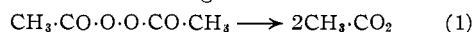# Kinetics of the Thermal Decomposition of Diacetyl Peroxide. I. Gaseous Phase

BY A. REMBAUM AND M. SZWARC

RECEIVED JUNE 9, 1954

The thermal decomposition of gaseous diacetyl peroxide has been investigated in a flow system in the presence of toluene or benzene. The reaction has been studied over a temperature range of about 100° (from 90 to 190°), and has been found to obey the first-order kinetics. The first-order rate constant is given by the equation $k = 1.8 \times 10^{14} \times \exp. (-29,500/RT)$ sec.$^{-1}$. The products of the decomposition are CO_2, C_2H_6 and small quantities of CH_4, the molar ratio $CO_2/(C_2H_6 + CH_4)$ being 2:1. It appears that methyl acetate is *not* formed in the decomposition of gaseous diacetyl peroxide. All the observations indicate that one measures the rate of the unimolecular dissociation, $CH_3 \cdot CO \cdot O \cdot O \cdot CO \cdot CH_3 \rightarrow 2CH_3 \cdot CO_2$, and it is concluded, therefore, that $D(CH_3 \cdot CO \cdot O\text{---}O \cdot CO \cdot CH_3) = 29.5$ kcal./mole.

The pioneering work of Kharasch and his colleagues[1] demonstrated conclusively that the decomposition of diacetyl peroxide is initiated by the O–O bond breaking reaction 1

$$CH_3 \cdot CO \cdot O \cdot O \cdot CO \cdot CH_3 \longrightarrow 2CH_3 \cdot CO_2 \qquad (1)$$

It follows, therefore, that one may obtain valuable information about the magnitude of the O–O bond dissociation energy in this compound by studying the kinetics of its decomposition in the gaseous phase.

The decomposition of gaseous diacetyl peroxide was investigated previously only by Walker and Wild,[2] who used a static system in which the partial pressure of the peroxide was kept constant by connecting the reaction vessel to a small tube containing a liquid or a solid diacetyl peroxide and maintained at a constant temperature (35 or 15°). The decomposition was studied at one temperature, namely, 100°, and only the composition of the products was recorded. Unfortunately, no data were published from which the rate of the gaseous reaction could be computed and, therefore, it was decided to study thoroughly the kinetics of this reaction in the gaseous phase. Furthermore, since reaction 1 determines the rate of the decomposition both in gaseous phase and in solution, one may profitably study the effects of various solvents on the kinetics of a unimolecular dissociation by comparing rates of the decomposition in a solution and in the gaseous phase.

The present paper reports the results of our studies of the decomposition of gaseous diacetyl peroxide, while the effects of solvents on the kinetics of the decomposition will be discussed in the following papers.

Experimental

Diacetyl peroxide was prepared according to the method described by Price and Morita[3] and modified by us in one detail only, namely, the ether solution of the peroxide was washed several times with a cold solution of sodium bicarbonate until the ether layer was completely neutral. Further operations, *i.e.*, the crystallization of the compound at −80° and its drying in a high vacuum, followed the procedures outlined by Price and Morita. The pure crystals of the peroxide were dissolved in toluene, and the solution used by us was made to be approximately 0.34 M. Concentrations were determined by the iodometric titration method described by Wagner, Smith and Peters.[4] A solution of peroxide, and not pure crystals, was used in our work because handling of crystals was considered a too dangerous operation. Moreover, pipetting of known volumes of solution was more accurate than weighing small quantities of peroxide.

The investigation of the kinetics of decomposition of gaseous diacetyl peroxide was carried out in a flow system similar to one described previously.[5] The apparatus is shown schematically in Fig. 1. One or two cc. of toluene solution of peroxide was pipetted into a U-tube denoted in Fig. 1 by a letter U. The solution was then frozen by surrounding the U-tube with a liquid air-bath, and the contents of the tube were thoroughly evacuated until a vacuum of 10^{-4} mm. or less was obtained. In experiments carried out in a lower temperature range the frozen liquid was thawed by immersing the U-tube in an acetone–solid carbon dioxide bath, then frozen and evacuated again. After evacuation the liquid air-bath was replaced by a water-bath and simultaneously the stopcock 1 was opened. In each experiment the water-bath was kept at a constant temperature, however, this temperature was varied from one experiment to another, the lowest being 10° while the highest was 22°. In this way we were able to vary the average partial pressure of the peroxide in the reaction vessel.

