

tween  $\text{UF}_6$  and  $\text{LiF}$ ,  $\text{KF}$ ,  $\text{CaF}_2$ ,  $\text{ZrF}_4$  and  $\text{AgF}$ . In no case was any physical evidence of compound formation observed. The  $\text{UF}_6$  did not appear to react with the fluoride and could be recovered at room temperature. The exchange values in Table II are calculated assuming complete exchange involving a statistical distribution of  $\text{F}^{18}$  among all the fluorine atoms. Data on the exchange between  $\text{UF}_6$  gas at high temperatures and  $\text{NaF}$  are included for comparison. Essentially no exchange is observed to occur between  $\text{UF}_6$  and  $\text{LiF}$ ,  $\text{ZrF}_4$  and  $\text{AgF}$ . The relatively large amount of uranium rendered permanently non-volatile by  $\text{KF}$  is probably due to reaction of the  $\text{UF}_6$  with potassium hydroxide or oxide formed during the drying of the  $\text{KF}$ . In an experiment using a prefluorinated sample of  $\text{KF}$ , 90% of the  $\text{UF}_6$  was recovered. Martin, Albers and Dust observed compound formation to the extent of  $3\text{KF} \cdot 2\text{UF}_6$  after prolonged contact of the reactants at  $67^\circ$ . The observations on  $\text{KF}$  in Table II therefore are not necessarily

directly contradictory with the results reported by Martin, Albers and Dust. However, the difficulty of preventing attack on the container over a period of many days, especially if any initial hydroxide is present, and the qualitative differences observed by Martin, *et al.*, between the behavior of  $\text{NaF}$  and  $\text{KF}$  suggest that compound formation between  $\text{UF}_6$  and  $\text{KF}$  has not been adequately established.

The situation with respect to calcium fluoride is different. Although no compound appeared to form, in agreement with the observations of Martin, Albers and Dust and over 96% of the  $\text{UF}_6$  was recovered at room temperature, a substantial amount of exchange occurred. If the assumption is made that all the  $\text{UF}_6$  has exchanged only once with the  $\text{CaF}_2$ , the  $\text{F}^{18}$  content of the  $\text{UF}_6$  can be accounted for by the exchange of each mole of  $\text{UF}_6$  with 2.3 moles of  $\text{CaF}_2$ .

The reasons for formation of complexes between  $\text{UF}_6$  and some non-volatile metal fluorides but not others remain obscure.

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## The Photolysis of Acetone in a Perfluorinated Solvent at Several Temperatures<sup>1</sup>

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The photolysis of acetone in perfluorodimethylcyclobutane solutions has been studied in the  $2537 \text{ \AA}$ . region at 2, 24 and  $41^\circ$ . Preliminary evidence is cited for self-quenching of acetone in solution. The ratio of the specific rate constants for hydrogen abstraction to recombination for methyl radicals was evaluated at each temperature and shown to be consistent with data obtained in other solvents and with a diffusion-controlled combination of methyl radicals. An apparent relationship between the material balance and the product quantum yields is noted and discussed.

### Introduction

The photolysis of acetone in the vapor phase has been the subject of many careful studies<sup>2</sup> and is well understood at temperatures over  $100^\circ$ . At lower temperatures complicating factors are evident<sup>3-5</sup> and the vapor phase photolysis is less certain. Liquid phase studies of the photolysis of acetone are generally limited to temperatures below  $100^\circ$  by the nature of the solvent, and, therefore, these investigations are theoretically as well as experimentally difficult. Early liquid phase studies<sup>6,7</sup> using pure acetone and acetone-hydrocarbon solutions demonstrated a very low quantum yield of gaseous products and indicated that reactions occurred between photo-excited acetone molecules and hydrogen-containing molecules in the liquid phase. A recent study<sup>8</sup> conducted in this laboratory using fluorocarbon solvents and acetone- $d_6$  showed the photolysis to proceed *via* a free radical

mechanism. A more recent study<sup>9</sup> of the photolysis of acetone in water solutions is in complete accord with a free radical interpretation.

The present study reports the results of the photolysis of dilute solutions of acetone in perfluorodimethylcyclobutane at several temperatures. It is expected that studies of ketone photolysis in low concentrations in inert solvents, such as those reported by Volman<sup>9</sup> and the present investigation, will contribute kinetic data for free radical reactions in the liquid phase and possibly give some insight into the effects of condensed media on the primary photochemical process.

