The Solvent Effect on the Reaction Selectivity in the Chlorination of Propionic Acid

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The chlorinations of propionic acid with chlorine were carried out at 70°C in various solvent mixtures with photo-irradiation or with initiation by benzoyl peroxide. Benzene - CCl_4, naphthalene - CCl_4, and anthracene - CCl_4 mixtures, and sulfur dioxide - CCl_4 were used as the solvents. In the benzene - CCl_4 mixtures, the relative reactivity, β/α, of the α and the β positions of propionic acid changed from 1.68 (CCl_4) to 1.11 (benzene), the ratio being inversely proportional to the electron-donor properties of the solvents. In the naphthalene - CCl_4 mixtures, the plot of the relative reactivity, β/α, *versus* the naphthalene content showed a minimun at *ca.* 0.1 mol/*l* of naphthalene; however, the total yield of the chlorinated acids decreased as the content of the naphthalene increased. No chlorinated acids were obtained in the anthracene - CCl_4 system. In the presence of sulfur dioxide, the α-position was more readily substituted than the β-position, the β/α ratio decreasing as the molar ratios of Cl_2/SO_2 were decreased, from 1.3 ($Cl_2/SO_2=0.286/0.036$) to 0.49 (0.286/0.858), by the initiation of benzoyl peroxide. However, dilution with CCl_4 or photo-irradiated chlorination cause no change in the selectivity in spite of the presence of sulfur dioxide. A mechanism to account for such a selectivity has been suggested.

It is well known[1] that the chlorine atom attacks hydrogen atoms more readily in this order: tertiary> secondary>primary hydrogen. However, when a compound bearing an electron-withdrawing substituent, such as propionic acid, is involved, the primary position (β-hydrogen) is more readily substituted than the secondary one (α-hydrogen) because of the lower electron density at the α-position, while the chlorine atom is an electrophilic reagent.

It has been generally assumed that a solvent has little effect upon the course and rate of the free radical reaction. Yet, it has also been accepted that chlorination by a chlorine atom has a remarkable selectivity varying with the solvent used. Chlorine forms a π-complex with the aromatic nucleus by a charge transfer-type interaction.[2] This complexed radical is less reactive and more selective than a free chlorine atom. Thus, the ratio of the relative rates, k_{tert}/k_{prim}, of 2,3-dimethylbutane rises more in benzene or in other donor solvent than in a hydrocarbon.[3]

The present paper is concerned with the study of the reaction and the selectivity of attacking radicals in the chlorination of propionic acid in various solvent mixtures.

Results and Discussion

The chlorination of propionic acid with chlorine was carried out at 70°C in various solvents with photoirradiation or with initiation by benzoyl peroxide (BPO). The solvents used were benzene - carbon tetrachloride mixtures, naphthalene - carbon tetrachloride mixtures, and anthracene - carbon tetrachloride mixtures. The chlorination was also undertaken in the presence of sulfur dioxide and sulfur dioxide - carbon tetrachloride mixtures.

The reactions were performed by passing chlorine gas through the reaction mixtures. As products, α-chloro-, α,α-dichloro-, β-chloro-, and β,β-dichloro- propionic acids and a cyclic anhydride of β-sulfopropionic acid[4] were obtained. A negligible amount of chlorinated aromatic compounds was also formed.

The products were analyzed by the NMR spectral method. In these experiments the authors paid special attention to establishing the relationship between the relative reactivity, β/α, and the concentration of the aromatic compound mixed into the solution or the quantity of sulfur dioxide used.

Table 1 summarizes the results of the chlorination where the effect of benzene in the reaction mixture was examined. The data in this table demonstrate that the relative reactivity, β/α, decreases from 1.68 to 1.11 as the mole fraction of benzene in the solvent (benzene - CCl_4) increases from zero to unity. The values of β/α are not affected by differences in the initiation, the photo-irradiation, or the BPO. The results of the addition of naphthalene to the solvent (CCl_4) are shown in Table 2. The plot of the relative reactivity *vs.* the concentration of naphthalene exhibits a minimum point at *ca.* 0.1 mol/*l* of naphthalene, as is seen in Fig. 2. Moreover, the total yield of the chlorinated products decreases as the concentration of naphthalene is increased.