The opening of stopcock 1 was considered as the beginning of the experiment. By this operation flask H is connected with the pumping system and the carrier gas begins to flow through the apparatus. The vapors of toluene or benzene were used as carrier gases, the respective liquid hydrocarbon being kept in flask H maintained at a constant temperature. The flow was continued until the solution introduced into the U-tube disappeared completely.

The vapor of diacetyl peroxide, picked up by the carrier gas, flowed through the reaction vessel maintained at a temperature constant within ±0.1°. The variation of temperature along the reaction vessel was not greater than ±0.75°, and a special correction was introduced to take care of this non-homogeneous temperature distribution. The temperature was measured with an accuracy better than 0.1° by means of a thermocouple and a potentiometer, the reading of the latter being standardized with the help of a precision thermometer calibrated by The National Bureau of Standards.

The vapor of the carrier gas and of the undecomposed diacetyl peroxide was condensed in trap T_1, cooled to −80°, while the gaseous products of the decomposition were pumped into the storage section by means of two mercury vapor pumps (I and II). Keeping trap T_2 in a liquid air-bath ensured the condensation of ethane and carbon dioxide formed in the reaction, and thus the pressure in the storage section determined the amount of permanent gases (CH_4) formed in the reaction. Thereafter, the liquid air-bath surrounding trap T_2 was replaced by an acetone–solid carbon dioxide bath; and the amount of CO_2 and ethane formed in the decomposition was then measured by the increase of pressure. Finally, the gaseous products were pumped, by means of a Toepler pump, into a gas analyzer and their composition was determined.

Results

The decomposition of diacetyl peroxide was studied from 90° up to 250°. Carbon dioxide, ethane and small quantities of methane were found

(1) M. S. Kharasch and M. T. Gladstone, THIS JOURNAL, 65, 15 (1943); M. S. Kharasch, E. J. Jensen and W. H. Urry, *J. Org. Chem.*, 10, 386 (1945).

(2) O. J. Walker and G. L. E. Wild, *J. Chem. Soc.*, 207 (1935).

(3) C. C. Price and H. Morita, THIS JOURNAL, 75, 3686 (1953).

(4) C. D. Wagner, R. H. Smith and E. D. Peters, *Ind. Eng. Chem., Anal. Ed.*, 19, 976 (1947).

(5) M. Szwarc, *J. Chem. Phys.*, 17, 431 (1949); *Proc. Roy. Soc. (London)*, 198A, 267 (1949).
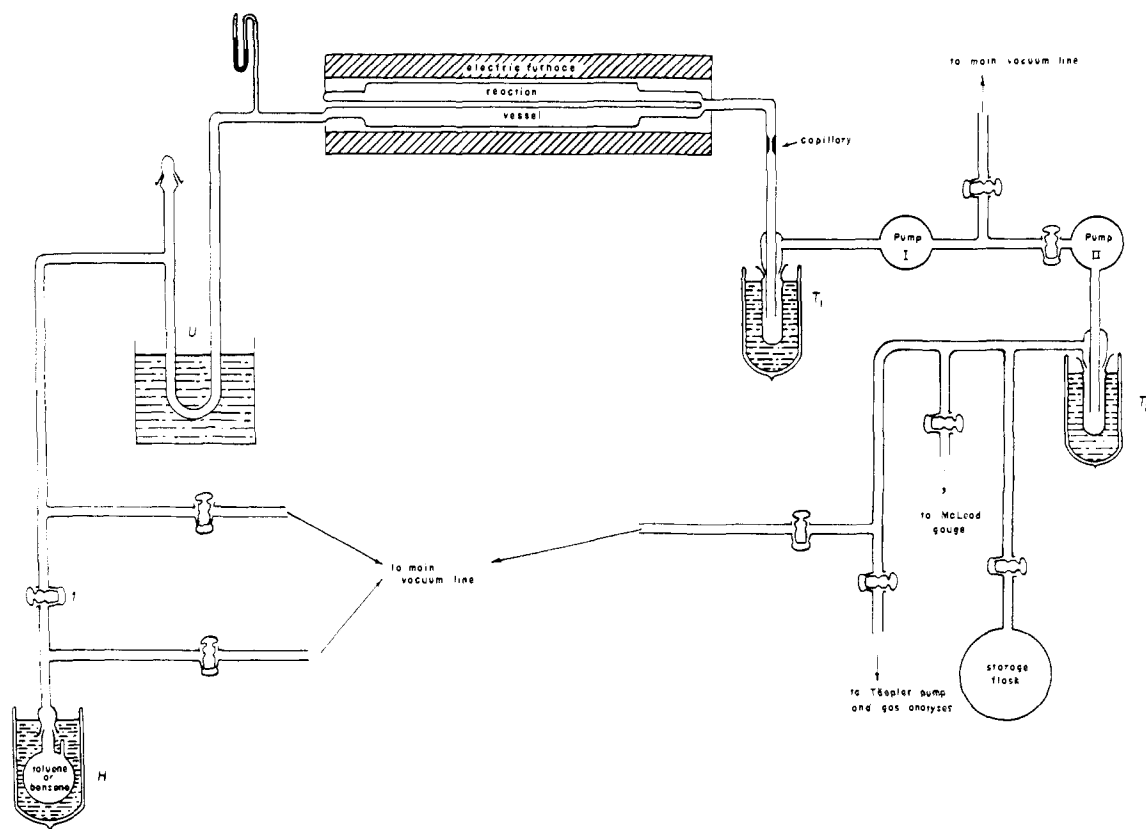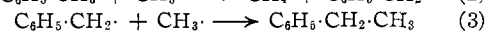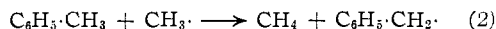
Fig. 1.