### Experimental

The solvent employed in this investigation was perfluorodimethylcyclobutane. While its purity has not been established, it is believed to consist of a mixture of *cis*- and *trans*-1,2-perfluorodimethylcyclobutane. The mass spectra of the vapor and liquid solvent indicated some fractionation in vaporization but failed to reveal more than very small possible traces of hydrogen in either fraction. The mass spectra were consistent with ions of the formula  $\text{C}_2\text{F}_7$ . Small side peaks which could arise from ions of the formula  $\text{C}_2\text{F}_7\text{H}_2$  were attributable to  $\text{C}^{13}$  isotopes to within 1% of the isotope peak. The ultraviolet absorption spectrum showed the solvent to be optically transparent out to  $2200 \text{ \AA}$ . Hence, the solvent was used without further purification. Viscosity measurements of perfluorodimethylcyclobutane were made over the temperature range  $2-42^\circ$  using an Ostwald viscometer.

(1) Based upon thesis research submitted by R. D. Doepker in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Carnegie Institute of Technology.

(2) W. A. Noyes, Jr., G. B. Porter and J. E. Jolley, *Chem. Revs.*, **56**, 49 (1956).

(3) J. Hecklen and W. A. Noyes, Jr., *THIS JOURNAL*, **81**, 3858 (1959).

(4) A. J. C. Nicholson, *ibid.*, **73**, 3981 (1951).

(5) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 47 (1955).

(6) R. Pieck and E. W. R. Steacie, *ibid.*, **33**, 1304 (1955).

(7) P. E. Frankenburg and W. A. Noyes, Jr., *THIS JOURNAL*, **75**, 2847 (1953).

(8) D. B. Peterson and G. J. Mains, *ibid.*, **81**, 3510 (1959).

(9) D. H. Volman and L. W. Swanson, *ibid.*, **82**, 4141 (1960).

TABLE I  
 PHOTOLYSIS OF ACETONE IN PERFLUORODIMETHYLCYCLOBUTANE

Temp., °C.	Acetone (molecules/cc. $\times 10^{-19}$ )	Irrad. (sec. $\times 10^{-4}$ )	Volume gas (cc. at S.T.P.)	$R_{CO}$	$R_{CH_4}$ (molecules/cc.-sec. $\times 10^{-12}$ )	$R_{C_2H_6}$	$R_{CH_4}/R^{1/2}C_2H_6$ $\times 10^{-6}$
2	2.35	1.62	0.302	2.06	1.01	5.72	0.423
2	3.49	1.44	.370	2.68	1.90	7.52	.693
2	4.82	1.44	.466	3.16	2.18	9.91	.692
2	6.50	1.26	.345	2.80	2.34	7.77	.839
2	7.71	1.20	.328	2.31	2.77	7.81	.993
24	1.33	1.62	.170	1.77	1.25	1.92	.899
24	1.75	1.44	.298	3.04	2.10	4.63	.977
24	2.83	1.20	.512	5.27	2.82	12.03	.813
24	5.54	1.08	.271	3.57	4.92	3.32	2.70
24	7.29	0.96	.327	3.24	7.50	5.31	3.26
24	7.89	0.99	.310	2.73	6.83	5.20	3.00
41	2.11	1.44	.453	6.08	3.50	5.25	1.53
41	3.07	1.26	.405	5.79	3.70	5.67	1.55
39	5.84	1.20	.324	4.37	5.80	2.56	3.63
41	6.14	1.27	.482	5.98	5.81	6.10	2.35
42	6.44	1.20	.404	5.41	6.90	3.55	3.67
41 <sup>a</sup>	6.57	1.44	1.157	13.11	11.35	13.88	3.05

<sup>a</sup> Analysis for CO, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> confirmed by mass spectrometry.

