

# Effect of pH on the $\gamma$ -Ray-Induced Chain Reaction between Formic Acid and Hydrogen Peroxide<sup>1</sup>

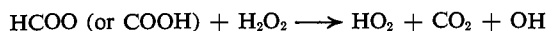
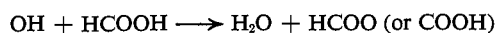
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Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois. Received November 16, 1964

The effect of pH on carbon dioxide, carbon monoxide, and hydrogen yields is reported for the chain radiolysis of dilute aqueous formic acid-hydrogen peroxide solutions. In the pH range from 1 to 13,  $G(\text{CO}_2)$  reaches a maximum yield of 300 at pH 4.4, and  $G(\text{CO})$  a maximum yield of 1.5 at pH 2.5.  $G(\text{H}_2)$  is unchanged from pH 0.4 to 3.0 and then decreases to a constant value of 0.6 at pH 5.0. Oxygen is a powerful inhibitor, but carbon monoxide, formaldehyde, and glyoxylic acid also retard the chain reaction. The mechanism is discussed in terms of ionization of the carboxyl, hydroperoxy, and hydroxyl radicals, as well as of the formic acid.

## Introduction

Formic acid solutions containing hydrogen peroxide react by a chain mechanism when exposed to ionizing radiations.<sup>3,4</sup> The net reaction is  $\text{HCOOH} + \text{H}_2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ . The suggested propagation steps in this mechanism are



This earlier work was carried out at pH 3.0 under such conditions that the effects of ionization of formic acid or of the intermediate free hydroperoxy or formate radicals were not studied. The effect of pH on  $G(\text{CO}_2)$ ,  $G(\text{CO})$ , and  $G(\text{H}_2)$  is now reported for the formic acid-hydrogen peroxide chain reaction. The present work covering the pH range from 1 to 13 reveals not only the effects of ionization of formic acid and the carboxyl radical but also of the hydroperoxy and hydroxy radicals.

## Experimental

**Irradiation Techniques.** The techniques used for evacuation and irradiation of solutions have already been reported.<sup>3-6</sup> The eight-cell evacuation chamber and 12-ml. cylindrical cells were usually used for gas-free solutions. For solutions of dissolved gases (oxygen, carbon monoxide, nitrogen, or argon), 100-ml. syringes were used, the dose being measured by the Fricke dosimeter using  $G(\text{Fe}^{3+}) = 15.6$ . Dosage rates used were between  $0.86 \times 10^{20}$  and  $3.13 \times 10^{17}$  e.v./l. min.

Carbon dioxide was measured in a Van Slyke micro gas apparatus by absorption in potassium hydroxide.

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

(2) International Institute of Nuclear Science and Engineering, Affiliate from Pakistan.

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

(4) G. E. Adams and E. J. Hart, *ibid.*, **84**, 3994 (1962).

(5) E. J. Hart, *ibid.*, **83**, 567 (1961).

(6) C. Senvar and E. J. Hart, *Proc. Intern. Conf. Peaceful Uses At. Energy*, 2nd, Geneva, 1958, **29**, 19 (1958).

The residual gases (hydrogen and carbon monoxide) were analyzed by a Chronofrac having a column of molecular sieve 13X packed in a copper tubing,  $\frac{3}{8}$  in. in diameter and 1 m. long. (Dry compressed air was used as a carrier.) Hydrogen peroxide was measured by triiodide absorption at 3500 Å.<sup>7</sup>

**Reagents.** Triply distilled water was used throughout,<sup>8</sup> and all irradiation equipment was heated to 550° before use to remove possible contamination. Matheson 98-100% formic acid was freshly distilled at 20 cm. through a 30-plate fractionating column at 59° to give a product having  $n_{\text{D}}^{20}$  of 1.3715. It was stored at 40° until used.

Reagent grade sulfuric acid, inhibitor-free 89% hydrogen peroxide, sodium and potassium hydroxide, formaldehyde, oxalic acid, glyoxylic acid, and barium hydroxide were used without further purification. Sodium hydroxide solution was made carbonate free by adding barium hydroxide; the supernatant solution free from carbonate was used. No additional buffer was added for making the solution up to the desired pH. For alkaline pH values, fresh stock solution of mild acidic pH was added to the evacuation chamber and thoroughly degassed. Next, a calculated amount of alkali was added, and the solution was evacuated again. This process minimized the amount of carbon dioxide present in the unirradiated control. Corrections were applied whenever a significant dark reaction occurred.