to be the *only* products of the reaction. The analyses of the gases showed invariably 66–67 mole per cent. of carbon dioxide in the products, *i.e.*, the molar ratio of $CO_2/(C_2H_6 + CH_4)$ was found to be 2:1. All these findings confirm essentially the results of Walker and Wild.

The presence of methane in the products of decomposition is significant. It indicates the occurrence of reactions 2 and 3.

$$C_6H_5 \cdot CH_3 + CH_3 \cdot \longrightarrow CH_4 + C_6H_5 \cdot CH_2 \cdot \quad (2)$$
$$C_6H_5 \cdot CH_2 \cdot + CH_3 \cdot \longrightarrow C_6H_5 \cdot CH_2 \cdot CH_3 \quad (3)$$

In our system a quantitative study of reaction 2 is considered as impractical since the quantity of methane formed is too small (in most experiments it amounts to not more than 2% of the total of the produced gases). Nevertheless, the extent to which reaction 2 participates in the over-all process seems to be consistent with our present knowledge of radical reactions. For example, at 445°K., the unimolecular rate constant for the decomposition of diacetyl peroxide was found to be 0.6 sec.$^{-1}$. Taking $2.5.10^{-9}$ mole/cc. as a typical value for the concentration of diacetyl peroxide in the reaction vessel, we compute the rate of formation of methyl (or acetate) radicals at 3×10^{-9} mole/cc./sec. The rate constant for the bimolecular recombination of methyl radicals is about $5 \cdot 10^{13}$ cc./mole/sec. Hence, the stationary concentration of methyl radicals is calculated at 8×10^{-12} mole/cc. Using the data of Trotman-Dickenson and Steacie[6] for the rate constant of reaction 2, we compute the

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

rate of formation of methane under our experimental conditions at

$$(1.2 \times 10^7)(8 \times 10^{-12}) (5 \times 10^{-7}) = 4.8 \times 10^{-11} \text{ mole/cc./sec.}$$

This means that the computed rate of formation of methane is equal to about 1.5% of the rate of formation of carbon dioxide, in agreement with our experimental findings. The same calculation shows that at 360°K. (the lowest temperature in which the decomposition was studied) the amount of methane formed should increase to about 10% of that of carbon dioxide. This value again is in fair accord with experimental results.

TABLE I

Run	% of decomposition based on the amount Of gas collected	On titration	Run	% of decomposition based on the amount Of gas collected	On titration
42	13.0	12.0	37	18.0	19.1
41	13.9	13.3	35	38.9	38.9
40	14.4	13.3	31	39.8	39.5
38	15.7	16.5	33	41.9	39.8

If each mole of diacetyl peroxide produces on decomposition two moles of carbon dioxide and one mole of ethane (or methane), then the number of moles of decomposed peroxide is given by 1/3 of the number of moles of gas produced. Hence the percentage of the decomposition can be calculated either from the amount of the gas collected, or by titrating the undecomposed diacetyl peroxide condensed in trap T_1. Data obtained by these two methods are listed in Table I, inspection of which shows that the agreement is satisfactory.