 TABLE II  
 QUANTUM YIELDS IN ACETONE PHOTOLYSIS AT 2537 Å. AND 25°

System	$\Phi_{CH_4}$	$\Phi_{CO}$	$\Phi_{C_2H_6}$	$\frac{1/2CH_4 + C_2H_6}{CO}$
Acetone vapor <sup>14</sup>	$10^{-3}$	0.25	0.35	1.4
Acetone liquid <sup>6</sup>	$2 \times 10^{-3}$	$10^{-4}$	$10^{-4}$	9.2
0.108 M Acetone in H <sub>2</sub> O <sup>9</sup>	$3.6 \times 10^{-2}$	$2.2 \times 10^{-3}$	$2.9 \times 10^{-2}$	21
0.023 M Acetone in perfluorodimethylcyclobutane <sup>3</sup>	$10^{-3}$	$10^{-3}$	$2 \times 10^{-3}$	3
0.096 M Acetone in perfluorodimethylcyclobutane	$3.5 \times 10^{-4}$	$2.6 \times 10^{-4}$	$2.5 \times 10^{-4}$	1.6

Fisher Certified Acetone was purified by techniques already described.<sup>3</sup> The purified acetone was distilled under vacuum into ampoules and stored in the dark until used.

The light source employed in this research was a Hanovia UA-15 lamp coiled into a helix. The quartz reaction vessel, previously described,<sup>8</sup> was located within the coils of the lamp. The temperature of the reaction cell was controlled to  $\pm 0.5^\circ$  during photolysis by circulating filter solution from a reservoir in a constant temperature bath through the outer jacket of the quartz reaction cell. The filter solution was a 0.02% solution of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene iodide described by Kasha.<sup>10</sup> This solution restricted the actinic radiation to the mercury lines at 2537 and 2652 Å. Uranyl oxalate was employed as the actinometer. Using the principle of equivalent optical densities,<sup>11,12</sup> a solution of 0.096 M acetone in perfluorodimethylcyclobutane was found to absorb  $1.3 \pm 0.1 \times 10^{16}$  quanta cc.<sup>-1</sup> sec.<sup>-1</sup> in the region transmitted by the filter solution.

The procedures of degassing, irradiation, removal of gaseous products and analysis were the same as those employed by Peterson and Mains.<sup>3</sup>

### Results

A series of seventeen experiments were conducted to ascertain the effects of acetone concentration and temperature on the yield and composition of the gaseous photolysis products. The majority of these experiments were carried out at three temperatures, 2, 24 and 41°, in a random order to lessen any cumulative effects arising from lamp aging. New solvent was used for each experiment. The gaseous products were analyzed by gas chromatography. The results of these experiments are summarized in Table I. Product identification and gas chromatographic analysis of one photolysis

(10) M. Kasha, *J. Opt. Soc. Am.*, **38**, 429 (1948).

(11) D. H. Volman and J. C. Chen, *THIS JOURNAL*, **81**, 756 (1959).

(12) I. M. Claesson, *Arkiv Kemi*, **10**, 1 (1956).

experiment was confirmed by mass spectrometry. These independent analyses for carbon monoxide, methane and ethane agreed to within 1%. However, the mass analysis found 5.7% hydrogen which was not detected in the gas chromatographic analysis. The failure to detect hydrogen in low concentrations in a gas chromatographic system employing helium gas carrier is attributed to the small difference in the thermal conductivity of these gases. The presence of this small amount of hydrogen cannot be explained in terms of accepted mechanisms for acetone photolysis in this wavelength region. Lossing<sup>13</sup> found small amounts of hydrogen in his study of the mercury-sensitized photolysis of acetone in the vapor phase. Since precautions were taken to keep mercury vapor from coming in contact with the solution of acetone in perfluorocarbon, this appears to rule out hydrogen formation *via* a mercury-photosensitized mechanism. However, this experiment yielded an abnormal amount of gas and mercury-sensitization may not be completely eliminated for this particular experiment.

Previous studies<sup>8</sup> indicated that liquid products such as biacetyl, methyl ethyl ketone and acetyl acetone could not be detected in the low percentage conversions employed in these experiments and no further attempt was made to analyze for them.

The quantum yields of gaseous products found in this study are given in Table II along with those of previous investigations. The quantum yields reported by Pieck and Steacie<sup>6</sup> and by Peterson

(13) F. Lossing, *Can. J. Chem.*, **35**, 305 (1957).