The addition of anthracene to the solvent (CCl_4) gave no chlorinated propionic acids, even when a very small quantity (0.117 mol/*l*) was present in the reaction mixture. As Table 3 indicates, the decrease in the relative reactivity was more accelerated in the presence of sulfur dioxide. When an equimolar amount of sulfur dioxide or more is mixed with the chlorine, the relative reactivity decreases below unity, indicating the reversal of the reactivities between the α- and β-positions. On the contrary, no change in the selectivity with the sulfur dioxide concentration was observed in the photo-initiated chlorination where the relative reactivity was kept constant, $\beta/\alpha=1.4$; this selectivity is very similar to the relative reactivity in the carbon tetrachloride only.

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[1] W. A. Pryor, "Free Radicals," McGraw-Hill, New York (1966), p. 181.

[2] R. E. Bühler, *Helv. Chim. Acta*, **51**, 1558 (1968).

[3] G. A. Russell, *J. Amer. Chem. Soc.*, **80**, 4987 (1958).

[4] M. S. Kharasch, T. H. Chao, and H. C. Brown, *ibid.*, **62**, 2393 (1940).

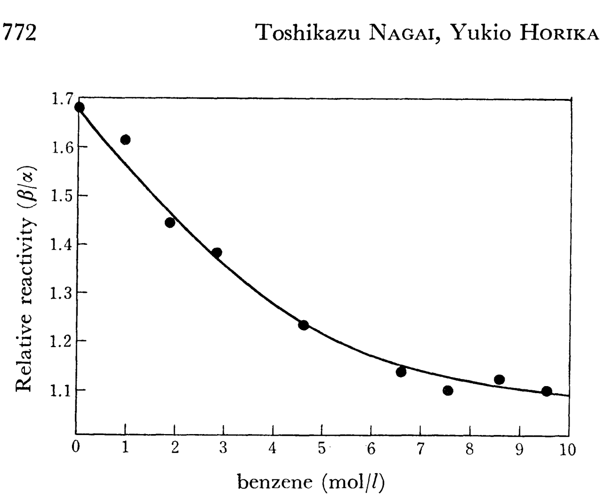


Fig. 1. Relative reactivity (β/α) in the chlorination of propionic acid with chlorine initiated by benzoyl peroxide in benzene - CCl_4 mixtures at 70°C.

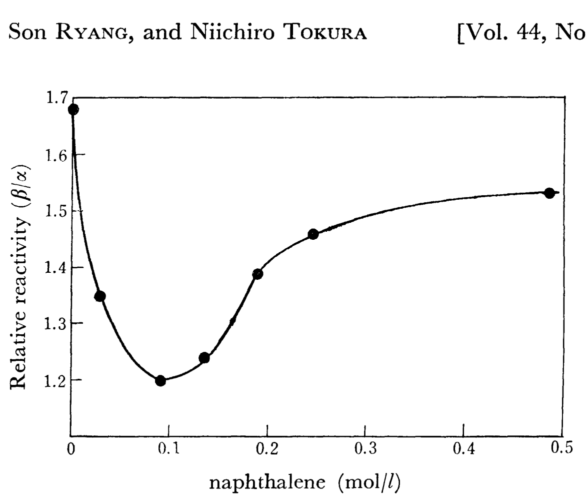


Fig. 2. Relative reactivity (β/α) in the chlorination of propionic acid with chlorine initiated by benzoyl peroxide in naphthalene - CCl_4 mixtures at 70°C.

TABLE 1. CHLORINATION OF PROPIONIC ACID IN BENZENE - CCl_4 AT 70°C

Initiation	Mole fraction of benzene in the mixed solvent	Product yield (mol %)				Relative reactivity(β/α)
		$CH_3CHClCO_2H$	$CH_3CCl_2CO_2H$	$CH_2ClCH_2CO_2H$	$CHCl_2CH_2CO_2H$	
BPO	0.0	10.9	16.0	10.8	56.9	1.68
	0.1	12.9	16.1	14.3	53.4	1.61
	0.2	16.1	12.5	16.8	44.9	1.44
	0.3	15.1	13.2	20.1	35.7	1.38
	0.5	18.0	9.6	25.0	26.4	1.23
	0.7	16.4	10.2	23.5	22.0	1.14
	0.8	16.3	8.0	22.6	18.2	1.11
	0.9	15.8	7.0	24.5	14.0	1.13
	1.0	18.5	7.8	28.9	14.5	1.11
hν	0.0	13.8	1.7	34.3	4.2	1.65
	0.5	14.6	4.3	30.4	3.1	1.23
	1.0	16.3	3.3	30.5	2.6	1.13

