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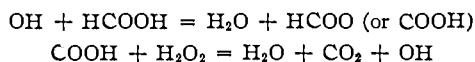
Free Radical Induced Reaction Between Formic Acid and Perdisulfuric Acid<sup>1</sup>

BY EDWIN J. HART

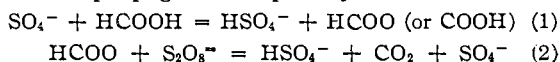
RECEIVED AUGUST 3, 1960

The effect of formic acid and perdisulfuric acid concentrations and of *pH* and dose rate on the Co<sup>60</sup>  $\gamma$ -ray initiated reaction of these compounds is reported.  $G(\text{CO}_2)$  as high as 680 is found. The chain reaction proceeds with the stoichiometry given by:  $\text{S}_2\text{O}_8^{2-} + \text{HCOOH} = 2\text{HSO}_4^- + \text{CO}_2$ .  $G(\text{CO}_2)$  increases with increasing formic acid concentration and with decreasing dose rate. At constant formic acid and perdisulfuric acid concentrations,  $G(\text{CO}_2)$  also increases rapidly in the *pH* range from 1.5 to 5.1, but subsequently decreases at *pH*'s in the range from 5.1 to 7 and again in the range from 9 to 11. The propagation steps proposed are:  $\text{COOH} \text{ (or } \text{HCOO}) + \text{S}_2\text{O}_8^{2-} = \text{HSO}_4^- + \text{CO}_2 + \text{SO}_4^-$  and  $\text{SO}_4^- + \text{HCOOH} = \text{HSO}_4^- + \text{COOH} \text{ (or } \text{HCOO})$ . Ionization of formic acid increases  $G(\text{CO}_2)$  whereas ionization of the COOH and OH radicals explains the decrease in yield for the *pH* ranges of 5 to 7 and 9 to 11, respectively. Permonosulfuric acid and hydrogen peroxide add to the complexity of the reaction. Three briefly discussed additional radiation induced reactions of perdisulfuric acids show the stoichiometry:  $\text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O} = 2\text{HSO}_4^- + \frac{1}{2}\text{O}_2$ ;  $\text{S}_2\text{O}_8^{2-} + \text{H}_2 = 2\text{HSO}_4^-$ ; and  $\text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O}_2 = 2\text{HSO}_4^- + \text{O}_2$  (chain).

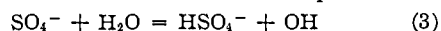
Blends of aqueous solutions of formic acid and hydrogen peroxide undergo a Co<sup>60</sup>  $\gamma$ -ray induced chain decomposition with these steps in the propagation reactions<sup>2</sup>



A similar chain radiolysis occurs when perdisulfuric acid replaces hydrogen peroxide. In this case, the propagation steps may be written as



although thermal persulfate studies support a conversion of the sulfate radical ion,  $\text{SO}_4^-$ , into a hydroxyl radical.<sup>3-5</sup> The formic acid-perdisulfuric



acid system is unaffected by dissolved oxygen in marked contrast to the strong oxygen inhibition of the formic acid-hydrogen peroxide reaction.

The present paper reports the effects of concentration, of *pH*, of dose rate and intermediate oxidizing species on the chain radiolytic decomposition of the formic acid-perdisulfate system. Some exploratory experiments are also included on the effects of hydrogen and hydrogen peroxide on the radiolysis of perdisulfuric acid. An attempt is made to explain some of the free radical reactions in aqueous perdisulfuric acid by using the free radical reactions with formic acid and hydrogen peroxide as a guide.

## Experimental

**Irradiation Techniques.**—The irradiations are carried out at room temperature (about 25°) in Pyrex cells of 12 to 14 ml. capacity at Co<sup>60</sup>  $\gamma$ -ray dosage rates in the range  $2.55 \times 10^{20}$  to  $0.0083 \times 10^{20}$  ev./l.min. and measured by the Fricke Dosimeter using the Hochanadel-Ghormley value of 15.6 ferric ions/100 ev.<sup>6</sup> Since about 3.0 water molecules are dissociated into hydrogen atoms and hydroxyl radicals by the  $\gamma$ -rays per 100 ev. of energy, at the above dosage rates, these free radical species are produced at steady rates varying from  $12.7 \times 10^{-6}$  to  $0.041 \times 10^{-6}$  *M*/min. The major portion of the irradiations were conducted at  $0.0535 \times 10^{20}$  ev./l.min. corresponding to the generation of

$0.266 \times 10^{-6}$  *M* hydrogen atoms and hydroxyl radicals/min.