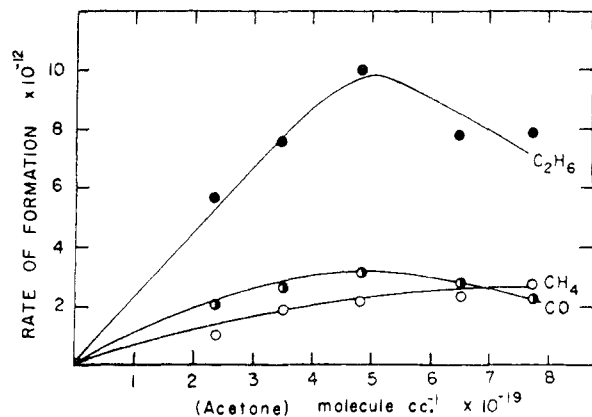


Fig. 1.—Rates of product formation as a function of acetone concentration at 2°.

and Mains<sup>8</sup> are uncertain by a factor of two or more. The vapor phase quantum yields of Herr and Noyes,<sup>14</sup> the aqueous solution quantum yields of Swanson and Volman<sup>9</sup> and the quantum yields reported here are much more accurate, probably uncertain by less than  $\pm 5\%$ .

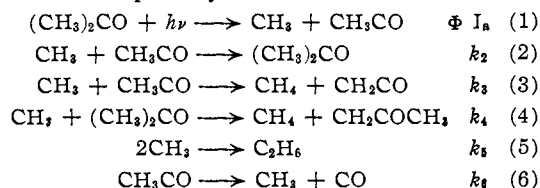
Because earlier studies<sup>9,9</sup> had indicated that ethane formation was a diffusion-controlled process, the viscosity of perfluorodimethylcyclobutane was measured as a function of temperature. The viscosity data are reported below. The activa-

Temperature, °C.	2.0	15.0	24.0	32.0	42.0
Viscosity, centipoise	1.5835	1.1961	0.9773	0.8500	0.7165

tion energy for viscosity, obtained from the slope of a semi-logarithmic graph of viscosity *versus*  $1/T$ , was found to be  $3.2 \pm 0.4$  kcal./mole.

### Discussion

The free radical mechanism postulated to account for the photolysis of acetone is



Additional reactions leading to the unobserved liquid products have not been included because their occurrence is largely speculative. Some of these reactions have been given previously.<sup>8</sup>

**The Concentration Effect.**—Based upon this mechanism the kinetic relationships predicted for the principal gaseous products are

$$R_{\text{CO}} = k_6 (\text{CH}_3\text{CO}) \quad (\text{I})$$

$$R_{\text{CH}_4} = k_3 (\text{CH}_3)(\text{CH}_3\text{CO}) + k_4 (\text{CH}_3)(\text{CH}_3\text{COCH}_3) \quad (\text{II})$$

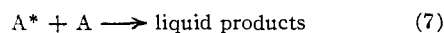
$$R_{\text{C}_2\text{H}_6} = k_5 (\text{CH}_3)^2 \quad (\text{III})$$

The experimentally determined rates of product formation at 2° are shown in Fig. 1. It is evident that the rate of formation of ethane and carbon monoxide pass through maxima which are not predicted by the preceding mechanism. The

(14) D. S. Herr and W. A. Noyes, Jr., *THIS JOURNAL*, **62**, 2052 (1940).

data at 24°, although showing more experimental uncertainty, also clearly indicate that  $R_{\text{C}_2\text{H}_6}$  and  $R_{\text{CO}}$  pass through maxima at higher acetone concentrations. The 41° data, although much less certain, indicate the possible existence of a slight maximum provided the last experiment is rejected for reasons previously mentioned. Earlier data<sup>8</sup> also exhibited a falling off of gaseous products which was then attributed to experimental error. The data reported in Table I indicate that the maxima are real in the rates of formation of carbon monoxide and ethane. Since methane is a minor product at 2° where the data are more precise, it is not possible to decide whether or not  $R_{\text{CH}_4}$  exhibits a small maximum.

The curvature of a graph of rates of product formation *versus* acetone concentration is subject to several explanations. The most reasonable interpretation of the maxima at high acetone concentrations is in terms of self-quenching of photo-excited acetone molecules, *viz.*



where  $\text{A}^*$  could represent either the excited singlet state or the excited triplet state of acetone (since both can presumably give rise to gaseous products<sup>8</sup>) and the liquid products are not precursors for gaseous products. Self-quenching to unexcited acetone molecules is well established in the vapor phase<sup>2,3</sup> whereas quenching to yield diacetone alcohol and other alcohols is known in the liquid phase.<sup>6,7</sup> The present data do not merit a detailed consideration of the self-quenching mechanism or the products of reaction 7.