TABLE 2. CHLORINATION OF PROPIONIC ACID IN NAPHTHALENE - CCl_4 AT 70°C

Mole fraction of naphthalene in the solvent	Product yield (mol %)				Relative reactivity(β/α)
	$CH_3CHClCO_2H$	$CH_3CCl_2CO_2H$	$CH_2ClCH_2CO_2H$	$CHCl_2CH_2CO_2H$	
0.00	10.9	16.0	10.8	56.9	1.68
0.006	19.1	8.6	26.3	29.8	1.35
0.010	21.0	6.8	32.4	18.1	1.20
0.014	24.5	3.7	39.7	13.0	1.24
0.019	18.1	4.3	33.2	14.6	1.39
0.025	19.2	2.5	38.1	9.8	1.46
0.050	19.6	0.6	40.4	5.7	1.53
0.10	8.2	0	19.7	0	1.59
0.20	0	0	0	0	—

However, the cyclic anhydride of β-sulfopropionic acid was obtained in both photo- and BPO- initiated processes, and neither the free acid nor the cyclic anhydride of α-sulfopropionic acid was detected in the reaction mixture; these results coincide with the earlier results of photochlorination by Kharasch *et al.*[4] This suggests that the formation of the cyclic anhydride of α-sulfopropionic acid is difficult because of the electronical and sterical effects of the carboxyl group.

Table 3 also lists the results of the reaction of propionic acid with sulfuryl chloride at 70°C. The relative reactivity by BPO initiation, β/α=0.76, resembles the result of equimolar chlorination with SO_2 and Cl_2 by BPO initiation, 0.87.

These data on the various reactions suggest several interesting things. First, the dependence of the relative reactivities upon the concentrations of aromatic compounds or the quantities of sulfur dioxide suggests that not only the chlorine radical, but also another radical species such as complexed radicals, take part in these reactions. Moreover, the species have more selectivities than the free chlorine atom. Secondly, the con-

TABLE 3. CHLORINATION OF PROPIONIC ACID IN THE PRESENCE OF SO_2 AND BY SO_2Cl_2 AT 70°C

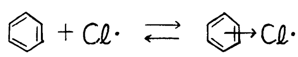
Initiation	Cl_2(mol)	SO_2(mol)	CCl_4(mol)	Product yield (mol%)[c)					Relative reactivity(β/α)
				CH_3CH-$ClCO_2H$	CH_3C-Cl_2CO_2H	CH_2ClC-H_2CO_2H	$CHCl_2C$-H_2CO_2H	Cyclic anhydride[a)	
BPO	0.286	0.036		24	2	41	8	3	1.3
	0.286	0.143		20	5	26	3	9	1.0
	0.286	0.286		24	2	15	1	18	0.87
	0.286	0.572		40	0	9	0	22	0.52
	0.286	0.858		20	6	3	0	16	0.49
	0.286	0.572	0.143	24	4	17	3	36	1.4
	0.195	(SO_2Cl_2 mol)		29	0	15	0	18	0.76[b)
hν	0.143	0.858		10	0	7	0	15	1.4
	0.286	0.858		20	4	13	0	37	1.4

a) The cyclic anhydride of β-sulfopropionic acid
b) Chlorination by SO_2Cl_2
c) No hydrogen rearrangement between the α- and β- position occurred under the present conditions, which was confirmed using propionic-α,α-d_2 acid-d_1 as the starting material.

tributions of these species to the reactions differ greatly among aromatic compounds.

Thirdly, in the presence of sulfur dioxide, the photo-initiated reaction proceeds quite differently from the BPO-initiated reaction, where there is no dependence of the relative reactivity on the concentration of sulfur dioxide used. Consequently, the chlorination mechanism in the former case should be discriminated.