**Thermal Reaction.** The thermal reaction between 0.01 *M* formic acid and  $5.0 \times 10^{-4}$  *M* hydrogen peroxide was studied at pH 4.4 in the dark for several days. The measurement of hydrogen peroxide left, as well as the carbon dioxide formed, showed that the thermal reaction is negligible as compared to the reaction under  $\gamma$ -irradiation. Corrections were necessary at alkaline pH values.

## Results

**Dosage Curves.** After a brief induction period, the dosage curves were usually linear over 60 to 80% of the reaction. In all cases the yield,  $G(\text{CO}_2)$ , was measured from the slope of these  $\Delta\text{CO}_2$  vs.  $\Delta E$  curves.  $\Delta(\text{CO}_2)$  equals  $\Delta(-\text{H}_2\text{O}_2)$  under these conditions and confirms the over-all reaction discussed above.

**Effect of pH on  $G(\text{CO}_2)$ .** In all these experiments a mixture of 0.01 *M* formic acid and  $\sim 500 \times 10^{-6}$  *M* hydrogen peroxide was used. At pH 2 (Figure 1) the chain length is low since  $G(\text{CO}_2) = 12$ ; however, as the hydrogen ion concentration decreases and ionization of formic acid ( $\text{p}K_a = 3.75$ ) sets in,  $G(\text{CO}_2)$  reaches a value of 60 at pH 3—and a maximum of 300 at pH 4.4.  $G(\text{CO}_2)$  decreases to 90 at pH 6.0 and remains at this value until it declines at pH 10. As in

(7) A. O. Allen, T. W. Davis, G. V. Elmore, J. A. Ghormley, B. M. Haines, and C. J. Hochanadel, ORNL-130 Report, Oct. 11, 1949.

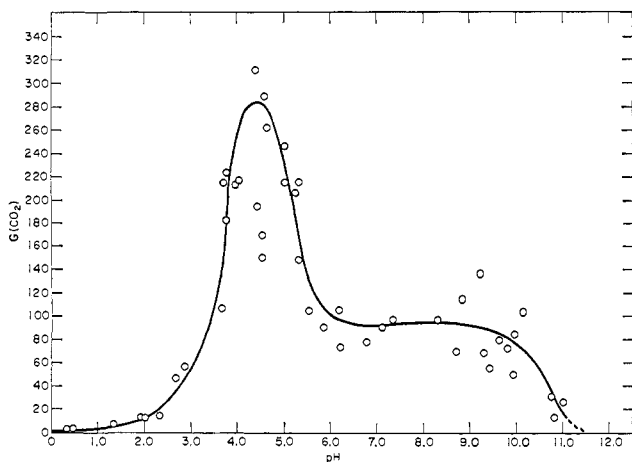


Figure 1. Effect of pH on the chain reaction between 0.01 *M* formic acid and 0.0005 *M* hydrogen peroxide.

the case of many chain reactions, it is difficult to obtain reproducible results for  $G(\text{CO}_2) > 80$  because of the high susceptibility of the reaction to traces of impurities.

As formic acid approaches its  $pK_a$  value of 3.75, there is an onslaught of chain radiolysis and an accompanying decrease in  $G(\text{CO})$ . Compare  $G(\text{CO}_2)$  in Figure 1 with  $G(\text{CO})$  in Figure 2 at pH 4.4 where the chain length reaches its maximum.

**Effect of pH on  $G(\text{CO})$  and  $G(\text{H}_2)$ .** The effect of pH on  $G(\text{CO})$  and  $G(\text{H}_2)$  in 0.01 *M* HCOOH and in 0.01 *M* HCOOH and  $5.0 \times 10^{-4}$  *M* hydrogen peroxide is shown in Figure 2. In 0.01 *M* formic acid solution, we find that carbon dioxide and hydrogen are produced in equimolar amounts up to a pH of about 3.5, and then the yield of carbon dioxide decreases until it reaches a value of  $G(\text{CO}_2) = 0.40$  at pH 6.5.  $G(\text{H}_2)$  decreases from 2.94 in acid solution to a constant value of  $G(\text{H}_2) = 1.2$  at pH 7.0.  $G(\text{CO})$  is appreciable only in the pH region below 2.0 in hydrogen peroxide-free solutions.