Nicholson<sup>4</sup> found curvature in a graph of  $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}$  *versus* acetone concentration in his vapor phase studies which was attributed to radical diffusion from the light beam. The effect observed in Fig. 1 is in the opposite direction to that observed by Nicholson and occurs at much higher acetone concentrations than Nicholson could obtain in the vapor. Therefore, it seems unreasonable to attribute the curvature in Fig. 1 to inhomogeneity in the free radical concentration. (Small concentration gradients may exist in the solution during photolysis in spite of rapid stirring. These would be in the form of three or four weak "zebra stripes" owing to the coiled nature of the lamp. However, the effect of these "stripes" is expected to be small.<sup>15</sup>)

Finally, it is possible to explain the curvature in Fig. 1 by proposing that methyl and acetyl radicals undergo an addition reaction with acetone to form some unobserved liquid products. While this alternative cannot be eliminated based upon the results of this study, it seems undesirable to postulate new reactions without better evidence. The precision and extent of the present data do not warrant such speculation. Reaction 7 adequately represents the situation in the light of presently available data.

**Evaluation of Rate Constants.**—Cautiousness in the application of homogeneous kinetics to liquid phase photolysis systems has been evident in earlier investigations.<sup>6,7</sup> In these earlier studies using pure acetone the radical concentration was

(15) R. M. Noyes, *ibid.*, **81**, 566 (1959).

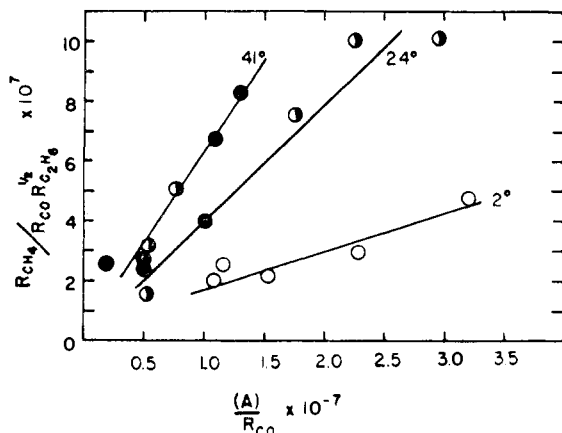


Fig. 2.—Plot according to the kinetic equation of Volman and Swanson.

very inhomogeneous and the reaction volume was poorly defined. In dilute solutions, such as used in this investigation and in the study of Swanson and Volman,<sup>9</sup> the whole solution is subjected to illumination and the radical concentration, while certainly not completely uniform, probably does not vary appreciably throughout the reaction cell. The specific rate constants calculated by assuming uniform radical concentrations throughout the cell will be subject to some error which will probably not exceed the experimental uncertainty of the data in this paper.

Bearing these limitations in mind the data of Table I may be used to estimate kinetic rate constants for reactions 4 and 5 relative to each other. Mains and Peterson<sup>8</sup> evaluated  $k_4/k_5^{1/2}$  from the slope of a graph of  $R_{CH_4}/R_{C_2H_6}^{1/2}$  versus acetone concentration. Swanson and Volman<sup>9</sup> have evaluated  $k_4/k_5^{1/2}$  from the slope of a graph of  $R_{CH_4}/R_{CO}R_{C_2H_6}^{1/2}$  versus the ratio of acetone concentration to  $R_{CO}$ . Both graphical methods give values of  $k_4/k_5^{1/2}$  which agree very well at 2 and 24° but which differ by 20% at 41°. Since the method of Swanson and Volman concentrate the data better and allow a more confident choice of the slope at 41°, the data are graphically presented in Fig. 2 using the Swanson and Volman method. Because of the scatter of points in the higher temperature experiments, owing to experimental difficulties concomitant to low quantum yields and the removal of small amounts of gas from liquids, it is not possible to draw straight lines with much certainty. The lines drawn in Fig. 2 were made by visually weighting the experimental points. For this reason a minimum error of  $\pm 10\%$  must be attached to the slopes of these lines. The ratio,  $k_4/k_5^{1/2}$ , estimated from Fig. 2 for each temperature is presented in Table III along with comparable liquid phase data obtained in other studies.