In the aromatic systems, the radical species different from the free radicals are probably complexed radicals between aromatic compounds and a chlorine radical. The formation of this π-complex had been suggested by Russel.[3) For benzene, it could be written as follows:


(1)

Recently,[2) such a π-complex was detected by means of the UV spectra as arising from a charge-transfer-type interaction. Thus, we presumed that these π-complexed radicals and free chlorine radicals are competitive in the present reaction series. The chain propagation reactions can be formulated thus, where Ar denotes aromatic compounds:

$$Cl_2 + Ini\cdot \longrightarrow IniCl + Cl\cdot \tag{2}$$

$$Cl\cdot + Ar \overset{K_1}{\rightleftarrows} Cl\cdot \rightarrow Ar \tag{3}$$

$$Cl\cdot + 2Ar \overset{K_2}{\rightleftarrows} Ar\rightarrow Cl\cdot \leftarrow Ar \tag{4}$$

$$CH_3CH_2CO_2H + Cl\cdot \xrightarrow{k_{\alpha0}} CH_3\dot{C}HCO_2H + HCl \tag{5}$$

$$CH_3CH_2CO_2H + Cl\cdot \xrightarrow{k_{\beta0}} \dot{C}H_2CHCO_2H + HCl \tag{6}$$

$$CH_3CH_2CO_2H + Cl\cdot \leftarrow Ar \xrightarrow{k_{\alpha1}} CH_3\dot{C}HCO_2H + HCl + Ar \tag{7}$$

$$CH_3CH_2CO_2H + Cl\cdot \leftarrow Ar \xrightarrow{k_{\beta1}} \dot{C}H_2CH_2CO_2H + HCl + Ar \tag{8}$$

$$CH_3CH_2CO_2H + Ar\rightarrow Cl\cdot \leftarrow Ar \xrightarrow{k_{\alpha2}} CH_3\dot{C}HCO_2H + HCl + 2Ar \tag{9}$$

$$CH_3CH_2CO_2H + Ar\rightarrow Cl\cdot \leftarrow Ar \xrightarrow{k_{\beta2}} \dot{C}H_2CH_2CO_2H + HCl + 2Ar \tag{10}$$

We could not explain the results of the naphthalene - CCl_4 system by considering merely the free chlorine radical or the 1 : 1 complexed radical between the chlorine radical and naphthalene as the reacting species. This is the reason why we wish to propose the presence of another complex, such as a 1 : 2 complex between the chlorine radical and the aromatic compound, in the reaction mixture.

The step of hydrogen abstraction must be rate-controlling in the chlorine substitution reaction. The formation rates of α-chloropropionic acid and β-chloropropionic acid are given by Eqs. (11) and (12) respectively:

$$\begin{aligned}\frac{d[CH_3CHClCO_2H]}{dt} &= k_{\alpha0}[Cl\cdot][Pr] + k_{\alpha1}[Ar\rightarrow Cl\cdot][Pr] \\ &\quad + k_{\alpha2}[Ar\rightarrow Cl\cdot\leftarrow Ar][Pr] \\ &= (k_{\alpha0}+k_{\alpha1}K_1[Ar] + k_{\alpha2}K_2[Ar]^2)[Pr][Cl\cdot]\end{aligned} \tag{11}$$

$$\begin{aligned}\frac{d[CH_2ClCH_2CO_2H]}{dt} &= k_{\beta0}[Cl\cdot][Pr] + k_{\beta1}[Ar\rightarrow Cl\cdot][Pr] \\ &\quad + k_{\beta2}[Ar\rightarrow Cl\cdot\leftarrow Ar][Pr] \\ &= (k_{\beta0}+k_{\beta1}K_1[Ar] + k_{\beta2}K_2[Ar]^2)[Pr][Cl\cdot]\end{aligned} \tag{12}$$

Hence, the relative formation rate may be represented as Eq. (13):

$$\frac{d[CH_2ClCH_2CO_2H]}{d[CH_3CHClCO_2H]} = \frac{k_{\beta0}+k_{\beta1}K_1[Ar]+k_{\beta2}K_2[Ar]^2}{k_{\alpha0}+k_{\alpha1}K_1[Ar]+k_{\alpha2}K_2[Ar]^2} \tag{13}$$

