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Kinetics of the Acid-Catalyzed α-Bromination of Aliphatic Acids

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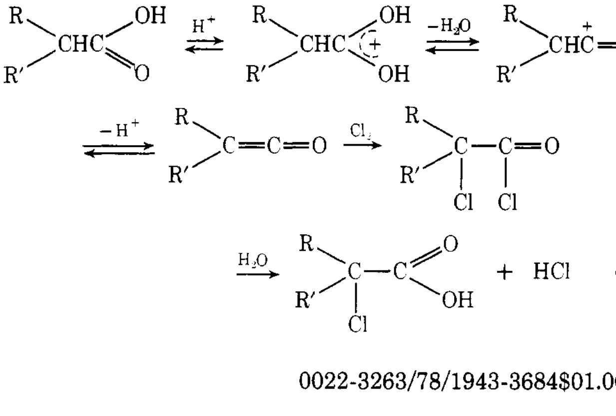
Aliphatic acids were found to be easily α-brominated in good yields (78–95%) by molecular bromine in the presence of chlorosulfonic acid as a catalyst in 1,2-dichloroethane as a solvent at 84 °C. Kinetic study shows that the rate is expressed as: $v = k_{\text{obsd}}[\text{RCO}_2\text{H}][\text{Br}_2]$, where k_{obsd} is proportional to the initial concentration of chlorosulfonic acid at an early stage. The substituent effect fits Taft's equation with little steric effect, giving $\rho^* = -0.97$ at 60 °C, which suggests that the reaction is accelerated by electron-releasing groups, thus the reactivity increases as follows: $CH_3CO_2H < CH_3CH_2CO_2H < CH_3CH_2CH_2CO_2H < (CH_3)_2CHCH_2CO_2H < (CH_3)_2CHCO_2H < (CH_3CH_2)_2CHCO_2H$. The mechanism involving ketene intermediates is discussed.

Ketones and aldehydes are α-halogenated by molecular halogen in the presence of acid or base catalysts;[2] the reaction mechanism is said to involve the corresponding enol which is in equilibrium with the keto form. The rate-determining step in most cases is the enolization, hence the rate is independent of the concentration and nature of halogen, i.e., chlorination, bromination, and iodination under the same conditions proceed at the same rate irrespective of their concentration.[2b,3]

In the Hell–Volhard–Zelinsky reaction the aliphatic acids are α-halogenated by halogen in the presence of phosphorus halides.[4] Little et al. have proposed that this reaction proceeds via enol or ketene intermediate with little evidence,[5] but most workers prefer the intermediacy of enol.[4] Only one kinetic study for the Hell–Volhard–Zelinsky reaction was reported, in which the rate was said to depend on the concentration of bromine,[4c] in contrast to the behavior of ketones.

We have reported previously that aliphatic acids can be α-chlorinated by a Cl_2–O_2 mixture in the presence of a strong acid such as chlorosulfonic or fuming sulfuric acid,[6] and we suggested that the reaction intermediate may be ketene on the basis of NMR and laser-Raman spectral data, deuterium tracer study, and trapping by aniline forming acetanilide.[7] However, no kinetic study could yet be done because of the low solubility of chlorine.

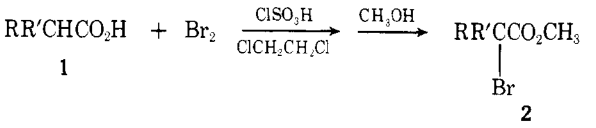


(1)

The present paper reports the application of this chlorination method to bromination of aliphatic acids and also the kinetics of bromination which presents further support and detailed information for the mechanism of reaction.

Results and Discussion

α-Bromination. It was found that aliphatic acids could also be easily α-brominated by molecular bromine in 1,2-dichloroethane using a strong acid catalyst, chlorosulfonic acid, as in the case of chlorination, but the presence of a radical trapper such as molecular oxygen was unnecessary. The yields and physical properties for identification of esters of α-bromo acids are listed in Tables I and II, respectively. The yields are satisfactory (78–95%) under these conditions except for bromination of acetic acid.



$$\underset{\mathbf{1}}{RR'CHCO_2H} + Br_2 \xrightarrow[ClCH_2CH_2Cl]{ClSO_3H} \xrightarrow{CH_3OH} \underset{\mathbf{2}}{RR'C(Br)CO_2CH_3} \qquad (2)$$