A graph of  $\log(k_4/k_5^{1/2})$  versus  $1/T$  is presented in Fig. 3. The slope of the best straight line corresponds to a difference in activation energies,  $E_4 - 1/2E_5$ , of 8.1 kcal./mole. This is, of course, in fortuitous agreement with the 8.1 kcal./mole value which can be predicted by assuming  $E_4 = 9.7$  kcal./mole from the vapor phase studies and taking  $E_5 = 3.2$  kcal./mole, the activation energy for viscosity in perfluorodimethylcyclobutane.

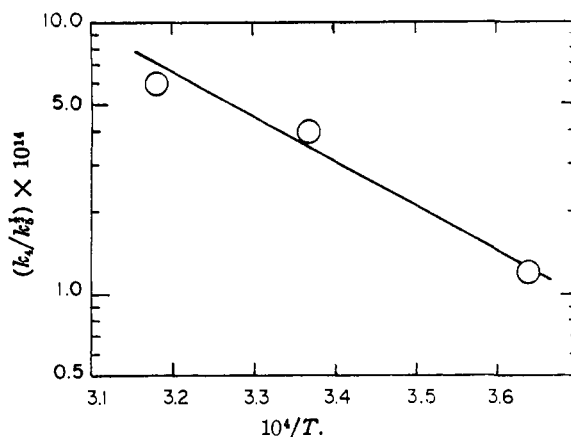


Fig. 3.—Arrhenius plot of the rate constant ratios derived from the slopes of Fig. 2.

It should be noted that the differences between the ratio of specific rate constants,  $k_4/k_5^{1/2}$ , reported in the present study and that found by Peterson and Mains<sup>8</sup> are real. The ratio of rate constants and the quantum yields reported by Peterson and Mains and listed in Table II and Table III have been reproduced using the last of their supply of fluorocarbon. A change in solvent composition appears to be the only reasonable explanation for these differences and, if this is correct, shows clear need for the use of solvents of constant composition in future studies.

TABLE III  
COMPARISON OF SPECIFIC RATE CONSTANTS

Solvent	Temp., °C.	$k_4/k_5^{1/2}$ (cc. <sup>1/2</sup> / molecule <sup>-1/2</sup> sec. <sup>-1/2</sup> ) $\times 10^{14}$	Viscosity activ. energy (kcal./mole)	Ref.
Acetone liquid	54	4.76	1.88	6
	24	2.30		6
	3	1.12		6
Perfluorodi- methylcyclo- butane	41	$6.0 \pm 0.6$	3.2	This work
	24	$4.0 \pm 0.4$		This work
	2	$1.2 \pm 0.2$		This work
Perfluorodi- methylcyclobutane	24	$12 \pm 1$		8
Water	73	200	5.1-3.4 <sup>a</sup>	9
	49	190		9
	27	99		9
	2	57		9

<sup>a</sup> Viscosity is not an exponential function for associated liquids such as water. The values for the viscosity activation energy of water are taken from the slopes of a graph of  $\log \eta$  versus  $1/T$  at 0 and 50°.

The agreement between the ratio of specific rate constants obtained by Pieck and Steacie in liquid acetone and those reported in Table III for this research is striking. If these differences are attributed to diffusion-control of reaction 5, for which an activation energy of the order of the viscosity activation energy may be assumed, there should be a factor of about 3.3 relating the perfluorodimethylcyclobutane ratio to the ratio obtained in acetone. The factor is less, *circa* 1.2-1.5. Also, the ratios of the specific rate constants obtained in water seem too large to be ascribed solely to viscosity activation energy.

These considerations indicate that the differences in the ratio of specific rate constants cannot be completely attributed to a diffusion activation energy for reaction 5, which is naively approximated by a viscosity activation energy. However, in view of the low precision to which the specific rate constant ratios are known, and the difficulties in estimating an activation energy for the diffusion of methyl radicals in these solvents, the agreement between these independent investigations is very satisfying.

**Comparison of Quantum Yields.**—It is interesting to note from Table II that water is least effective in reducing the quantum yields. Perfluorodimethylcyclobutane is singularly effective in reducing the quantum yields below those obtained in liquid acetone. This order of reduction is difficult to reconcile in terms of a "cage-effect" mechanism since water, possessing considerable structure in the liquid, would be expected to act as a very efficient "cage" for acetone. While these data are explainable in terms of solvent quenching concepts, the explanation requires that acetone be less effective than perfluorodimethylcyclobutane in quenching excited acetone molecules. Whether the quenching act places the photo-excited acetone molecule in its ground electronic state or in a low vibrational level of the excited singlet or lowest triplet state is not known. The order of variation of the quantum yields with solvent is not unreasonable if the solvent quenching involves the removal of vibrational energy. Neither the "cage-effect" nor solvent quenching offer very satisfying explanations of the observed trends.