In solutions containing 0.01 *M* formic acid and  $5.0 \times 10^{-4}$  *M* hydrogen peroxide,  $G(\text{H}_2)$  is 2.94 at pH 3 and lower, and then, during the rise of  $G(\text{CO}_2)$ , it drops rather sharply at pH 3 to a constant yield of 0.6 in the pH region from 5 to 11.  $G(\text{CO})$  is a maximum at pH values of 2 to 3.

**Effect of Dose Rate on  $G(\text{CO}_2)$ .** As the dose rate is lowered,  $G(\text{CO}_2)$  at pH 4.4 increases in the manner expected for bimolecular termination of one of the propagation radicals. In Figure 3, the effect of dose rate in the range  $3.13 \times 10^{17}$  to  $0.86 \times 10^{20}$  e.v./l. min. is shown. Initially, a plot of  $G(\text{CO}_2)$  vs.  $(\text{dose rate})^{-1/2}$  is linear. Near  $10^{19}$  e.v./l. min.  $G(\text{CO}_2)$  begins to decline and falls to half-value at  $10^{18}$  e.v./l. min. We ascribe this drift to lower values to an impurity-catalyzed decomposition of hydrogen peroxide forming oxygen, a powerful chain inhibitor. As mentioned above, all dosage curves show a brief induction period. At sufficiently low dosage rates, the steep linear part of the curve is never reached.

**Effect of Oxygen, Carbon Monoxide, and Added Substances.** The effect of oxygen ( $3.5\text{--}11.5 \times 10^{-6}$  *M*) at pH 4.4 is shown in Figure 4. Oxygen delays the chain reaction, but, as soon as it is consumed, the expected  $G$  value is obtained. This is similar to earlier

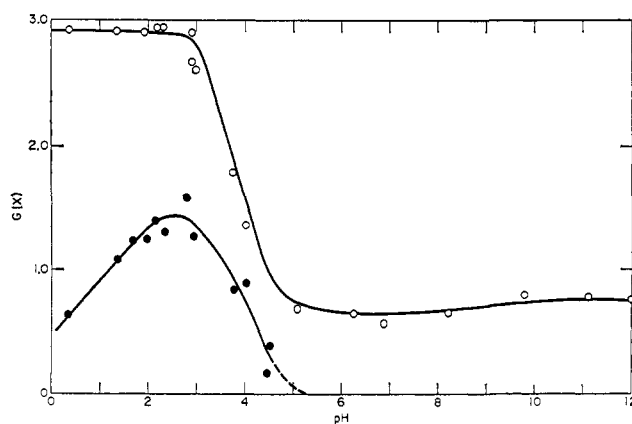


Figure 2. Effect of pH on hydrogen and carbon monoxide yields in 0.01 *M* formic acid–0.0005 *M* hydrogen peroxide solutions: O,  $G(\text{H}_2)$ ; ●,  $G(\text{CO})$ .

results reported for studies carried out at pH 3 using 0.01 *M* formic acid and 0.030 *mM* hydrogen peroxide.

The effect of other added substances appears in Table I. It seems that carbon monoxide and formaldehyde decrease the chain by almost the same extent.

Table I. Effect of Formic Acid Radiolysis Products in the Formic Acid–Hydrogen Peroxide Reaction

Substance	Concn., mM	pH	$G(\text{CO}_2)$	$R^a$
None	...	4.3	$300 \pm 20$	1.0
CO	0.116	4.3	36	0.12
CO <sub>2</sub>	3.8	4.3	175	0.57
HCHO	0.5	4.24	34	0.11
CHOCOOH	0.5	4.23	14	0.047
CHOCOOH	0.5	7.5	15	0.15
COOH–COOH	0.5	4.02	79	0.27
COOH–COOH	0.5	4.32	125	0.40
COOH–COOH	0.5	7.07	110	1.1
COOH–COOH	0.5	7.28	77	0.71
COOH–COOH	0.5	9.7	38	0.42
COOH–COOH	0.5	10.9	5	0.12

<sup>a</sup>  $R$  is ratio of  $G(\text{CO}_2)$  of column 4 to  $G(\text{CO}_2)$  of Figure 1 at pH of column 3.