If the concentration of the aromatic compounds is constant during the reaction time, the relative reactivity can be expressed as the following Eq. (14):

$$\begin{aligned}\frac{\beta}{\alpha} &= \frac{[CH_2ClCH_2CO_2H]}{[CH_3CHClCO_2H]} \times \frac{2}{3} \\ &= \frac{k_{\beta0}+k_{\beta1}K_1[Ar]+k_{\beta2}K_2[Ar]^2}{k_{\alpha0}+k_{\alpha1}K_1[Ar]+k_{\alpha2}K_2[Ar]^2} \times \frac{2}{3}\end{aligned} \tag{14}$$

Many interesting suggestions about these reaction series were obtained from the differential equation of Eq. (14) with respect to the aromatic concentration (Eq. (15)):

$$\frac{\mathrm{d}\left(\dfrac{\beta}{\alpha}\right)}{\mathrm{d}[\mathrm{Ar}]} = \frac{(k_{\alpha0}k_{\beta1}\mathrm{K}_1 - k_{\alpha1}k_{\beta0}\mathrm{K}_1) + 2(k_{\alpha0}k_{\beta2}\mathrm{K}_2 - k_{\alpha2}k_{\beta0}\mathrm{K}_2)[\mathrm{Ar}] + (k_{\alpha1}k_{\beta2}\mathrm{K}_1\mathrm{K}_2 - k_{\alpha2}k_{\beta1}\mathrm{K}_1\mathrm{K}_2)[\mathrm{Ar}]^2}{(k_{\alpha0} + k_{\alpha1}\mathrm{K}_1[\mathrm{Ar}] + k_{\alpha2}\mathrm{K}_2[\mathrm{Ar}^2])^2} \times \frac{2}{3} \tag{15}$$

First, the relation (16) can be derived for the benzene - CCl_4 system, which shows a monotonous decreasing curve in the β/α *vs*. Ar (aromatic) plot, as is indicated in Fig. 1:

$$\frac{k^{\mathrm{B}}_{\beta0}}{k^{\mathrm{B}}_{\alpha0}} > \frac{k^{\mathrm{B}}_{\beta1}}{k^{\mathrm{B}}_{\alpha1}} > \frac{k^{\mathrm{B}}_{\beta2}}{k^{\mathrm{B}}_{\alpha2}} \tag{16}$$

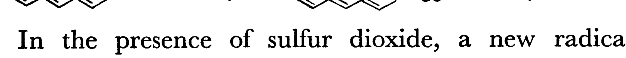
The relation (16) demonstrates that the relative reactivities decrease in this order: the free chlorine radical, the 1:1 complexed radical, and the 1:2 complexed radical. Such a prediction makes it clear that the reactivities of these radical species diminish in this order, so the reactivity of secondary hydrogen in propionic acid increases as compared with the primary hydrogen according to the above order.

The approximate value of each term in the relation (16) can be obtained from the curve of Fig. 1. That is, in benzene - CCl_4 systems the relative reactivities of the free radical, the 1:1 complex radical, and the 1:2 compelx radical are estimated to be 1.68, 1.12, and 1.01 respectively.

Secondly, in the naphthalene - CCl_4 series a minimum point in the plot is seen as shown in Fig. 2, where the relation (17) may be derived similarly as in the above case:

$$\frac{k^{\mathrm{N}}_{\beta0}}{k^{\mathrm{N}}_{\alpha0}} > \frac{k^{\mathrm{N}}_{\beta1}}{k^{\mathrm{N}}_{\alpha1}} \qquad \frac{k^{\mathrm{N}}_{\beta1}}{k^{\mathrm{N}}_{\alpha1}} < \frac{k^{\mathrm{N}}_{\beta2}}{k^{\mathrm{N}}_{\alpha2}} \tag{17}$$

The relation (17) points out the striking tendency that the relative reactivity of the 1:2 complexed radical is larger than that of the 1:1 complexed radical. Thus, it is anticipated that the hydrogen abstraction in the α-position suffers from more steric hindrance, largely because of the bulk of the 1:2 complexed radical. Accordingly, this steric effect will accelerate the increase in the selectivity, indicating a reversal of the reactivity tendency. Thirdly, the two equilibrium constants in the naphthalene - CCl_4 system, K_1 and K_2, are much larger than those in the benzene - CCl_4 system, because the relative reactivity of the former changes in a much lower concentration of aromatic compounds than that of the latter. Fourthly, the equilibrium constants of the anthracene - CCl_4 systems are so large that the free chlorine radical could scarcely participate in this reaction. Moreover, the recativity of the formed complexed radicals is too low to be able to abstract a hydrogen atom of propionic acid.