Hydrogen peroxide and/or permonosulfuric acid are determined by triiodide ion absorption at 3500 Å. When perdisulfuric acid is present, the optical density of the solution increases linearly with time of standing in the spectrophotometer cells. The sum of hydrogen peroxide and permonosulfuric acid concentrations are calculated from the optical density at zero time by the method previously described.<sup>2,7</sup> The slope of the optical density-time curve is proportional to the perdisulfuric acid concentration. Hydrogen peroxide is determined from oxygen liberated by reaction with ceric sulfate in acid solution.<sup>8</sup> Total oxidizing power is determined by the oxidation of ferrous sulfate and measures the sum of perdisulfuric acid, permonosulfuric acid and hydrogen peroxide. From these three analyses, one may estimate each of these three species. The ferric ion concentration of the resulting solution is measured in the Beckman quartz spectrophotometer at 3020 Å. using a molar extinction coefficient of 2225 to calculate the concentration of ferric ion formed.

The carbon dioxide and oxygen concentrations are measured in the Van Slyke micro gas apparatus.<sup>2</sup> Carbon dioxide is absorbed by potassium hydroxide and oxygen is absorbed by an alkaline sodium hydrosulfite solution. Hydrogen, assumed to be the residual gas after absorption of carbon dioxide and oxygen, is usually present in trace amounts. Consequently  $G(\text{H}_2)$ , particularly at high  $G(\text{CO}_2)$  is not very reliable.

**Reagents.**—The purification of the water has been described previously.<sup>2</sup> In order to prevent further contamination of the reagents, all irradiations are carried out in cells heated to 550°. Reagent grade sulfuric acid, potassium persulfate, 90% hydrogen peroxide and perchloric acid are used without further purification. Matheson 98-100% formic acid is distilled at 20 cm. pressure through a 30-plate fractionation column at 59° to give a product having an  $n_{\text{D}}^{20}$  of 1.3715. Permonosulfuric acid is obtained by heating of 0.1 *M* potassium persulfate in 1.0 *M* sulfuric or perchloric acid for 60 minutes at 50° according to the method of Kolthoff and Miller.<sup>3</sup>

**Thermal Reaction.**—A correction is made to the  $\gamma$ -ray reaction for the thermal reaction taking place between perdisulfuric acid and formic acid. A log-log plot of the thermal rate of carbon dioxide evolution versus perdisulfuric acid concentration is linear in the range from  $0.46 \times 10^{-3}$  to 0.1 *M* with a slope of unity, showing a first order reaction as is reported by Srivastava and Ghosh.<sup>9</sup> The correction for the thermal reaction normally amounts to less than a few per cent. of the  $\gamma$ -ray induced reaction. However, in 0.1 *M* perdisulfuric acid, the thermal correction amounts to two-thirds of the irradiated yield.

## Results and Discussion

**Dosage Curves.**—At formic acid concentrations of 0.001 to 1.0 *M*, carbon dioxide and hydrogen

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

2 E. J. Hart, *J. Am. Chem. Soc.*, **73**, 68 (1951).

(3) I. M. Kolthoff and I. K. Miller, *ibid.*, **73**, 3055 (1951).

(4) M. Tsao and W. K. Wilmarth, *J. Phys. Chem.*, **63**, 346 (1959).

(5) C. R. Giuliano, N. Schwartz and W. K. Wilmarth, *ibid.*, **63**, 353 (1959).

(6) C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **21**, 880 (1953).

(7) E. J. Hart, *THIS JOURNAL*, **76**, 4198 (1954).

(8) E. J. Hart, S. Gordon and D. A. Hutchison, *J. chim. phys.*, **52**, 570 (1955).

(9) S. P. Srivastava and S. Ghosh, *Z. physik. Chem. (Leipzig)*, **211**, 149 (1959).