Kinetics of α-Bromination. The rate of α-bromination of isobutyric acid in 1,2-dichloroethane at 60 °C using 0.05 M chlorosulfonic acid as a catalyst fits eq 3.

$$v = k_{\text{obsd}}[\text{RR'CHCO}_2\text{H}][\text{Br}_2] \qquad (3)$$

The first-order dependence of rate on bromine concentration was confirmed at various concentrations of bromine (Table III). Equation 3, which depends on $[Br_2]$, suggests that

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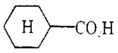
Table I. Yields of Esters of α-Bromo Acids by the Reaction of Aliphatic Acids with Br_2 in 1,2-Dichloroethane at 85 °C[a]

	registry no.	substrate acid	yield, %
1a	64-19-7	CH_3CO_2H	10.9
1b	79-09-4	$CH_3CH_2CO_2H$	78.1
1c	107-92-6	$CH_3CH_2CH_2CO_2H$	85.9
1d	503-74-2	$(CH_3)_2CHCH_2CO_2H$	83.5
1e	79-31-2	$(CH_3)_2CHCO_2H$	95.3 15.1[b]
1f	88-09-5	$(CH_3CH_2)_2CHCO_2H$	92.4
1g	98-89-5		90.4

[a] Substrate acid (10 mmol) was treated with bromine (10 mmol) in the presence of chlorosulfonic acid (10 mmol) in 1,2-dichloroethane (50 mL) at 85 °C for 2 h and refluxed with methanol (30 mL) for 10 h. [b] Concentrated sulfuric acid (18 mmol) was used in place of chlorosulfonic acid.

bromine adds to ketene intermediate **3** at the rate-determining step.

Effect of Concentration of Chlorosulfonic Acid. The initial rate constant k_{obsd} for bromination of isobutyric acid was found to be proportional to the initial concentration of chlorosulfonic acid (Figure 1).

Hence, the rate in eq 3 can be rewritten as follows, where $[\ ]_0$ means initial concentration.

$$v = k[\mathrm{ClSO_3H}]_0[\mathrm{RR'CHCO_2H}][\mathrm{Br_2}] \quad (4)$$

Mechanism. As stated above, there are evidences for the formation of ketenes from aliphatic acids in $ClSO_3H$ or fuming H_2SO_4.[7] These results may be explained by the following scheme.

$$\mathrm{RR'CHCO_2H + ClSO_3H \overset{fast}{\rightleftarrows} RR'C{=}C{=}O + HCl + H_2SO_4} \quad (5)$$

$$\mathrm{RR'C{=}C{=}O + Br_2 \xrightarrow{k_6} RR'CBrCOBr} \quad (6)$$

$$\mathrm{RR'CBrCOBr + CH_3OH \rightarrow RR'CBrCO_2CH_3 + HBr} \quad (7)$$

Step 5 for formation of ketene is irreversible or at least shifts greatly to the right side and this reaction competes with other reactions of aliphatic acids such as the formation of $RR'CH(OH)_2^+$, $RR'CHCO^+$, $RR'C(SO_3H)CO_2H$, $RR'CHCOOSO_3H$, and ketene dimer as discussed below. At an early stage of the reaction, the concentration of ketene may be proportional to the initial concentration of $ClSO_3H$. If the rate is determined by eq 6, then the above mechanism leads to the observed rate equation as shown below.

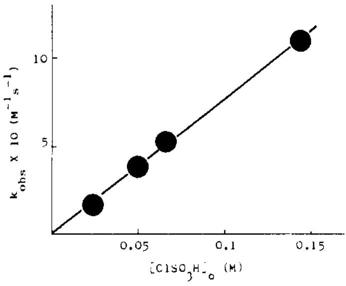


Figure 1. Correlation between concentration of chlorosulfonic acid and rate constant (k_{obsd}) for bromination of isobutyric acid at 60 °C.

$$\begin{aligned} v &= k_6[\mathrm{RR'C{=}C{=}O}][\mathrm{Br_2}] \\ &= k[\mathrm{ClSO_3H}]_0[\mathrm{RR'CHCO_2H}][\mathrm{Br_2}] \quad (8) \end{aligned}$$

There may be the following steps before formation of ketene.

$$\mathrm{RR'CHCO_2H + ClSO_3H \rightleftarrows RR'CHC(OH)_2^+ + ClSO_3^-} \quad (9a)$$