In the presence of sulfur dioxide, a new radical such as $SO_2Cl\cdot$ may be formed, as is seen in Scheme 1:

$$\begin{tikzcd}[column sep=small]
\mathrm{Ini}\cdot + \mathrm{Cl}_2 \arrow[r] & \mathrm{IniCl} + \mathrm{Cl}\cdot \\
\mathrm{SO}_2 + \mathrm{Cl}\cdot \arrow[r, shift left] \arrow[d, "\mathrm{RH}"] & \mathrm{SO}_2\mathrm{Cl}\cdot \arrow[l, shift left] \arrow[d, "\mathrm{RH}"] \\
\mathrm{R}\cdot + \mathrm{HCl} & \mathrm{R}\cdot + \mathrm{HCl} + \mathrm{SO}_2
\end{tikzcd}$$

$$\begin{tikzcd}[column sep=small]
\mathrm{SO}_2 + \mathrm{R}\cdot \arrow[r, shift left] & \mathrm{RSO}_2\cdot \arrow[l, shift left] \arrow[d, "\mathrm{Cl}_2"] \\
\mathrm{RCl} + \mathrm{Cl}\cdot \arrow[u, leftarrow, "\mathrm{Cl}_2"] & \mathrm{RSO}_2\mathrm{Cl} + \mathrm{Cl}\cdot \arrow[d, "-\mathrm{SO}_2"] \\
 & \mathrm{RCl} + \mathrm{SO}_2
\end{tikzcd}$$

Scheme 1

The chlorine radical has so large an electrophilicity that the reaction is very sensitive to the electron density of the substrate as well as to the solvent used. The relative reactivity (β/α) or the selectivity varies according to the polar effect of the substituent in the substrate and the medium with which the radical may form a complex or a new attacking species.

The present authors have confirmed that propionic acid does not react with chlorine in either *n*-heptane, anisole, or dioxane, where the hydrogens of the solvent molecules have high electron densities. Thus, the relative reactivity (β/α) of propionic acid will diminish upon the decrease in the electrophilicity of the attacking radical, because the electron density at the α-position hydrogen atom is expected to have a lower electron density than that at the β-position in propionic acid.

Ordinarily, a rise in such a selectivity is accompanied by a decrease in the reactivity of the attacking radical.

It has been reported that the sulfochlorine radical is less reactive than the chlorine radical.[5] The increase in the content of the aromatic compound in the reaction mixture results in a proportionate decrease in the total yield of the reaction product. The decrease in the reactivity of the attacking radical will cause an increase in the energy difference due to selectivity (E_s) between primary (β) and secondary (α) hydrogens. On the other hand, the energy difference due to the polar effect (E_p) will decrease as the chlorine radical forms another complex or a new complexed radical, because the nucleophilic character of the latter will increase. The energy difference between the α and the β-positions would be reduced by the compensation of both the effects. If E_s is very large and if E_p is small, as in the sulfochlorine radical, it can be expected that the reversal of the relative reactivity may easily happen.

The energy-level diagram in the reaction course is illustrated in Fig. 3.

In the chlorine - sulfur dioxide system the present authors assumed that a sulfochlorine radical was formed. However, we could not completely rule out the interaction between the carboxyl group of the substrate and the sulfur dioxide molecule. The oxygen atom of sulfur dioxide is bonded with the α-hydrogen atom by a hydrogen bonding, as is indicated in Fig. 4. Thus, the α-hydrogen-carbon bond is weakened and is easily attacked by a chlorine radical to abstract the α-hydrogen atom.

The difference in the results of the photoreactions between the Cl_2 - aromatics - CCl_4 and Cl_2 - sulfur dioxide systems is probably caused by the following factors.

