \longrightarrow CH_4 + C_6H_4COCF_3 \quad (22)$$

An increase in rates of formation of CH_3–containing species in the mixture photolyses would provide evidence for CH_3 generation from CF_3. In Table II the product rates for each pure component are summed and can be compared with the rates in the mixture photolyses for three sets of data at three different CH_3COCF_3 concentrations. The interpretation of the results is not simple, but several general features are clear. The rates of CO and CF_3H formation are much higher in the mixture photolysis than in the rate sums of individual runs. The effect of increased concentration on the decomposition of the CF_3CO radical is consistent with this finding. The rates of formation of CH_4, C_2H_6 and CH_3CF_3 in mixture photolyses are slightly larger in some runs, slightly smaller in others, but no consistent trend is apparent. Conflicting conclusions are possible concerning the CH_3 steady-state concentration in these systems. It is evident that the simple reaction schemes which appear to explain pure component photolyses are not entirely adequate for mixture photolyses. The most reliable criterion of change in rate of CH_3 formation in these systems available from the present data is the sum of the rates of the total CH_3-containing species which appear as gaseous products, ΣR_{CH_3}. This function is very nearly the same in the mixture and sums of individual pure component runs when account is taken of the slightly different intensities of light absorbed by the CH_3COCF_3 component. However there are two effects which have not been considered in this simple interpretation which would tend to mask the regeneration of CH_3 radicals from CF_3 in this system. A reaction similar to 16 is expected to occur to lower the CH_3 concentration in the mixture photolyses. In addition, the photolysis of CH_3COCF_3 appears to involve an excited state which would undergo more extensive collisional deactivation at the higher pressures involved in the mixture photolyses.[3] The fact that gaseous CH_3– containing species were formed at essentially the same rate in pure CH_3COCF_3 and in the mixtures provides very indirect evidence that CF_3 radicals regenerate CH_3 by interaction with CH_3COCF_3. Obviously, a more definitive test of this point is necessary.

The Mechanism of CH_3COCF_3 Photolysis.—The chain mechanism involving CH_3–containing molecules and CO is confirmed by the quantum yields of products and quantum yield summations shown in runs 43, 46 and 49 of Table II and runs 53 and 54 of Table III. The results of run 54 at 348° are most striking; 31.6 CH_3–groups appear in the gaseous products for every quantum of light absorbed by CH_3COCF_3. A previously undetected short chain involving CF_3–containing gaseous products is indicated also. The relatively large quantum yield of CF_3CH_3 suggests that the reaction

$$CF_3 + CH_3COCF_3 \longrightarrow CF_3CH_3 + COCF_3 \quad (23)$$

---

[22] H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, 589 (1939).

may become important at the very high temperatures. Although the general chain photodecomposition scheme suggested by Sieger and Calvert[3] is in accord with this work, the specific reactions 1 and 2 appear unlikely; a careful analysis of the products of run 46 and 54 failed to reveal detectable quantities of CF_3COCF_3, although the method of analysis was sufficiently sensitive to find even 5% of the total quantity expected from the reaction scheme. There is no obvious alternative mechanism to replace 1 and 2. The undefined reaction sequence

$$CF_3 + CH_3COCF_3 \longrightarrow X \longrightarrow CH_3 + \text{non-volatile products} \quad (24)$$

must be subjected to further experimentation. The absolute magnitude of the quantum yields of products of run 54 differ from those found by Sieger and Calvert[3] using a different photolysis system but under similar conditions of temperature, pressure, wave length and at a slightly higher light intensity; for example, Φ_{CO} was 1.95 compared to 7.42 found in this work. The variability of the length of the chain process with change in reaction system coupled with the fact that homogeneous reactions similar to 1, 2, 3, 23 and 24 have not been observed in analogous systems, suggest strongly that these chain steps are at least in part heterogeneous reactions.