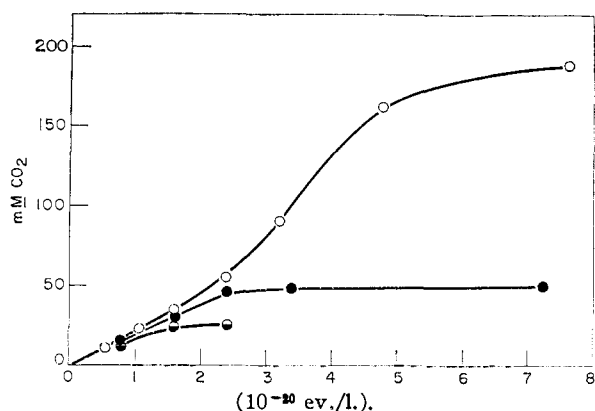
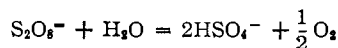


Fig. 1.—Carbon dioxide formation in deaerated solutions of formic acid and persulfuric acid at pH 2.08: O, 0.0002M HCOOH, 0.003M  $K_2S_2O_8$ ; ●, 0.000050M HCOOH, 0.001M  $K_2S_2O_8$ ; ●, 0.000025M HCOOH, 0.001M  $K_2S_2O_8$ ; dosage rate =  $0.053 \times 10^{20}$  ev./l. min.

dosage curves are linear at persulfate concentrations of 0.001 in 0.01 M sulfuric acid. But at low ratios of formic acid to persulfate, non-linear carbon dioxide dosage curves may result. Figure 1 shows an autocatalytic dosage curve for a solution containing 0.0002 M formic acid, 0.003 M potassium persulfate and 0.01 N sulfuric acid. In this experiment the initial carbon dioxide yield,  $G_i(CO_2)$ , of 13.1 increases to a maximum  $G(CO_2)$  of 33. At lower formic acid-persulfate ratios, the formic acid is consumed before autocatalysis becomes important. Some intermediate is generated, possibly permonosulfuric acid, that is more reactive than perdisulfuric acid. Later we shall see that permonosulfuric acid is, indeed, more effective than perdisulfuric acid in the radiolysis of formic acid.

All of the formic acid in the irradiations of Fig. 1 is consumed rapidly. Note how closely the amount of carbon dioxide evolved approaches the initial concentration of formic acid. This result shows that there can be no important reaction liberating carbon monoxide.

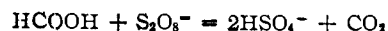
**Stoichiometry and Effect of Formic Acid Concentration.**—The radiolysis of 0.001 M perdisulfuric acid is a non-chain reaction.  $G(O_2)$  at pH 2.9 is 1.32 and  $G(-S_2O_8^{2-})$  is 2.55. Neither hydrogen nor hydrogen peroxide is present in the irradiated solution. This result indicates the proportions



But even at formic acid concentrations of  $25 \times 10^{-6}$  M,  $G(CO_2)$  becomes 9.1, revealing a short chain reaction. This result further shows the importance of eliminating organic impurities from the persulfuric acid for thermal studies on the perdisulfuric acid systems.

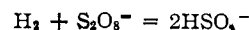
$G(CO_2)$  increases from 9.1 in  $25 \times 10^{-6}$  M formic acid to 416 in 1 M formic acid in solutions containing 0.001 M potassium persulfate and 0.01 N sulfuric acid. Since these results show a chain reaction for a pair of substances, neither of which separately undergoes a chain radiolysis, we explain this result by the alternating radical sequence of reactions 1 and 2. As will be discussed later, either the formic acid or the formate radical,

COOH, may react in either the un-ionized or ionized forms. Carbon dioxide generation closely equals persulfate disappearance in 0.01 M formic acid solutions and so the over-all reaction is



In the concentration range from  $2 \times 10^{-4}$  to 0.1 M formic acid in 0.01 N sulfuric acid,  $G(CO_2)$  increases from 10 to 252 substantially as  $(HCOOH)^{1/2}$ . In unbuffered solutions, too,  $G(CO_2)$  increases as  $(HCOOH)^{1/2}$  reaching 497 in 0.125 M solutions (see Fig. 2).

Hydrogen yields in the range of 2.8 to 3.7 are obtained for formic acid-persulfate ratios of one or greater. Therefore hydrogen atoms generated in the water with a  $g(H)$  of about 3.0 react with the formic acid in preference to the persulfate ion.<sup>2</sup> At ratios less than one,  $G(H_2)$  decreases and approaches zero. In some cases hydrogen builds up to low steady state concentrations proving that this molecule, too, reacts with the sulfate radicals in the solution. In the absence of formic acid, 0.73 mM hydrogen and 0.91 mM perdisulfuric acid react and consume hydrogen with a yield  $G(-H_2)$  of 7.24. Oxygen is also liberated and the total persulfate consumption amounts to  $G(-S_2O_8^{2-})$  of 8.06. The hydrogen-persulfate relationship is



**Effect of Perdisulfuric Acid Concentration.**—Relatively little effect of perdisulfuric acid concentration is found in the irradiation of 0.01 M formic acid as the concentration increases from  $0.028 \times 10^{-3}$  to 0.01 M.  $G(CO_2)$  varies from 50 at the lower limit to 92 at the higher limit at a dosage rate of  $0.053 \times 10^{20}$  ev./l.min. A rapid increase in  $G(CO_2)$  occurs between 0.01 and 0.1 M perdisulfate and is coincident with a relatively large increase in the dark reaction.