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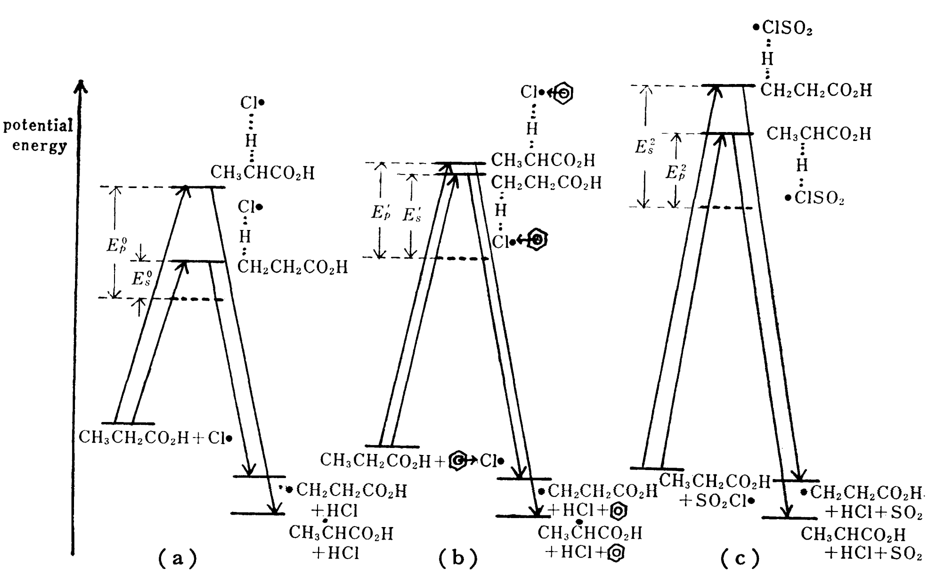
[5] G. A. Russell and H. C. Brown, *J. Amer. Chem. Soc.*, **77**, 4031 (1955).



$E_p^0 > E_p^1 > E_p^2 \quad E_s^0 < E_s^1 < E_s^2$

Fig. 3. Schematic energy diagram of chlorination reaction of propionic acid with chlorine, in the absence of solvent (a), in the presence of benzene (b) or sulfur dioxide (c).

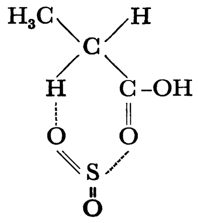


Fig. 4

In the Cl_2-aromatics - CCl_4 system, photo-irradiation has little influenece upon the stabilities of the formed complexed radicals, while photo-irradiation may hinder the formation or may quickly decompose the sulfochlorine radical, as is shown by the following scheme:

$$SO_2 + Cl\cdot \rightleftarrows SO_2Cl\cdot$$

$$SO_2Cl\cdot \xrightarrow{h\nu} SO_2Cl\cdot^{*} \longrightarrow SO_2 + Cl\cdot$$

As has been mentioned above, the relative reactivity in the photoreactions by the $Cl_2 - SO_2$ system was similar to that of the attack by the chlorine radical alone, in spite of the presence of sulfur dioxide.

The selectivity in the reaction of SO_2–Cl_2 diluted with carbon tetrachloride has also indicated no dependence upon the concentration of sulfur dioxide as in the case of the photo-irradiation. The reason for this probably lies in the instability of the $SO_2Cl\cdot$ radical as a result of its dilution by carbon tetrachloride.

The formation of the $SO_2Cl\cdot$ radical as the attacking species in the $Cl_2 - SO_2$ - BPO system may be proved by the results shown in Table 3, where the relative reactivity, β/α, is 0.76, this value being close to the result in the equimolar ($Cl_2 : SO_2 = 1 : 1$) chlorination, $\beta/\alpha = 0.87$.

Experimental

Chlorination of Propionic Acid Initiated by Benzoyl Peroxide in a Benzene - Carbon Tetrachloride Mixed Solvent. Propionic acid (10.59 g, 0.143 mol), a solvent (1.0 mol), and BPO (0.087 g, 0.00036 mol) were placed in a four-necked flask (200 m*l* volume) immersed in a water bath equipped with a thermostat. The solvents used were mixtures of benzene and carbon tetrachloride, mole fractions of benzene varying as 0.0, 0.1, 0.2, 0.3, 0.5, 0.7, 0.8, 0.9, and 1.0. Chlorine gas (0.286 mol), which had been washed and dried by the use of water, concentrated sulfuric acid, calcium oxide and phosphorus pentoxide, was blown into the reaction mixtures at 70°C for three hours. The amount of flowing chlorine gas was set by a flow meter. In these reactions, all the entire reaction apparatus was sheltered from light, and the reaction apparatus was filled with nitrogen gas before the reactions in order to eliminate the effect of oxygen. The solvents were removed by distillation, and the residue was analyzed by means of the NMR spectra. The following compounds were obtained for chlorinated propionic acids.

