

## Kinetics of the Chlorosulfonic Acid Promoted $\alpha$ Iodination of Propionic Acid<sup>1</sup>

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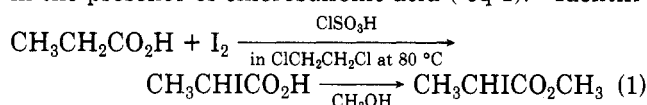
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Propionic acid was found to be  $\alpha$  iodinated by molecular iodine in the presence of chlorosulfonic acid in 1,2-dichloroethane as a solvent at 80 °C. In view of the easy oxidation of hydrogen iodide to molecular iodine by chlorosulfonic acid as well as the detection of SO<sub>2</sub> during the iodination, the stoichiometry of the reaction may be  $\text{CH}_3\text{CH}_2\text{CO}_2\text{H} + 0.5\text{I}_2 + \text{ClSO}_3\text{H} \rightarrow \text{CH}_3\text{CHICO}_2\text{H} + \text{HCl} + 0.5\text{H}_2\text{SO}_4 + 0.5\text{SO}_2$ . Kinetic study shows that the initial rate is expressed as  $v = k_{\text{obsd}}[\text{CH}_3\text{CH}_2\text{CO}_2\text{H}][\text{I}_2]$ , where  $k_{\text{obsd}}$  is proportional to the initial concentration of chlorosulfonic acid at an early stage. A mechanism involving addition of molecular iodine to a ketene intermediate and re-formation of molecular iodine by chlorosulfonic acid is discussed. The yield (ca. 80%) of  $\alpha$  iodination is comparable to that of the literature (ca. 80%) and the procedure is simpler for synthesis.

We have reported previously that aliphatic acids can be  $\alpha$  chlorinated by a Cl<sub>2</sub>-O<sub>2</sub> mixture in the presence of a strong acid such as chlorosulfonic acid or fuming sulfuric acid;<sup>2</sup> at that time we suggested that the reaction intermediate may be a ketene on the basis of NMR and laser Raman spectral data, a deuterium tracer study, and trapping by aniline forming acetanilide.<sup>3</sup> Thereafter, the kinetic study of analogous  $\alpha$ -bromination suggested the rate-determining addition of molecular bromine to the ketene intermediate.<sup>4</sup> The present paper deals with the iodination of propionic acid with molecular iodine in the presence of chlorosulfonic acid. For the iodination of aliphatic acids, a procedure which employs thionyl chloride as a solvent affording a yield of ca. 80% has been reported.<sup>5</sup> The stoichiometry and mechanism of this iodination will be discussed on the basis of the product analysis and kinetic study.

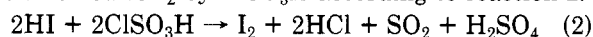
### Results and Discussion

**$\alpha$  Iodination.** It was found that propionic acid could be  $\alpha$  iodinated by molecular iodine in 1,2-dichloroethane in the presence of chlorosulfonic acid (eq 1). Identifi-



cation of product was done after its conversion to methyl  $\alpha$ -iodopropionate by comparison of NMR and GLC peaks with those of the authentic sample.

**Stoichiometry.** Assuming that 1 mol of iodine yields 1 mol of propionic acid, the yield reaches ca. 160% as shown in Figure 1. This phenomenon may be explained by the oxidation of hydrogen iodide produced during the reaction to molecular iodine which is again used for the reaction. Indeed, on addition of chlorosulfonic acid to KI, molecular iodine was liberated quantitatively. Therefore, HI is oxidized to I<sub>2</sub> by ClSO<sub>3</sub>H according to reaction 2.<sup>6</sup>



The formation of SO<sub>2</sub>, as apparent from eq 2, was confirmed by decolorization of fuchsine paper for the

**Table I. Effect of Concentration of Reactants on the Second-Order Rate Constant (eq 3) for  $\alpha$  Iodination of Propionic Acid in 1,2-Dichloroethane at 80 °C<sup>a</sup>**

[CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> H] <sub>0</sub> , M	[I <sub>2</sub> ] <sub>0</sub> , M	10 <sup>3</sup> k <sub>obsd</sub> , M <sup>-1</sup> s <sup>-1</sup>
2.00	0.14	1.19
1.50	0.14	1.19
1.30	0.14	1.18
1.00	0.14	1.19
0.50	0.14	1.27
1.30	0.14	1.18
1.30	0.12	1.11
1.30	0.07	1.27

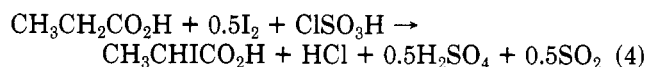
<sup>a</sup> The initial concentration of ClSO<sub>3</sub>H was 0.5 M.

reaction of KI with ClSO<sub>3</sub>H and also for the iodination of propionic acid according to this procedure.