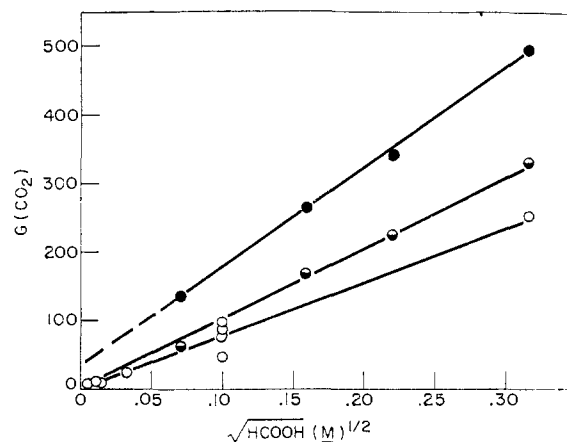


Fig. 2.— $G(CO_2)$  as a function of formic acid concentration in 0.001M perdisulfuric acid: O, 0.01 N  $H_2SO_4$ ,  $0.053 \times 10^{20}$  ev./l. min.; ●, 0.01 N  $H_2SO_4$ ,  $0.078 \times 10^{20}$  ev./l. min.; ●, unbuffered HCOOH,  $0.078 \times 10^{20}$  ev./l. min.

**Effect of Dosage Rate of  $\gamma$ -Rays.**—There is less than a two-fold change in  $G(CO_2)$  as the dosage rate ( $I$ ) is varied 300-fold from  $2.55 \times 10^{20}$  to  $0.0083 \times 10^{20}$  ev./l.min. (see Fig. 3). This work was carried out on solutions containing 0.01 M

TABLE I  
EFFECT OF OXYGEN, HYDROGEN PEROXIDE, PERMONOSULFURIC ACID AND PERCHLORIC ACID ON THE OXIDATION OF 0.01 *M* FORMIC ACID

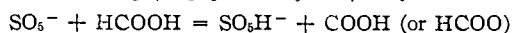
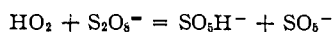
Expt.	Acid ( <i>N</i> )	Initial concentrations ( <i>M</i> )				<i>G</i> (CO <sub>2</sub> )	<i>G</i> (H <sub>2</sub> )
		(O <sub>2</sub> )	(H <sub>2</sub> O <sub>2</sub> )	(H <sub>2</sub> SO <sub>6</sub> )	(H <sub>2</sub> S <sub>2</sub> O <sub>8</sub> )		
1	H <sub>2</sub> SO <sub>4</sub> 0.01	.....	.....	.....	0.0010	86	...
2	H <sub>2</sub> SO <sub>4</sub> .01	0.00043	.....	.....	.0010	84	0.65
3	H <sub>2</sub> SO <sub>4</sub> .01	.....	0.000069	.....	.0010	67	3.5
4	H <sub>2</sub> SO <sub>4</sub> .01	.....	.0000075	0.0000427	.000938	91(1) <sup>a</sup>	<i>G</i> (-P) = 88
5	H <sub>2</sub> SO <sub>4</sub> .01	.....	.000460	.000032	.000473	73	<i>G</i> (O <sub>2</sub> ) = 7.0
6	HClO <sub>4</sub> .01	.....	.000028	.000054	.000892	~300i	
7	HClO <sub>4</sub> .01	.....	.000090	.000164	.000619	64(1) <sup>a</sup>	<i>G</i> (-P) <sub>1</sub> = 74 <i>G</i> (-P) <sub>tot.</sub> = 232 <i>G</i> (-H <sub>2</sub> SO <sub>6</sub> ) = 161
8	H <sub>2</sub> SO <sub>4</sub> .01	.....	< .000006	< .000006	.000967	78	...
9	HClO <sub>4</sub> .01	.....	< .000006	< .000006	.000967	112	...