NMR: $CH_3CHClCO_2H$, τ, 5.70 (quartet) 8.29, (doublet).
$CH_3CCl_2CO_2H$ 7.70 (singlet),
$CH_2ClCH_2CO_2H$ 6.12 (triplet), 7.18 (triplet).
$CHCl_2CH_2CO_2H$ 3.98 (triplet), 6.72 (doublet).

The yields of these compounds were calculated from the areas of their respective peaks. A small white crystal was gained as the by-product. The crystal was recrystallized from ethanol melted at 157—158°C. This product was confirmed as α-benzene hexachloride by a comparison of the IR and NMR spectra, and the retention time in gas-liquid chromatography, with those of an authentic specimen. In addition to this, a very small amount of chlorobenzene was obtained; it was identified by a study of the IR spectrum and by glc.

Chlorination in Naphthalene - Carbon Tetrachloride and Anthracene - Carbon Tetrachloride. The reactions were performed in the same apparatus and using the same procedure as have been described above. The mole fractions of naphthalene in the solvent (CCl_4) used were 0.006, 0.01, 0.014, 0.019, 0.025, 0.05, 0.10, and 0.20, and that of anthracene was 0.0129.

Chlorination with Photo-initiation in Benzene - Carbon Tetrachloride. In a reaction flask we placed propionic acid (10.59 g, 0.143 mol) and solvents (1.0 mol). This reaction flask was then illuminated by a 300-watt unfrosted tungsten light bulb placed near it. The mole fraction of benzene in the mixed solvents were 0.0, 0.5, and 1.0 respectively. Identification and quantitative analysis were done by the previously-described procedures.

Chlorination Initiated by BPO in the Presence of Sulfur Dioxide. To a four-necked vessel with a volume of 50 m*l* immersed in a water bath and equipped with a thermostat, we added propionic acid (10.59 g, 0.143 mol) and BPO (0.087 g, 0.00036 mol). Dried chlorine gas (0.286 or 0.572 mol) and sulfur dioxide gas were then passed through the reaction mixtures at 70°C for three hours. The total amounts of sulfur dioxide used were 0.036, 0.142, 0.286, 0.572, and 0.858 mol respectively. Soon after the reaction, white crystals were formed. These crystals were separated from benzene - ligroin (1:4) mixtures. The compound was identified as the cyclic anhydride of β-sulfopropionic acid by a comparison of its melting point, NMR, and mass spectra with those of an authentic specimen. Mp, 76—77°C. NMR: centered at 6.97 (multiplet) and 7.38 (multiplet). Mass: exhibited a molecular ion peak at m/e 136 with those of fragment ions. The soluble compounds in the solvent were distilled under pressure (10 mm Hg) after the solvents had been removed. The three portions of the distillate at 50—70, 70—80 and 80—90°C were submitted to NMR analyses.

Photochlorination in the Presence of Sulfur Dioxide. Sulfur dioxide (0.858 mol) was passed with chlorine gas (0.143 or 0.286 mol) through a reaction vessel containing propionic acid (0.143 mol). Identification and quantitative analysis were done as has been described in the experimental section concerning initiation with BPO.

Reaction of Propionic Acid with Sulfuryl Chloride. Propionic acid (0.143 mol) was reacted with sulfuryl chloride (0.195 mol) at 70°C with BPO (0.00036 mol).

NMR Spectra. The proton resonance spectra were run on a Nihondenshi spectrometer at 60 MHz.

IR Spectra. The infrared spectra were recorded on an EPI-S2-TYPE Hitachi spectrometer.

Mass Spectra. The mass spectra were run on a Hitachi RMU-6E single-focusing instrument.

Gas-liquid Chromatography. Glc was carried out on a K53-TYPE Hitachi chromatograph, using Silicone SE-30 as the column.