On the whole, we find that the percentage of decomposition based on the amount of gas formed in the reaction is much more reliable than that obtained by titration.[7] Consequently, all the data presented in the following tables are calculated from the rates of formation of the gaseous product.

A further check on the stoichiometry of the reaction was obtained by carrying the decomposition of diacetyl peroxide to completion. From the data, presented later in this paper, we calculated the percentage of the decomposition at 240° and 0.7 sec. time of contact as exceeding 99.9%. Actually, the following results were obtained:

Amount of diacetyl peroxide introduced   0.176 mmole

Products $\begin{cases} CO_2 = 0.361 \text{ mmole} & = 66.8\% \\ C_2H_6 = 0.169 \text{ mmole} & = 30.7\% \\ CH_4 = 0.011 \text{ mmole} & = 2.5\% \end{cases}$

Total = 0.541 mmole, i.e., % of decomposition 102.5%

Thus, the assumed stoichiometry of the reaction is fully confirmed. Furthermore, this result proves that no methyl acetate is formed in the decomposition of diacetyl peroxide in gaseous phase, a point which will be of importance in discussing the mechanism of the decomposition of this compound in solution.

The decomposition of diacetyl peroxide in the gaseous phase is shown to be a first-order reaction. This conclusion follows from experiments in which the partial pressure of the compound[8] was varied from 0.035 up to 0.150 mm. and the time of contact

TABLE II

VARIATION OF THE PARTIAL PRESSURE OF THE PEROXIDE

Run	Pperoxide, mm.	$k,^a$ sec.$^{-1}$	Dev. from the mean, %
56	0.035	0.650	+8.3
55	.037	.645	+7.5
57	.051	.603	+0.5
54	.051	.600	0.0
53	.101	.605	+0.8
52	.111	.610	+1.7
32	.141	.576	−4.0
33	.156	.620	+3.3

VARIATION OF THE PARTIAL PRESSURE OF TOLUENE

Run	Ptoluene, mm.	$k,^a$ sec.$^{-1}$	Dev. from the mean, %
57	9.27	0.603	+0.5
58	9.42	.600	0.0
32	14.50	.576	−4.0
33	14.90	.620	+3.3

VARIATION OF TIME OF CONTACT

Run	Time of contact, sec.	$k,^a$ sec.$^{-1}$	Dev. from the mean, %
64	0.446	0.587	−2.2
63	.453	.582	−3.0
57	.830	.603	−0.5
58	.843	.600	0.0

Using benzene instead of toluene as a carrier gas

54		0.600	0.0
55		.645	+7.5
56		.650	+8.3

^{a} The rate constants are interpolated to a common temperature 444°K.

(7) Presence of greater quantity of toluene interferes somehow with the analytical procedure.

(8) The "partial pressure" of diacetyl peroxide denotes the average partial pressure.

was changed from 0.40 to 0.84 sec. The relevant data are collected in Table II which includes also the data demonstrating that the first-order rate constants are independent of the partial pressure of toluene, and of the nature of the carrier gas. The data collected in Table II result from 17 experiments carried out in a narrow temperature range of 4° only, and the rate constants k were recalculated to a common temperature for the sake of comparison. The deviations, listed in the last column of Table II, refer to the mean value obtained from all 17 experiments (see also Table III).