<sup>a</sup> 1 indicates linear part of the dosage curve.

formic acid, 0.001 *M* potassium persulfate in 0.01 *N* sulfuric acid. But as the formic acid concentration is increased to 0.06 *M* and as the chain length of the reaction increases, *G*(CO<sub>2</sub>) is inversely proportional to *I*<sup>1/2</sup> (see Fig. 3). At *pH* 5.48 the curve extrapolates to *G*(CO<sub>2</sub>) = 0 at high intensities. At *pH* 2.58, in 0.06 *M* formic acid and at *pH* 2.20 in 0.01 *M* formic acid, there is relatively little effect of dose rate.

#### Effect of Oxygen and Hydrogen Peroxide.—

Oxygen is a powerful inhibitor of the chain reaction between hydrogen peroxide and formic acid.<sup>2</sup> In contrast, oxygen has no effect on the decomposition of 0.01 *M* formic acid in 0.001 *M* persulfuric acid solutions (expt. #2, Table I). Oxygen is consumed in this reaction with *G*(-O<sub>2</sub>) = 2.7 and the hydrogen yield is reduced from 3.2 to 0.65. Since *G*(H<sub>2</sub>) is only slightly above the molecular yield *g*(H<sub>2</sub>), of 0.45, the low yield of 0.65 proves that hydrogen atoms react mainly with oxygen instead of formic acid. The resulting hydroperoxy radical is also capable of initiating a chain reaction between persulfuric acid and formic acid since *G*(CO<sub>2</sub>) is unaltered by oxygen. Since the hydroperoxy radical does not promote chain reactions in the hydrogen peroxide-formic acid system,<sup>2</sup> it must form a chain propagating radical by reaction with the perdisulfuric acid perhaps as



Since oxygen disappears from the solution, oxygen probably is not liberated in a reaction such as



although hydroperoxy radical termination, if substituted for bisulfate radical termination (see mechanism), explains the observed decrease in oxygen. Performic acid intermediates may also be important.

Hydrogen peroxide (0.069 *mM*) has a small inhibitory effect on the formic acid-persulfuric acid reaction. *G*(CO<sub>2</sub>) is reduced slightly whereas *G*(H<sub>2</sub>) is unaffected by hydrogen peroxide. At peroxide concentrations of 0.46 *mM*, normal decomposition of 0.01 *M* formic acid is observed (expt. 5, Table I). However, oxygen, an unexpected additional product, forms with a net *G*(O<sub>2</sub>) of 7.0. This oxygen originates from another chain

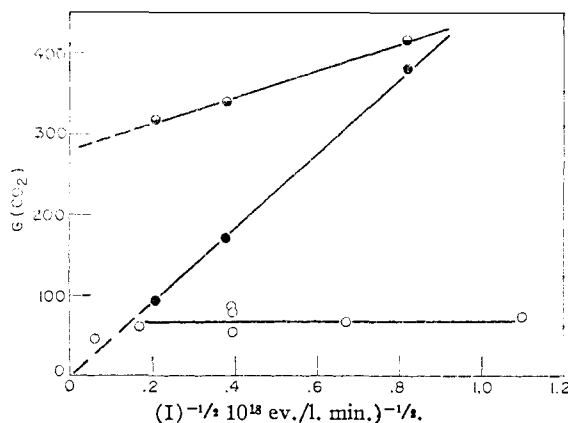
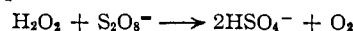


Fig. 3.—Effect of  $\gamma$ -ray dosage rate on *G*(CO<sub>2</sub>) in formic acid-0.001*M* persulfuric acid solutions: O, 0.01*M* HCOOH, 0.01 *N* H<sub>2</sub>SO<sub>4</sub>; ●, 0.06*M* HCOOH, *pH* = 5.48; ●, 0.06*M* HCOOH, *pH* = 2.58.

reaction between hydrogen peroxide and perdisulfuric acid, a reaction already studied by Tsao and Wilmarth.<sup>10</sup> *G*(O<sub>2</sub>) of 117 has been found by the irradiation of  $0.956 \times 10^{-3}$  *M* perdisulfate plus permonosulfate and  $0.37 \times 10^{-3}$  *M* hydrogen peroxide at a *pH* of 2.89. This over-all reaction is



And this result is consistent with the non-interference of oxygen in the formic acid-perdisulfuric acid chain reaction.