Acknowledgment.—Grateful acknowledgment is made of research fellowships provided R. M. S. by the Allied Chemical and Dye Corporation and the Socony-Vacuum Oil Company, and a Grant-in-Aid from E. I. du Pont de Nemours and Company, Inc.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Comparison of the Organic Products from the Br^{80m} (4.4 hr.) $\xrightarrow{\text{I.T.}}$ Br^{80} (18 min.) Process in the Propyl Bromides with Those from the $Br^{79}(n,\gamma)Br^{80}$ Process

BY GERRIT LEVEY[1] AND JOHN E. WILLARD

RECEIVED NOVEMBER 11, 1955

It has been shown previously that activation of Br_2 by the (n,γ) and by the isomeric transition processes in solutions of Br_2 in CCl_4 yields the same distribution of organic products. The present paper shows a similar result for five products (CH_2Br_2, C_2H_5Br, n-C_3H_7Br, i-C_3H_7Br and 1,2-$C_3H_6Br_2$) from the (n,γ) and I. T. activation of bromine in n-C_3H_7Br and i-C_3H_7Br, thus lending support to the conclusion that the product determining steps are the same for the two methods of activation.

Introduction

The $Br^{79}(n,\gamma)Br^{80}$(4.4 hr. and 18 min.) and $Br^{81}(n,\gamma)Br^{82}$(36 hr.) processes yield product atoms with a recoil energy sufficient to break chemical bonds[2] (some 4000 kcal. per mole if all of the nuclear energy is lost as one photon) and, in at least an appreciable fraction of the events, a positive charge.[3] The isomeric transition of $Br^{80m}(Br)^{80m}$(4.4 hr.) $\xrightarrow{\text{I.T.}}$ Br^{80}(18 min.)) gives daughter atoms with an average charge[4] of +10. This charge may spread over the parent molecule and as a result of coulombic repulsion cause the bromine atom to split out with considerable kinetic energy (about 80 e.v. in the case of Br_2 with +10 charge). In liquid or solid organic media bromine atoms which have ruptured their parent bonds as a result of either the (n,γ) process or the isomeric transition process are able to enter organic combination, apparently by producing a random fragmentation[2] of bonds in the surrounding molecules and combining with radicals so formed. From the available facts about such processes it is impossible to say whether the kinetic energy or the energy from charge neutralization, or both, are primarily responsible for the chemical fate of the tagged atom, although it has been customary to assume that recoil energy is the important factor in (n,γ) activation and charge in activation by isomeric transition.

If the determining factor in chemical activation by the two processes is the same, the distribution of chemical products would be expected to be the same in the same chemical system; if the activating step is different, the product distribution might be different. It has been shown[5] that the ratios of CCl_3Br to CCl_2Br_2 and to higher boiling components in the organic products from the (n,γ) and isomeric transition processes of Br_2 in CCl_4 are identical within the accuracy of the determinations. This is not, however, conclusive evidence that the mechanism of chemical activation is the same for the two processes. It may be that the possible types of bond rupture in a simple molecule like CCl_4 are so few that fragmentation occurs in an identical fashion whether it results from charge neutralization processes or from the dissipation of recoil energy. It was therefore important to test more complex molecules than the Br_2–CCl_4 system. In the work reported below normal and isopropyl bromide have been chosen for this purpose because the yields of a variety of products from the (n,γ) process on these compounds have been studied carefully.[6,7]

Experimental

Liquid Br_2 irradiated in the CP5 pile of the Argonne National Laboratory at a flux of 2×10^{12} neutrons cm.$^{-2}$ sec.$^{-1}$

---

[1] Department of Chemistry, Berea College, Berea, Kentucky.

[2] For reviews of the literature on chemical effects of nuclear transformations see: J. E. Willard, *Ann. Rev. Nucl. Sci.*, **3**, 193 (1953); J. E. Willard, *Ann. Rev. Phys. Chem.*, **6**, 141 (1955).

[3] S. Wexler and T. H. Davies, *J. Chem. Phys.*, **20**, 1688 (1952).

[4] S. Wexler and T. H. Davies, *Phys. Rev.*, **88**, 1203 (1953).

[5] J. F. Hornig and J. E. Willard, THIS JOURNAL, **75**, 461 (1953).

[6] M. S. Fox and W. F. Libby, *J. Chem. Phys.*, **20**, 487 (1952).

[7] J. C. W. Chien, Ph.D. Thesis, University of Wisconsin, 1954.