A clue to the variation of the quantum yields in changing from one solvent to another is perhaps to be found in the material balance ratio ( $1/2\text{CH}_4 +$

$\text{C}_2\text{H}_6$ )/CO. It is evident from Table II that the material balance ratio, a measure of the carbon monoxide deficiency, increases in the same order that the quantum yields increase. This is understandable in terms of the "cage-effect" mechanism if once an acetyl and methyl radical escape geminate recombination they result in product formation. (This is a reasonable assumption at low radical concentrations where homogeneous recombination must compete with many other reactions.) Since the acetyl radical usually results in liquid products, the carbon monoxide deficiency is then a measure of the ability of the methyl and acetyl radical pair to escape geminate recombination. Alternately, in terms of the solvent quenching concepts, the carbon monoxide deficiency is a measure of the probability of the dissociation of  $\text{A}^*$ , the photo-excited state of acetone, prior to solvent quenching. Since the variation is explainable from both a "cage-effect" viewpoint and a solvent quenching viewpoint, it contributes little to the present understanding of the primary photochemical process in solution. Furthermore, a possible relationship between the carbon monoxide deficiency and the liquid phase quantum yields of acetone photolysis, while interesting, can scarcely be considered established based upon the limited data presently available. Many more quantum yield studies seem necessary to gain some insight into the factors influencing the magnitude of the quantum yield in the liquid phase.

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## Bis-(pentafluorosulfur) Peroxide

BY CLAUDE I. MERRILL AND GEORGE H. CADY

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Preparation of bis-(pentafluorosulfur) peroxide,  $(\text{SF}_5)_2\text{O}_2$ , has been achieved by allowing pentafluorosulfur hypofluorite ( $\text{SF}_5\text{OF}$ ) to react with thionyl fluoride ( $\text{SOF}_2$ ) or with thionyl tetrafluoride ( $\text{SOF}_4$ ) and by subjecting  $\text{SF}_5\text{OF}$  to ultraviolet light. Bis-(pentafluorosulfur) peroxide is a dense, colorless liquid that boils at  $49.4^\circ$  and freezes at  $-95.4^\circ$ . It reacts very slowly with base and shows oxidizing character by slowly producing free iodine when contacted with potassium iodide solution. Thermal decomposition of  $\text{S}_2\text{O}_2\text{F}_{10}$  results ultimately in the products  $\text{SF}_6$ ,  $\text{SO}_2\text{F}_2$  and  $\text{O}_2$ , although  $\text{SOF}_4$  is one of the materials produced initially. Chemical, mass spectrographic, infrared and nuclear magnetic resonance data contribute evidence consistent with a peroxide structure for this substance.

A small amount of bis-(pentafluorosulfur) peroxide,  $\text{SF}_5\text{OOSF}_5$ , was produced a few years ago by J. W. Dale and D. A. McLeod of the Defense Research Chemical Laboratories, Ottawa, Canada. They obtained the substance as one of the products of the reaction of fluorine with sulfur. The structure of the compound has been determined by Harvey and Bauer,<sup>1</sup> using the electron diffraction method, and found to consist of two  $\text{F}_5\text{SO}$ -octahedra joined by the two oxygen atoms. Some physical

(1) R. B. Harvey and S. H. Bauer, *THIS JOURNAL*, **76**, 859 (1954).

properties determined by Dale and McLeod are given in the paper of Harvey and Bauer.

Hypofluorites are known to be useful reagents for producing certain peroxides. For example,  $\text{CF}_3\text{OF}$  combines with  $\text{COF}_2$  to form  $\text{CF}_3\text{OOCF}_3$ <sup>2</sup>

or with  $\text{SO}_3$  to form  $\text{CF}_3\text{OOS-F}$ .<sup>3</sup> By analogy with



(2) R. S. Porter and G. H. Cady, *ibid.*, **79**, 5628 (1957).

(3) W. P. Van Meter and G. H. Cady, *ibid.*, **82**, 6005 (1960).