**Effect of Permonosulfuric Acid.**—The autocatalytic form of the dosage curves of Fig. 1 for 0.2 *mM* formic acid shows an intermediate of greater chain oxidation potential than perdisulfuric acid. The series of experiments from 4 to 7 of Table I is carried out using low concentrations of permonosulfuric in addition to perdisulfuric acid. Permonosulfuric acid is obtained by the hydrolysis of perdisulfuric acid in 1 *N* sulfuric acid (expts. 4 and 5) or perchloric acid (expts. 6 and 7).

An increase in yield from *G*(CO<sub>2</sub>) of 112 to 238 occurs on the replacement of part of the perdisulfuric acid by permonosulfuric acid in 0.01 *N* perchloric acid solutions. (Compare irradiations 7 and 9 of Table I where the effect of 0.164 *mM* permonosulfuric acid is shown.) A smaller in-

(10) M. Tsao and W. K. Wilmarth, private communication.

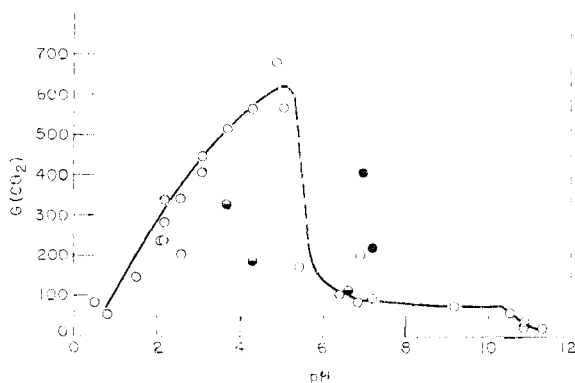
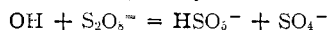


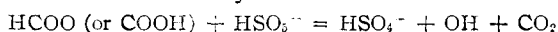
Fig. 4.—Effect of  $pH$  on the chain radiolysis of 0.06M formic acid-0.0001M potassium persulfate solutions: O, initial yields (HCOOH + NaOH); ●, maximum experimental yields; ●, reagent grade HCOONa.

crease takes place in sulfuric acid solutions containing low concentrations of permonosulfuric acid. After depletion of the permonosulfuric acid a linear oxidation rate characteristic of the prevailing perdisulfuric acid concentration is obtained.

A first step in the radiolysis of formic acid-perdisulfuric acid solutions may be the formation of permonosulfuric acid. At low formic acid-perdisulfuric acid ratios the hydroxyl radical may react as



thereby producing permonosulfuric acid and a sulfate radical. Subsequent reaction of the permonosulfuric acid may be



thereby continuing the chain.

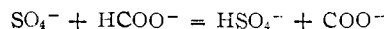
**Effect of  $pH$ .**— $pH$  was studied in the range from 0.52 to 11.3 using 0.06 M formic acid-sodium formate concentrations with 0.001 M potassium persulfate. The reaction is characterized by a rapid rise in  $G(CO_2)$  in the acid range to  $pH$  5.1, a rapid decrease in  $G(CO_2)$  in the  $pH$  range 5.1 to 7.3 and another lesser decrease at  $pH$  10-11 (see Fig. 4).

$G(CO_2)$  increases from 60 to 600 as the  $pH$  is increased from 0.52 to 5.1. However  $G(CO_2)$  is dependent on the substances present. Blends of formic acid and sodium formate lead to lower yields than formic acid-sodium hydroxide in the  $pH$  range 3.1 to 4.3 (see Fig. 4). Impurities introduced with the sodium formate or sodium hydroxide produce a major effect.

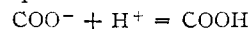
Results in the  $pH$  range from 5.5 to 7.3 are most uncertain. With a boric acid buffer around a  $pH$  of 7.0, there is a pronounced autocatalytic form to the dosage curves. The yield increases as the reaction proceeds. The initial yields are represented by the open circles in Fig. 4, whereas the maximum yields are given by the solid circles. Lower  $G(CO_2)$  yields are obtained in using phosphate buffers than in those using blends of formic acid and sodium hydroxide or with borate buffers.

$G(CO_2)$  decreases from 600 to about 80 in the  $pH$  range of 5 and 7. Above a  $pH$  of 7 the yield remains constant, decreasing again in the  $pH$  region of 10.5 to 11.5.