**Kinetics of  $\alpha$  Iodination.** The initial rate of  $\alpha$  iodination of ca. 1.3 M propionic acid in 1,2-dichloroethane at 80 °C with 0.5 M chlorosulfonic acid as a promoter fits eq 3.

$$v = k_{\text{obsd}}[\text{CH}_3\text{CH}_2\text{CO}_2\text{H}][\text{I}_2] \quad (3)$$

Here, the stoichiometry of eq 4 was assumed on the basis of eq 2.



The first-order dependence of rate on iodine concentration and on propionic acid concentration (second order overall) was confirmed at various concentrations of reactants (Table I).

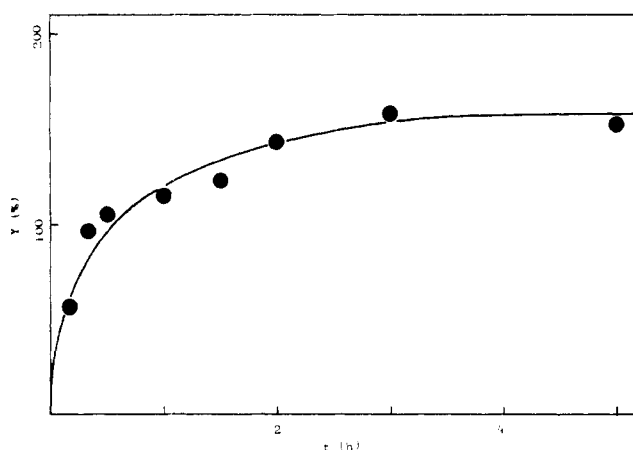
The rate constant tended to decrease with the progress of the reaction, so that the initial rate was measured by a graphical method. The decrease of the  $k_{\text{obsd}}$  is probably due to the consumption of chlorosulfonic acid by eq 4 and as described below. Since the rate of iodination is much less than that of bromination, the decreasing tendency of  $k_{\text{obsd}}$  is much more remarkable in iodination. Equation 3, which depends on [I<sub>2</sub>], suggests that iodine adds to the ketene intermediate at the rate-determining step.

**Effect of Concentration of Chlorosulfonic Acid.** The initial rate constant  $k_{\text{obsd}}$  for iodination of propionic acid was found to be proportional to the initial concentration of chlorosulfonic acid (Figure 2). Hence, the rate in eq 3 can be rewritten as in eq 5, where [ ]<sub>0</sub> means initial concentration.

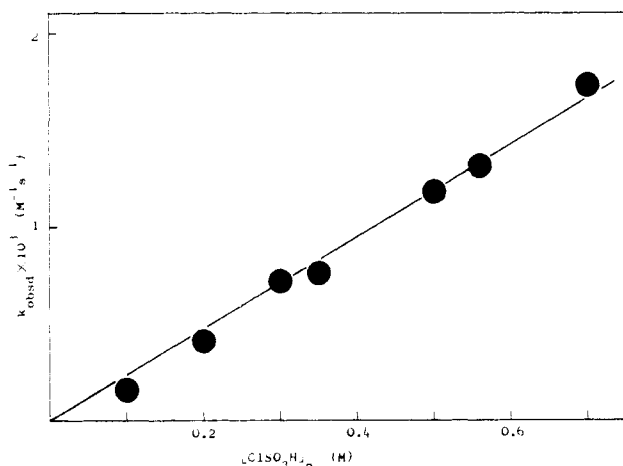
$$v = k[\text{ClSO}_3\text{H}]_0[\text{CH}_3\text{CH}_2\text{CO}_2\text{H}][\text{I}_2] \quad (5)$$

**Mechanism.** There is evidence for the formation of ketene from aliphatic acids in ClSO<sub>3</sub>H or fuming H<sub>2</sub>SO<sub>4</sub>.<sup>3</sup>