The same intermediate species ( $\text{H}\dot{\text{C}}\text{O}$ ) is probably involved. On the other hand, inhibition by oxalic acid is much more pronounced in alkaline medium than in neutral medium. The inhibition owing to glyoxylic acid (and consequently of species derived from the  $\dot{\text{C}}\text{HO}$ ) is very remarkable. Neglecting the thermal reaction between glyoxylic acid and hydrogen peroxide, glyoxylic acid seems nearer to a true chain inhibitor in this reaction.

## Discussion of Results

**Carbon Dioxide Chain Reaction.** The principal characteristics of this reaction are (1) a rapid rise in  $G(\text{CO}_2)$  in the pH range from 2 to 4.4, then a rapid drop in  $G(\text{CO}_2)$  in the range to pH 5.5, followed by an appreciable chain reaction and constant yield to pH 11, (2) a rise in  $G(\text{CO})$  to a maximum of 1.5 at pH 2.5, followed by a decline to zero at pH 5.0, and (3)  $G(\text{H}_2)$  remaining essentially constant to pH 3.0 and then decreasing to a yield of  $\sim 0.6$ . These results may be

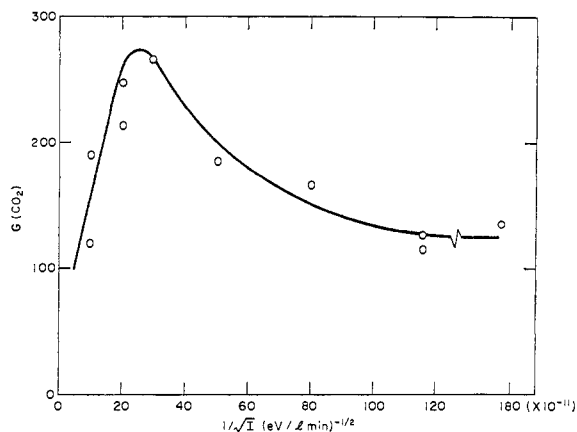
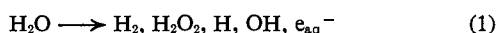
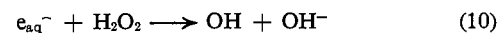
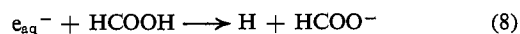
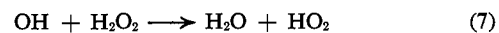
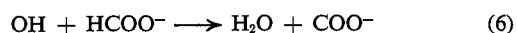
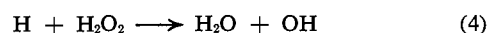
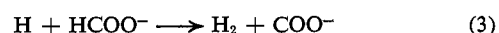
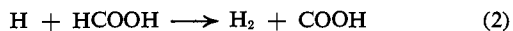


Figure 3. Effect of  $\gamma$ -ray dose rate on the chain reaction between formic acid and hydrogen peroxide (0.01 M HCOOH, 0.0005 M H<sub>2</sub>O<sub>2</sub>, pH 4.4).

accounted for by the mechanism



Possible reactions of these species with formic acid, formate ion, hydrogen ion, and hydrogen peroxide are



From available absolute and relative rate constants it is possible to determine the relative importance of these reactions as pH is varied since the formic acid and hydrogen peroxide concentrations are known.<sup>8</sup> In most experiments (HCOOH) = 0.01 M and (H<sub>2</sub>O<sub>2</sub>) = 5 × 10<sup>-4</sup> M.