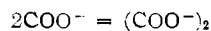
Perdisulfuric acid is a strong acid and we may assume it to be completely ionized at 0.001 M in the  $pH$  range above 1.5. Therefore the increase in  $G(CO_2)$  from 140 to 600 can be attributed to formic acid ionization and if we assume the ion to be more reactive than the neutral molecule, we may write the reaction



to replace the un-ionized radical in the propagating series. Since the dissociation constant for formic acid is  $1.76 \times 10^{-4}$ , dissociation is essentially complete at 5.1, the  $pH$  where maximum  $G(CO_2)$  is observed. We can account for the rapid subsequent decrease in  $G(CO_2)$  between  $pH$  5.1 and 7 by assuming the equilibrium

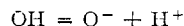


with the COOH radical as the reactive chain propagating species. Low yields at  $pH$ 's 6 to 8 can then be ascribed to the terminating reaction



forming oxalic acid.<sup>11,12</sup>

The further decrease beyond  $pH$  9 may be due to the equilibrium



with the  $O^{\cdot -}$  radical ion as the new reactive species.

**Mechanism.**—The complex behavior of the formic acid-persulfate system is difficult to explain, although an attempt has been made above to write reactions to interpret its over-all behavior. The high  $G(CO_2)$  and its dependence on  $(I)^{-1/2}$  and  $(HCOOH)^{1/2}$  are indicative of the radiolytic decomposition of hydrogen peroxide.<sup>13</sup> This similar mechanism explains these facts.

	Rate constants $k_{II}, k_{OH}$
$H_2O = H_2, H_2O_2, H, OH$	
$H + HCOOH = H_2 + COOH \text{ (or } HCOO)$	$k_1$
$OH + HCOOH = H_2O + COOH \text{ (or } HCOO)$	$k_2$
$COOH + S_2O_8^{2-} = CO_2 + HSO_4^- + SO_4^{\cdot -}$	$k_3$
$SO_4^{\cdot -} + HCOOH = HSO_4^- + COOH$	$k_4$
$2SO_4^{\cdot -} + HCOOH = S_2O_8^{2-} + HCOOH$	$k_5$

Here we assume that only the hydrogen atoms and hydroxyl radicals initiate radical formation by attacking formic acid since the  $I^{-1/2}$  dependence holds only at high ratios of formic acid to persulfate.  $k_3$  and  $k_4$  are the rate constants for the propagating reactions and  $k_5$  is the rate constant for the termolecular termination reaction. For convenience, all reactions of formic acid and its radical ions are shown in acid form. Treatment of the above mechanism by steady state kinetic analysis yields the equation

$$G(CO_2) = g(H) + g(OH) + k_4 \left[ \frac{g(H) + g(OH)}{2k_5} \right]^{1/2} \frac{(HCOOH)^{1/2}}{J_a^{1/2}}$$

where  $g(H)$  and  $g(OH)$  are the free radical yields of H and OH, respectively, at formic acid concentration (HCOOH) in moles/l.  $J_a$  is the rate of energy input in  $ev./6.02 \times 10^{25}$  l.sec. This equation pro-

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vides us with the basic behavior observed in Figs. 2, 3 and 4 if we assume that the formate ion, too, reacts with the sulfate radical  $\text{SO}_4^-$ , as shown in the above propagation and termination reactions. In fact, since  $G(\text{CO}_2)$  at complete formic acid ionization reaches a value of 680 at a  $p\text{H}$  of 4.9 compared to 80 at a  $p\text{H}$  of 0.5, the ratio  $(k_4/2k_6)^{1/2}$  must be 8.5 times as great for the formate ion reactions as for the neutral molecule reactions. The higher carbon dioxide yields are therefore associated with a more efficient propagation reaction (greater  $k_4$ ) or with a less efficient termination reaction (lower  $k_6$ ).