TABLE III

Run	T, °K.	P_{total} mm.	$P_{peroxide}$ mm.	Time of contact, sec.	% decomposition	k, sec.$^{-1}$	
68	361.3	18.0	0.390	41.2	1.27	3.12 × 10^{-4}	
70	363.4	17.9	.380	36.8	1.42	3.8 × 10^{-4}	k_{408} sec.$^{-1}$
48	407.5	13.7	.100	0.79	2.43	0.031	0.033
45	408.0	13.7	.095	.75	2.53	.034	.034
46	408.0	13.9	.096	.76	2.34	.031	.031
47	408.0	14.0	.097	.77	2.24	.029	.029
50	409.0	14.7	.148	.76	2.73	.036	.032
51	409.5	13.8	.157	.715	2.53	.038	.032
43	424.0	13.6	.094	.74	8.37	.118	Av.
44	424.5	13.4	.095	.72	8.57	.124	k = 0.032
42	429.9	13.5	.082	.72	13.0	.195	± 0.001
41	431.0	13.2	.083	.70	13.9	.212	
39	431.7	13.5	.075	.71	14.4	.218	
40	431.7	13.5	.080	.72	14.4	.217	
38	432.5	13.3	.073	.70	15.7	.244	
36	435.0	13.4	.071	.73	18.2	.277	
37	435.0	13.2	.070	.72	18.0	.276	k_{444} sec.$^{-1}$
63	442.7	10.9	.074	.45	21.3	.528	0.582
64	443.2	10.7	.061	.45	21.9	.554	.587
59	443.2	11.5	.065	.51	24.6	.554	.587
60	443.7	11.7	.071	.57	25.6	.568	.580
52	444.0	13.6	.111	.69	34.2	.610	.610
57	444.4	9.3	.051	.83	40.3	.621	.603
53	444.5	13.5	.101	.68	35.0	.632	.605
32	444.5	14.5	.141	.71	34.8	.600	.576
58	444.7	9.4	.052	.84	41.6	.637	.600
54*	445.5	13.2	.051	.69	37.2	.673	.600
62	445.5	11.0	.061	.48	26.6	.647	.579
61	445.7	11.2	.062	.49	27.4	.655	.575
55*	446.0	12.6	.037	.69	40.2	.748	.645
35	446.0	13.7	.067	.71	38.9	.697	.601
34	446.2	13.9	.071	.72	39.8	.705	.597
56*	446.2	12.4	.035	.68	40.6	.769	.650
33	447.0	14.9	.156	.69	41.9	.775	.620
65	457.5	9.8	.060	.39	49.8	1.76	Av.
66	457.7	9.7	.060	.39	50.0	1.79	0.600 ± 0.005

* Experiments carried out with benzene instead of toluene.

Table III contains all the data obtained for the whole temperature range from about 90 up to 190°. The reproducibility of the experiments is very good, and the plot of the logarithms of the first-order rate constant versus reciprocal of temperature gives an excellent straight line. The activation energy is computed at 29.5 ± 0.2 kcal./mole, and the frequency factor at 1.8 × 10^{14} sec.$^{-1}$. Two experiments were performed at a temperature of about 90° to provide a direct comparison between the rate of the decomposition in gaseous phase and in solution. (The decomposition of diacetyl peroxide in solution has been investigated in the temperature range of 55–85°.) In the latter experiments the time of contact was about 40 sec., nevertheless, the first-order rate constants agree very well with the values extrapolated from the other experiments.

Discussion

The results reported above suggest strongly that the decomposition of diacetyl peroxide is a unimolecular reaction, and the work of Kharasch and his school implies that we measure the rate of the unimolecular dissociation

$$CH_3 \cdot CO \cdot O \cdot O \cdot CO \cdot CH_3 \longrightarrow 2CH_3 \cdot CO_2 \qquad (1)$$
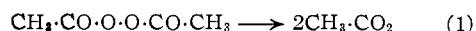
The present work adds the following evidence in favor of this assumption:

1. Some methane *is* produced in the decomposition and its quantity is consistent with the assumption that it results from reactions which involve methyl radicals. This observation indicates that ethane is *not* produced by a direct decomposition of diacetyl peroxide according to equation 4

$$CH_3 \cdot CO \cdot O \cdot O \cdot CO \cdot CH_3 \longrightarrow C_2H_6 + 2CO_2 \qquad (4)$$
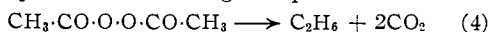
but by the recombination of methyl (or perhaps acetate) radicals.

2. It seems that the same reaction initiates the thermal decomposition of diacetyl peroxide in gas phase and in solution, since the rate of decomposition and the activation energy are essentially the same in both phases (see the following paper). On the other hand, there is no doubt that the decomposition in solution involves radicals.

We may conclude, therefore, that the observed activation energy represents the O–O bond dissociation energy in diacetyl peroxide, *i.e.*

$$D(CH_3 \cdot CO \cdot O \cdot O \cdot CO \cdot CH_3) = 29.5 \text{ kcal./mole}$$
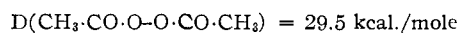
From this value one may calculate the heat of formation of acetate radical

$$\Delta H_f(CH_3 \cdot CO_2) = \tfrac{1}{2}\{29.5 + \Delta H_f (CH_3 \cdot CO \cdot O \cdot O \cdot CO \cdot CH_3)\}$$

and subsequently, the related bond dissociation energies, like $D(CH_3 \cdot COO-H)$. At present the heat of formation of diacetyl peroxide is not known, but we hope that it will be determined in the near future.