(1) Contribution No. 260.  
 (2) (a) Y. Ogata, T. Harada, K. Matsuyama, and T. Ikejiri, *J. Org. Chem.*, **40**, 2960 (1975); (b) Y. Ogata and K. Matsuyama, *Tetrahedron*, **26**, 5929 (1970); (c) Y. Ogata and T. Sugimoto, *Chem. Ind. (London)*, 538 (1977); (d) Y. Ogata and T. Ikejiri, *Nippon Kagaku Kaishi*, 1517 (1975).  
 (3) Y. Ogata, T. Harada, and T. Sugimoto, *Can. J. Chem.*, **55**, 1268 (1977).  
 (4) Y. Ogata and T. Sugimoto, *J. Org. Chem.*, **43**, 3684 (1978).  
 (5) D. N. Harpp, L. Q. Bao, C. J. Black, J. G. Gleason, and R. A. Smith, *J. Org. Chem.*, **40**, 3420 (1975).  
 (6) *Gmelins Handbuch*, **8**, 291 (1933).

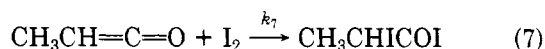
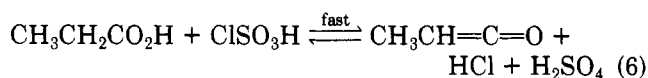


**Figure 1.** Yields ( $Y$ ) of methyl  $\alpha$ -iodopropionate at various times ( $t$ ) at 80 °C. Initial concentrations:  $[\text{CH}_3\text{CH}_2\text{CO}_2\text{H}] = 1.7 \text{ M}$ ,  $[\text{I}_2] = 0.13 \text{ M}$ ,  $[\text{ClSO}_3\text{H}] = 0.63 \text{ M}$ .

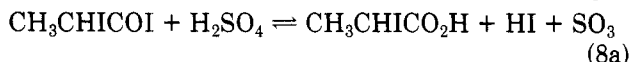


**Figure 2.** Effect of initial concentration of chlorosulfonic acid on the second-order rate constant ( $k_{\text{obsd}}$ ) for iodination of propionic acid in 1,2-dichloroethane at 80 °C.

Analogously,  $\alpha$  iodination may be explained by eq 6 and 7.



As a salient feature for this iodination, subsequent oxidation of HI occurs (eq 8a–c). As stated above, eq 8c



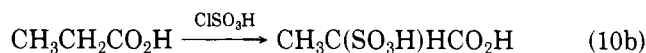
is confirmed by thiosulfate titration of liberated iodine and fuchsin test of  $\text{SO}_2$ .

Step 6 for the formation of ketene competes with other reactions of propionic acid such as the formation of  $\text{CH}_3\text{CH}_2\text{C}(\text{OH})_2^+$ ,  $\text{CH}_3\text{CH}_2\text{CO}^+$ ,  $\text{CH}_3\text{CH}(\text{SO}_3\text{H})\text{CO}_2\text{H}$ ,<sup>8</sup>  $\text{CH}_3\text{CH}_2\text{COOSO}_3\text{H}$ ,<sup>8</sup> and ketene dimer. However, these species and also other side reactions in  $\text{ClSO}_3\text{H}$  would be not so serious in view of the high yield of  $\alpha$  iodination and

the observed single GLC peak of the product. At an early stage of reaction, the concentration of ketene may be proportional to the initial concentration of  $\text{ClSO}_3\text{H}$ . If the rate is determined by step 7, then the above mechanism leads to the observed rate equation (9).

$$v = k_7[\text{CH}_3\text{CH}=\text{C}=\text{O}][\text{I}_2] = k[\text{ClSO}_3\text{H}]_0[\text{CH}_3\text{CH}_2\text{CO}_2\text{H}][\text{I}_2] \quad (9)$$

The rate constant decreases with the progress of the reaction, which suggests the disappearance of promoter chlorosulfonic acid by the reaction with water<sup>7</sup> (which is produced via ketene formation and/or which comes from atmospheric moisture) (10a), by  $\alpha$  sulfonation of aliphatic acid<sup>8</sup> (10b), and by oxidation of HI<sup>6</sup> (8c).



The iodination mechanism via enol,  $\text{CH}_3\text{CH}=\text{C}(\text{OH})_2$ , which has been suggested by most workers,<sup>9</sup> is less probable since this hydroxylic species should be dehydrated in these strong acid media.