Reaction 3, the conversion of the sulfate radical ion into a hydroxyl radical, need not be assumed in any of the present reactions. However, the inclusion of reaction 3 does not affect the kinetics of the decomposition reactions since hydroxyl radicals react efficiently with formic acid. In fact a point in favor of reaction 3 is that  $G(\text{CO}_2)$  is lower in strong acid solutions than in weakly acid solutions. This result accords with the bisulfate inhibition of the photolytic decomposition of persulfuric acid observed by Tsao and Wilmarth.<sup>4</sup>

**Acknowledgments.**—The technical assistance of Miss P. D. Walsh is gratefully acknowledged.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY]

## Microwave Absorption and Molecular Structure in Liquids. XXXVII. The Relaxation Times of Spherical Polar Molecules in Carbon Tetrachloride Solution<sup>1,2</sup>

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RECEIVED AUGUST 15, 1960

Measurements of dielectric constant and loss of dilute solutions of five spherical polar molecules in carbon tetrachloride at temperatures between 20 and 60° have been carried out at various wave lengths between 1.25 and 50 cm. Measurements of dielectric constant alone were made at 577 m, and refractive indices were measured using the sodium d-line. Mutual viscosities were determined for seven polar solutes in carbon tetrachloride solution. The influence of solute size and rigidity on the relaxation times found is discussed. Dipole moments of two adamantane halides are reported.

In order to test the application of the Debye equation to a system where one would expect it to be valid, the dielectric behavior of solutions of spherical polar molecules in carbon tetrachloride was analyzed. Two approaches were considered. Since the macroscopic viscosities of the solutions are approximately equal at a given temperature, one might suppose that the internal friction coefficients as well would be independent of solute.<sup>5</sup> In this case, at constant temperature,  $\tau$  (the relaxation time) should vary as the molar volume from solute to solute. Alternatively, the internal friction factor could be replaced by the mutual viscosity  $\eta_m$  defined by Hill.<sup>6</sup> If this is done,  $\tau/\eta_m$  would be expected to vary as the molar volume.

**Purification of Materials.**—Carbon tetrachloride and the solutes were purified as shown in Table I. The substances investigated were obtained from (A) Matheson, Coleman and Bell, Inc., (B) Eastman Kodak Company, (C) Mr. Robert D. Nicholas, Princeton University. The authors express their appreciation to Mr. Nicholas for the preparation of adamantane bromide and adamantane chloride.

### Experimental Results

The apparatus and various methods of measurement have been described previously.<sup>7-9</sup> The slopes for dependence

(1) This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

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(3) National Science Foundation Fellow, 1957-1960.

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TABLE I  
PURIFICATION OF MATERIALS

	Source	—B.p., °C.—	
		Obsd.	Lit.
Carbon tetrachloride <sup>a</sup>	A	76.5	76.7 <sup>f</sup>
Fluorobenzene <sup>b</sup>	B	84	84.7 <sup>f</sup>
<i>t</i> -Amyl alcohol <sup>c</sup>	A	102	102.3 <sup>f</sup>
		—M.p., °C.—	
<i>dl</i> -Camphor <sup>d</sup>	A	177	178.6 <sup>f</sup>
Adamantane chloride <sup>e</sup>	C	165	165 <sup>g</sup>
Adamantane bromide <sup>e</sup>	C	120	119-120 <sup>h</sup>

<sup>a</sup> Fractionally distilled and stored over Drierite. <sup>b</sup> Dried over barium oxide and fractionally distilled. <sup>c</sup> Distilled and dried over anhydrous sodium sulfate. <sup>d</sup> Recrystallized from aqueous ethanol and sublimed. <sup>e</sup> Recrystallized from methanol at acetone-Dry Ice temperatures. <sup>f</sup> J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishers, 1950. <sup>g</sup> H. Stetter, M. Schwarz and A. Hirschorn, *Chem. Ber.*, **92**, 1629 (1959). <sup>h</sup> S. Landa, S. Kriebel and E. Knoblock, *Chem. Listy*, **48**, 61 (1954).

of dielectric constants and losses upon mole fraction of solute are shown in Table II. The concentration range in mole fraction is given in parentheses for each set of solutions in Table II. Cole-Cole arc plots fit the data satisfactorily in every case.<sup>10</sup> Values of  $a_\infty$ , the high frequency intercept, determined from the arc plot,  $\alpha$  the distribution parameter,  $\tau$  the relaxation time and  $V$ , the molar volume, are listed in Table III.

The percentage of monomer for solutions of *t*-amyl alcohol in carbon tetrachloride was determined in the concentration range 0.005 to 1 *M* at a temperature of 20°, using a Perkin-Elmer double beam infrared spectrophotometer with a lithium fluoride prism. The mole fraction equilibrium constant for dimer formation  $K_x = \frac{X_{\text{dimer}}}{X_{\text{monomer}}^2}$  was determined by the method of Liddel and Becker assuming a closed dimer.<sup>11</sup> Evidence for this assumption from nuclear magnetic resonance studies is given by Becker.<sup>12</sup> Smith and

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