Kinetics of the Thermal Decomposition of Diacetyl Peroxide. II. Effects of Solvents on the Rate of the Decomposition

By M. Levy, M. Steinberg and M. Szwarc

The kinetics of the thermal decomposition of diacetyl peroxide has been studied in 9 solvents in the temperature range 55–85°. In sufficiently dilute solutions (*i.e.*, less than 0.1 M), the decomposition is essentially first order. At higher concentrations the induced second-order reaction begins to be significant, and it has been shown that the latter reaction is caused mainly by the solvent radicals. The comparison of the decomposition carried out in solutions with that taking place in the gaseous phase suggests that some recombination $2CH_3COO \rightarrow (CH_3COO)_2$ takes place in the "cage." This cage recombination probably is responsible for the observed changes in the apparent activation energy of the process.

In the present communication we shall try to elucidate the influence of a solvent on the rate and on the activation energy of the decomposition of acetyl peroxide. The kinetics of this decomposition has been studied in the temperature range 55–85° in the following solvents: isoöctane, cyclohexane, benzene, toluene, glacial acetic acid, propionic acid and in three fluorochemicals.

Experimental

The method of preparation of diacetyl peroxide is described in part I of this series. Crystals of the peroxide were dissolved in the required solvent and its concentration was determined by the iodometric titration method described by Wagner, Smith and Peters.[1] The solvents were acquired commercially. Isoöctane was of "spectroscopically pure" grade, benzene, toluene and acetic acid were of "analytically pure" grade, while propionic acid was of "chemically pure" grade. Three fluorochemicals were used, namely: a cyclic ether corresponding probably to a formula $CF_3 \cdot C_5F_9O$ manufactured by Minnesota Mining Co. (Trade name Fluorochemical 0–75), fluorinated methylcyclohexane ($CF_3 \cdot C_6F_{11}$) manufactured by Columbia Organic Chemicals Co., and fluorinated dimethylcyclohexane ($(CF_3)_2 \cdot C_6F_{10}$, manufactured by du Pont Co. (denoted as FCX 327). The solvents were distilled before use, and it was shown that all but fluorochemicals do not contain any peroxides.[2]

The following procedure was adopted in most experiments. Five cc. of the peroxide solution followed by 5 cc. of the pure solvent was pipetted into a 30-cc. flask provided with a constriction and an inner ground joint. The flask was attached to a high vacuum line, its contents frozen by immersing it into a solid carbon dioxide–acetone bath, and then evacuated until a vacuum of about 10^{-5} mm. was attained. Thereafter the contents of the flask were thawed, and then the freezing and evacuation procedure repeated for two more times. After the third evacuation the flask was sealed off at the constriction and immersed into a constant temperature bath. The temperature of the bath was kept constant within a limit better than ±0.1°, and the reading of the thermometer was compared with the reading of a precision thermometer calibrated by The National Bureau of Standards.

After a predetermined period of time (2–64 hours),[3] the flask was removed from the bath, cooled in a solid carbon dioxide–acetone bath, opened, and the contents analyzed for the undecomposed peroxide. The experimental results, expressed in the form of first-order rate constants are listed in Table I.

Some experiments were carried out in an apparatus from which aliquots of the solution could be withdrawn without admitting air to the reaction chamber.

Results

The first-order kinetics of the decomposition of diacetyl peroxide was confirmed by two methods. Using the apparatus mentioned previously the fraction of decomposition f was determined as a

(1) C. D. Wagner, R. H. Smith and E. D. Peters, *Ind. Eng. Chem.*, *Anal Ed.*, **19**, 976 (1947).

(2) We found that 10 cc. of $CF_3 \cdot C_6F_{11}$ liberates 0.75 × 10^{-2} millimole of iodine. 10 cc. of FCX 327 liberates 1 × 10^{-2}, and 10 cc. of 0–75 liberates 4.1 × 10^{-2} millimole of iodine.

(3) It was shown that the contents of the flask attain the temperature of the bath within 5 minutes.