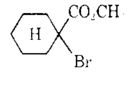
$$\mathrm{RR'CHC(OH)_2^+ + ClSO_3H \rightleftarrows RR'CHCO^+ + HCl + H_2SO_4} \quad (9b)$$

$$\mathrm{RR'CHCO^+ \rightleftarrows RR'C{=}C{=}O + H^+} \quad (9c)$$

Aliphatic acid is readily converted to the corresponding oxonium ion $RR'CHC(OH)_2^+$ in concentrated sulfuric acid but hardly to the corresponding acylium ion $RR'CHCO^+$.[13] On the other hand, aliphatic acid in fuming sulfuric acid is rather easily converted to the acylium ion.[13] Since the acidity of chlorosulfonic acid is analogous to fuming sulfuric acid,[14] chlorosulfonic acid can also convert aliphatic acid to acylium ion and thence to ketene by deprotonation. This lower acidity of sulfuric acid[14] may be the reason why sulfuric acid as a catalyst in α-halogenation gave yields far less than chlorosulfonic or fuming sulfuric acid (Table I and ref 6).

An equimolar amount of sulfuric acid, which should be a large enough amount for converting aliphatic acid to the oxonium ion $RR'CHC(OH)_2^+$, gave only poor yield, while an

Table II. Physical Properties for Identification of Methyl Esters of α-Bromo Acids

ester	registry no.	bp, °C (mm)	NMR chemical shift,[a] δ (J in Hz)	IR[b] $\nu_{C=O}$, cm^{-1}
$CH_2BrCO_2CH_3$	96-32-2	72–73 (40)[c]	3.73 (s, 3 H, CO_2CH_3), 3.79 (s, 2 H, CH_2)	1740
$CH_3CHBrCO_2CH_3$	5445-17-0	62–63 (36)[d]	1.80 (d, J = 6.8, 3 H, β-H), 3.74 (s, 3 H, CO_2CH_3), 4.29 (quart, J = 6.8, 1 H, 7α-H)	1745
$CH_3CH_2CHBrCO_2CH_3$	3196-15-4	76–77 (42)[e]	1.02 (t, J = 7.2, 3 H, γ-H), 2.04 (quart, J = 6.8, 2 H, β-H), 3.74 (s, 3 H, CO_2CH_3), 4.08 (t, J = 7.0, 1 H, α-H)	1735
$CH_3CH(CH_3)CHBrCO_2CH_3$	26330-51-8	82–83 (42)[f]	1.03 (d, J = 7.2, 3 H, γ-H),[h] 1.10 (d, J = 7.2, 3 H,γ′-H),[h] 2.14 (oct, J = 6.5, 1 H, β-H), 3.72 (s, 3 H, CO_2CH_3), 3.92 (d, J = 7.2, 1 H, α-H)	1740
$CH_3C(CH_3)BrCO_2CH_3$	23426-63-3	81–82 (70)[g]	1.89 (s, 6 H, β-H), 3.73 (s, 3 H, CO_2CH_3)	1745
$CH_3CH_2C(CH_2CH_3)BrCO_2CH_3$	2399-18-0	104–105 (42)	0.97 (t, J = 6.9, 6 H, γ-H), 2.09 (quart, J = 6.8, 4 H, β-H), 3.75 (s, 3 H, CO_2CH_3)	1735
	3196-23-4	123–124 (34)	1.03 (br, 6 H, γ, δ-H), 2.13 (t, J = 6.5, 4 H, β-H), 3.76 (s, 3 H, CO_2CH_3)	1740

[a] CCl_4. [b] Neat. [c] Lit.[8] bp 63.4–64.4 °C (33 mm). [d] Lit.[9] bp 56.5 °C (21 mm). [e] Lit.[10] bp 165–172 °C. [f] Lit.[11] bp 64–65 °C (11 mm). [g] Lit.[11] bp 52.2 °C (21 mm). [h] γ and γ′ protons are not equivalent magnetically.[12]

Table III. Effect of Concentration of Bromine on Second-Order Rate Constant (eq 3) for α-Bromination of Isobutyric Acid in 1,2-Dichloroethane at 60 °C[a]

$[Br_2]_0$, M	k_{obsd}, $M^{-1}\,s^{-1}$
0.025	3.89×10^{-3}
0.050	3.98×10^{-3}
0.100	3.93×10^{-3}

[a] Initial concentration of $ClSO_3H$, 0.05 M.