**Hydrogen Yields.** At pH 3, reaction 9 generating H atoms dominates reaction 10 since the ratio  $k_9(\text{H}^+)/k_{10}(\text{H}_2\text{O}_2) = 3.8$  at pH 3. ( $k_9 = 2.36 \times 10^{10}$  and  $k_{10} = 1.23 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ .)<sup>9</sup> Hydrated electron rate constants for reaction with formic acid and formate ion are  $1.43 \times 10^8$  and  $<10^6 \text{ M}^{-1} \text{ sec}^{-1}$ , respectively. Consequently, reaction 8 in the above mechanism may be neglected compared to (9) and (10) at all pH values.  $G(\text{H}_2)$  is constant below pH 3, a fact consistent with relative rate constant data since  $k_3/k_4 = 5.8$  and the ratio  $[\text{HCOOH}]/[\text{H}_2\text{O}_2] \geq 20$ . Above pH 3 reaction 9 becomes less important and the H atom yield is lowered because of reaction 10. Above pH 5  $G(\text{H}_2)$  decreases to 0.7–0.8 corresponding to the sum of the molecular hydrogen and H atom yields.

**Carbon Dioxide Yields.** Hart<sup>3</sup> explained the chain reaction between formic acid and hydrogen peroxide by primary reactions 2 and 5 generating a COOH

(8) A. O. Allen, *Radiation Res., Suppl.*, 4, 54 (1964).

(9) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *J. Am. Chem. Soc.*, 85, 1375 (1963); *Discussions Faraday Soc.*, 36, 193 (1963).

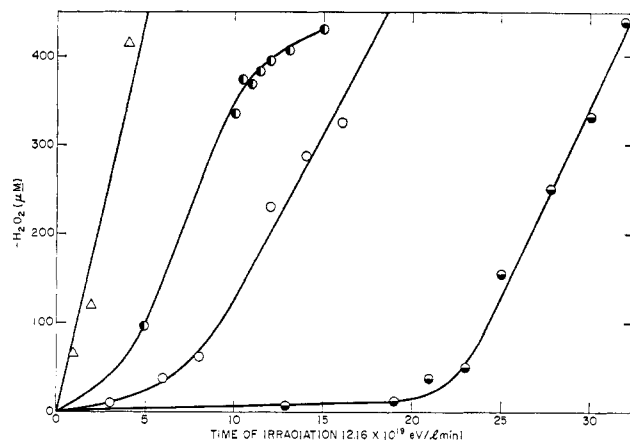
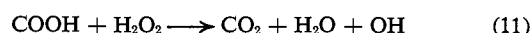


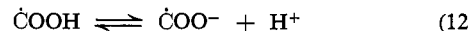
Figure 4. Inhibition of the formic acid-hydrogen peroxide chain reaction by oxygen (0.01 M HCOOH, 0.0005 M H<sub>2</sub>O<sub>2</sub>, pH 4.4):  $\Delta$ , N<sub>2</sub>; O, O<sub>2</sub>, 6.8  $\mu\text{M}$ ;  $\bullet$ , O<sub>2</sub>, 3.5  $\mu\text{M}$ ;  $\circ$ , O<sub>2</sub>, 11.5  $\mu\text{M}$ .

or HCOO radical followed by propagation reaction 11.

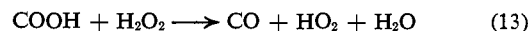


Because increased hydrogen peroxide lowered  $G(\text{CO}_2)$ , reaction 7 was suggested as leading to chain termination since the hydroperoxy radical does not propagate the chain. The present work confirms these earlier findings and supports the results of Rabani and Stein,<sup>10</sup> who reported that  $k_{\text{OH}+\text{HCOO}^-}/k_{\text{OH}+\text{HCOOH}} = 4.0$  in the pH range, 2.5–4.0. The greater reactivity of the formate ion with the hydroxyl radical explains part of the rise in  $G(\text{CO}_2)$  with dissociation of formic acid ( $\text{p}K = 3.75$ ).