The initial rate constant for  $\alpha$  iodination of propionic acid is  $2.4 \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$  at 80 °C and that for  $\alpha$  bromination is  $2.6 \times 10^{-1} \text{ M}^{-2} \text{ s}^{-1}$  at 60 °C.<sup>4</sup> This shows that the  $\alpha$  iodination is much slower than the  $\alpha$  bromination. This may be due to (1) the larger steric hindrance for  $\alpha$  iodination than for  $\alpha$  bromination because of the bulkier iodine atom and (2) lower electrophilicity of molecular iodine than that of molecular bromine on addition to the ketene intermediate. This lower rate of iodination causes the observed decrease of rate constant with the progress of reaction because of the faster consumption of chlorosulfonic acid.

## Experimental Section

**Materials.** Commercial first grade propionic acid [bp 73–75 °C (53 mm)] and chlorosulfonic acid [bp 86–88 °C (33 mm)] were distilled before use. Authentic methyl  $\alpha$ -iodopropionate [bp 72–73 °C (27 mm)] was prepared by the iodination in thionyl chloride.<sup>5</sup>

**Products.** A solution of propionic acid (20 mL), iodine (10 g), and chlorosulfonic acid (10 mL) in 1,2-dichloroethane (100 mL) was refluxed for 4 h at 80 °C. After completion of the reaction, the product was esterified by refluxing with methanol (50 mL) for 3 h. The ester solution was successively washed with water and aqueous  $\text{Na}_2\text{S}_2\text{O}_3$ , dried ( $\text{Na}_2\text{SO}_4$ ), and distilled in vacuo after removal of methanol and 1,2-dichloroethane. The isolated methyl  $\alpha$ -iodopropionate was identified by GLC and NMR (on a 60-MHz Hitachi R-24B NMR spectrometer) comparison with the authentic sample.

**Kinetics.** A solution of 1,2-dichloroethane (48.35 mL) containing propionic acid (65 mmol) and iodine (6.5 mmol) was thermostated at 80 °C. Chlorosulfonic acid (25 mmol, 1.65 mL) was then introduced into the solution to start the reaction. The concentration of iodine was estimated by iodometry; i.e., each 2 mL of the solution was pipetted out at appropriate intervals of time and poured into water, and then excess aqueous KI was added. Liberated iodine was titrated with 0.02 N  $\text{Na}_2\text{S}_2\text{O}_3$ . The second-order rate constants were calculated by means of the second-order integrated equation (11). Here,  $a$  and  $b$  are initial

$$\ln \frac{a-x}{b-x/2} = \frac{k_2}{2}(a-2b)t - \ln \frac{b}{a} \quad (11)$$

concentrations of propionic acid and iodine, respectively, and  $x/2$  is the molar concentration of consumed iodine at time  $t$ .

(7) T. M. Lowry, "Inorganic Chemistry", 2nd ed., Macmillan, London, 1931, p 387.

(8) (a) F. Gunther and J. Hetzer, U. S. Patent 1926 442 [Chem. Abstr., 27, 6001 (1933)]; (b) J. K. Weil, L. P. Witnauer, and A. J. Stirton, J. Am. Chem. Soc., 75, 2526 (1953); (c) E. E. Gilbert, Chem. Rev., 62, 549 (1962).

(9) (a) N. O. Sontag, Chem. Rev., 52, 358 (1953); (b) H. B. Watson, ibid., 7, 173 (1930); (c) H. Kwart and F. V. Scalzi, J. Am. Chem. Soc., 86, 5496 (1964); (d) D. N. Harpp, L. Q. Bao, C. J. Black, J. G. Gleason, and R. A. Smith, J. Org. Chem., 40, 3420 (1975); (e) R. L. Rodin and H. Gershon, ibid., 38, 3919 (1973).

The rate was also measured by estimation of  $\alpha$ -iodopropionic acid. The pipetted out mixture was poured into water, and unreacted iodine was removed by washing with aqueous  $\text{Na}_2\text{S}_2\text{O}_3$ . The residual mixture was esterified by an ethereal solution of diazomethane. The resulting methyl  $\alpha$ -iodopropionate was identified and estimated by means of GLC by using a Yanagimoto GCG-550 gas chromatograph equipped with a copper column packed with PEG 20 M (10%) on Chromosorb (WAW (60-80

mesh) and employing methyl caprate as an internal standard.

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**Registry No.** Propionic acid, 79-09-4; iodine, 7553-56-2; chloro-sulfonic acid, 7790-94-5; methyl  $\alpha$ -iodopropionate, 56905-18-1.