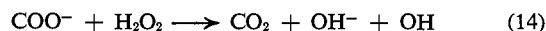
However, ionization of the formate radical may be a much more important factor in the effect of pH on  $G(\text{CO}_2)$ . Earlier, it was suggested that carbon monoxide formation is associated with H atom attack on formic acid.<sup>4</sup> Notice in Figure 2 how  $G(\text{CO})$  decreases as  $G(\text{H}_2)$  decreases in the pH range from 3 to 4.5. But, since  $G(\text{CO})$  is only 0.01 at pH 2 to 3 in hydrogen peroxide-free formic acid solutions, hydrogen peroxide contributes significantly to carbon monoxide formation in the pH region from 0.5 to 4.3. We suggest that dissociation of the carboxyl radical is important, not only in accounting for carbon monoxide formation but also in explaining the carbon dioxide chain reaction. We assume the dissociation equilibrium



As suggested earlier, the acid form of the carboxyl radical produces carbon monoxide.<sup>4</sup>



If reaction 13 is the only one forming carbon monoxide,  $G(\text{CO})$  is expected to rise with an increase in  $G(\text{CO}_2)$ . Because of propagation reactions 5 and 12, a certain fraction of COOH radicals will be channeled into reaction 13, thereby producing carbon monoxide. On this basis  $G(\text{CO})$  should be proportional to  $G(\text{CO}_2)$ . However, since  $G(\text{CO})$  reaches a maximum when  $G(\text{CO}_2)$  is only  $\sim 50$  at pH  $\sim 2.7$  and carbon monoxide is not formed in neutral solution, we conclude that the ionic form,  $\dot{\text{C}}\text{OO}^-$ , does not give carbon monoxide. We write its reaction as



(10) J. Rabani and G. Stein, *Trans. Faraday Soc.*, 58, 2150 (1962).

effective at pH values as low as 2.7. As reaction 14 gains in importance, terminating reaction 13 diminishes in importance. Consequently,  $G(\text{CO}_2)$  rises with increasing pH.

Therefore, on the basis of our kinetic evidence, the  $pK$  of ionization reaction 12 may be  $2.5 \pm 0.5$ . This conclusion is supported by recent pulsed electron beam studies of the aqueous formic acid and carbon dioxide systems.<sup>11</sup> In each of these systems one transient absorbing species with  $\lambda_{\text{max}} \sim 2600 \text{ \AA}$ . forms in solutions in the pH range from 3.5 to 6.25. Below pH 2.5, not only is the intensity of this band greatly diminished, but the second-order decay is also altered, facts that support our conclusion about the ionization of the carboxyl ion.

The decrease in  $G(\text{CO}_2)$  above pH 4.4, after nearly complete ionization of formic acid and the carboxyl radical, indicates further modification in the mechanism. Since the  $pK^{12}$  of the  $\text{HO}_2$  radical is 4.5 and corresponds almost exactly with our maximum  $G(\text{CO}_2)$ , we suggest participation of  $\text{O}_2^-$  as an important terminating species. A possible reaction is  $\text{CO}_2^- + \text{O}_2^- \rightarrow \text{CO}_2 + \text{O}_2^{2-}$ ,

(11) E. J. Hart and S. Gordon, unpublished results.

(12) G. Czapski and L. M. Dorfman, *J. Phys. Chem.*, **68**, 1169 (1964).

which may be relatively much faster than  $\text{CO}_2^- + \text{HO}_2 \rightarrow \text{CO}_2 + \text{HO}_2^-$ , thereby shortening the kinetic chain length of reaction sequence 6 and 14. Until further information is available on the rate constants of these termination processes, further speculation seems unwarranted.

The decrease in  $G(\text{CO}_2)$  above pH 10 is probably associated with the ionization of the hydroxyl radical previously postulated to explain the chain conversion of  $\text{O}^{16}\text{O}^{18}$  to  $\text{O}^{16}\text{O}^{16}$  in alkaline solutions.<sup>13</sup> Recent work has shown that the  $pK$  for OH dissociation is 11.9.<sup>14</sup> Under these conditions, if the ratio  $k_{\text{O}^- + \text{H}_2\text{O}_2} / k_{\text{O}^- + \text{HCOO}^-}$  is greater than the ratio  $k_{\text{OH} + \text{H}_2\text{O}_2} / k_{\text{OH} + \text{HCOO}^-}$ ,  $G(\text{CO}_2)$  will decrease with increasing pH. Ionization of hydrogen peroxide may be involved at pH values above 11, too.

*Acknowledgment.* A. H. gratefully acknowledges a fellowship and maintenance from the Agency for International Development, Washington, D. C., and from the Pakistan Atomic Energy Commission, Karachi.