## Photoinduced Decomposition of Peracetic Acid in Ethylbenzene

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The photolysis of peracetic acid in ethylbenzene has been conducted by using three sorts of light sources at room temperature. Photolyses at both 2537-Å light and over 2900-Å light give substantially the same products, namely, carbon dioxide, oxygen, water, methane, ethane, methanol, propylbenzene, ethyltoluenes, phenethyl alcohols, ethylphenols, and 2,3-diphenylbutane. The distribution of products depends on light wavelength; products from methyl radical (propylbenzenes) were formed preferentially in 2537-Å photolysis, while those from hydroxyl radical (phenethyl alcohols) were preferred in >2900-Å photolysis. This difference is discussed in relation to the mechanism of peracetic acid decomposition.

The photolysis of peracetic acid in aromatic hydrocarbons was initiated by two pathways: one path is the singlet-singlet energy transfer from excited aromatic solvent (ArH) to peracetic acid followed by its decomposition to methyl and hydroxyl radicals and carbon dioxide (2537-Å photolysis) and the other path is the direct decomposition of peracid (>2900-Å photolysis). In 2537-Å photolysis, methylated aromatic compounds were preferred to hydroxylated products, while in >2900-Å photolysis, the formation of hydroxylated compounds was favored. These facts suggest a difference of radical concentration with wavelength.<sup>1,2</sup>

In this experiment, we controlled the decomposition rate of peracid to compare the reactivity of radicals at the same or different radical concentration. The data which follow summarize our data on the photolysis of peracetic acid in ethylbenzene using 2537-Å (30 W) and >2900-Å (300 W and 1 kW) light sources. Products and effects of conditions on the product distribution suggest the mechanism of photolysis.

### Results and Discussion

The products resulting from the photolysis of peracetic acid (1) in ethylbenzene are listed in Tables I and II; Table I shows the results with a 30-W low-pressure Hg lamp (2537-Å light) and Table II shows the results with 300-W (>2900-Å light) and 1-kW high-pressure Hg lamps (>2900-Å light). These products were identified by GLC and GC/MS comparison with authentic samples.

The yields of propylbenzenes indicate the summation of those of two isomers, propyl- and isopropylbenzene, the latter predominates markedly. Ethyltoluenes, which were formed by an attack of methyl radical on the ring, include three isomers in the order ortho > meta > para in both 2537-Å and >2900-Å photolyses.

Hydroxylation of the side chain gives  $\alpha$ - and  $\beta$ -phenethyl alcohols, where the yields are  $\alpha \gg \beta$ . Hydroxylation of the ring gives three isomers of ethylphenols with the order of yields ortho > para > meta. 2,3-Diphenylbutanes, coupling products of  $\alpha$ -phenethyl radicals, were composed of *dl* and meso isomers with comparable yields.

The light wavelength affects largely the distribution of products; methylated compounds (propylbenzenes and ethyltoluenes) are more favored with 2537-Å light (Table I) than with >2900-Å light (Table II), while the yields of phenethyl alcohols were much higher with >2900-Å than with 2537-Å light. On the other hand, the light intensity gave only a small effect on the distribution of products as apparent from Table IIa (300 W) and Table IIb (1 kW).

The product distribution was little affected by irradiation time except for the yields of oxygen, water, and methanol in both 2537-Å and >2900-Å photolyses. These results show that a further reaction, such as oxidation of  $\alpha$ -phenethyl alcohol to acetophenone, does not occur under these conditions.

To study the dependency of radical concentration on the yields, we changed the initial concentration of peracetic acid (1) from 0.4 mmol/25 mL to 13.7 mmol/25 mL. Tables III and IV show the results in 2537-Å (30 W), >2900-Å (300 W), and >2900-Å (1 kW) photolyses.

In 2537-Å photolysis, the yields of ethane, methanol, and propylbenzenes decrease while the yields of phenethyl alcohols and 2,3-diphenylbutanes increase with decreasing peracid concentration; however, the yields of ethyltoluenes and ethylphenols are almost unchanged. The yields of methylated compounds (propylbenzenes and ethyltoluenes) are higher than those of hydroxylated compounds (phenethyl alcohols and ethylphenols).

In >2900-Å (300 W) photolysis, the yields of propylbenzenes (3-4%) are much lower than those (22-28%) in 2537-Å photolysis. Also radical addition to the ring (ethyltoluenes and ethylphenols) with >2900-Å light is less favored than that with 2537-Å light, whereas the yields of

(1) Y. Ogata and K. Tomizawa, *J. Org. Chem.*, 43, 261 (1978).

(2) Y. Ogata and K. Tomizawa, *J. Org. Chem.*, 43, 1920 (1978).