(13) E. J. Hart, S. Gordon, and D. A. Hutchison, *J. Am. Chem. Soc.*, **75**, 6165 (1953).

(14) J. Rabani and M. S. Matheson, *ibid.*, **86**, 3175 (1964).

## Kinetics of Addition of Vinyl lithium to 1,1-Diphenylethylene in Tetrahydrofuran Solution

Richard Waack and Philip E. Stevenson

*Contribution from the Dow Chemical Company, Eastern Research Laboratory, Framingham, Massachusetts. Received October 29, 1964*

From a kinetic analysis of the reaction,  $\text{CH}_2=\text{CHLi} + \text{CH}_2=\text{C}(\text{C}_6\text{H}_5)_2$  (THF)  $\rightarrow \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)_2\text{Li}$ , it is concluded that vinyl lithium is aggregated in tetrahydrofuran solution. Over a vinyl lithium concentration of  $5 \times 10^{-3}$  to  $2 \times 10^{-1} \text{ M}$  the kinetic law  $dA/dt = k'[\text{DPE}][\{\text{ViLi}\}_i/3]^{1/3}$  is obeyed, where  $k' = 5.7 \text{ l.}^{0.34} \text{ mole}^{-0.34} \text{ hr.}^{-1}$  and  $\{\text{ViLi}\}_i$  is the total initial concentration. Rates were measured spectroscopically.

The relative reactivities of organolithium compounds as polymerization initiators<sup>1</sup> or as metalating reagents<sup>2</sup> in tetrahydrofuran solution are found to vary markedly with their structure. Changes in reactivity with structure are probably, in part, a consequence of inherent reactivity differences. Effective reactivities might also vary owing to different extents of aggregation of the organolithium reagents,<sup>2,3</sup> presuming that the associated form is unreactive relative to the less associated reagent.

Vinyl lithium is one of the least reactive of the simple organolithium reagents.<sup>1,2</sup> For example, it is less reactive than *n*-butyllithium, benzyl lithium, allyl lithium,

and phenyllithium. The rate of addition of vinyl lithium to 1,1-diphenylethylene (DPE) in tetrahydrofuran (THF) solution is slow enough to be followed by spectroscopic techniques. In contrast, *n*-butyllithium adds to DPE essentially instantaneously under these conditions.

The majority of kinetic measurements reported for organolithium compounds have concerned *n*-butyllithium in hydrocarbon solution.<sup>4</sup> These kinetic experiments, which are substantiated by colligative measurements,<sup>5</sup> establish that *n*-butyllithium is predominantly hexameric in hydrocarbon solution throughout the concentration range  $10^{-4}$  to  $3 \text{ M}$ . Ethyllithium is also indicated to be hexameric in hydrocarbon solution,<sup>6</sup> and *t*-butyllithium is reported to be tetrameric.<sup>7</sup>

There are no reported physical measurements of the degree of aggregation of organolithium reagents in

(1) R. Waack and M. A. Doran, *Polymer*, **2**, 365 (1961).

(2) R. Waack and P. West, *J. Am. Chem. Soc.*, **86**, 4494 (1964).

(3) R. Waack and M. A. Doran, *Chem. Ind. (London)*, 496 (1964).

(4) (a) F. J. Welch, *J. Am. Chem. Soc.*, **81**, 1345 (1959); (b) K. F. O'Driscoll and A. V. Tobolsky, *J. Polymer Sci.*, **35**, 259 (1959); (c) D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **38**, 1891 (1964); (d) A. G. Evans and D. B. George, *J. Chem. Soc.*, 4653 (1961); (e) R. C. P. Cubbon and D. Margerison, *Proc. Roy. Soc. (London)*, **A268**, 260 (1962); (f) A. G. Evans and N. H. Rees, *J. Chem. Soc.*, 6039 (1963).

(5) D. Margerison and J. P. Newport, *Trans. Faraday Soc.*, **59**, 2058 (1963).

(6) J. Berkowitz, D. A. Bafus, and T. L. Brown, *J. Phys. Chem.*, **65**, 1380 (1961).

(7) M. Weiner, G. Vogel, and R. West, *Inorg. Chem.*, **1**, 654 (1962).