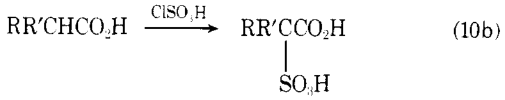
Table IV. Initial Rate Constants for α-Bromination of Aliphatic Acids in 1,2-Dichloroethane at 60 °C

	substrate acid		relative rate constant		
	$RR'CHCO_2H$				
	R	R'	k, $M^{-2}\,s^{-1}$	k_{rel}	log k_{rel}
1a	H	H	0.037	0.046	−1.330
1b	CH_3	H	0.256	0.321	−0.492
1c	CH_3CH_2	H	0.362	0.454	−0.342
1d	$(CH_3)_2CH$	H	0.458	0.575	−0.240
1e	CH_3	CH_3	0.796	1.000	0.000
1f	CH_3CH_2	CH_3CH_2	1.242	1.560	0.193
1g	hexahydrobenzoic acid		1.224	1.537	0.186

equimolar chlorosulfonic acid gave a pretty high yield. This fact suggests that the actual intermediate for bromination would not be the corresponding enol $RR'C{=}C(OH)_2$, because these geminal alcohols should easily be dehydrated in strong acids such as $ClSO_3H$ to form ketene in analogy with the other gem alcohols. Other cationic species, which may exist in equilibrium with ketene, e.g., $RR'CHCO^+$ and $RR'CH(OH)_2^+$, would not be attacked by electrophilic bromine, whereas ketene bearing a double bond is known to add easily to molecular halogen in the gas phase to form α-haloacyl halide,[15] which is confirmed also by us in a solution.[16]

The rate constant decreases with the proceeding of the reaction, which suggests the disappearance of chlorosulfonic acid by the reaction with water[17] produced during formation of ketene (eq 10a) and α-sulfonation of aliphatic acid (eq 10b).[18]

$$H_2O + ClSO_3H \longrightarrow HCl + H_2SO_4 \qquad (10a)$$



$$RR'CHCO_2H \xrightarrow{ClSO_3H} RR'\underset{\displaystyle SO_3H}{\underset{|}{C}}CO_2H \qquad (10b)$$

Substituent Effect. The rates of bromination of a number of aliphatic acids were measured in a homogeneous solution of 1,2-dichloroethane at 60 °C (Table IV).

A plot of relative rates (log k_{rel}) vs. summation of Taft's σ^* values ($\Sigma\sigma^*$)[19] gave a straight line with a slope (ρ^*) of −0.97 (Figure 2).

The negative ρ^* value suggests that acid-catalyzed α-bromination is accelerated by an electron-releasing group; the negative ρ value is expected for rate-determining electrophilic addition of bromine to the carbon–carbon double bond of ketene. A similar behavior was reported in the addition of bromine to alkene ($\rho = -4.1$ in 2,2,4,4-tetrachloroethane at 25 °C).[20] The reactivity of ketene may depend mostly on the inductive effect, but little on the steric hindrance effect.

The observed small steric effect on our reaction, which is rather different from the behavior in the addition of bromine to alkenes,[20,21] may be explained as follows: Addition of bromine to ketene may also proceed via a bromonium ion intermediate 4 as in the bromine addition to alkenes.[22] As postulated for the epoxidation of alkyl-substituted alkenes, an electrophilic oxygen atom should attack on the less hindered site of the double bond in view of both less steric hindrance and more stabilization of developing positive charge.[23] Similarly, Br^+ should attack primarily on the carbonyl carbon to produce bromonium ion (**4a**) which is stabilized by steric and polar effects. Since **4b** and **4c** are less stable than **4a**, the path via **4a** is favored, thus exerting little steric hindrance. A bromide ion attack on 4 gives α-bromoacyl bromide (**5**).

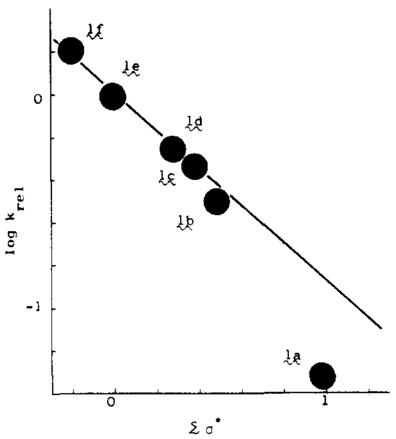
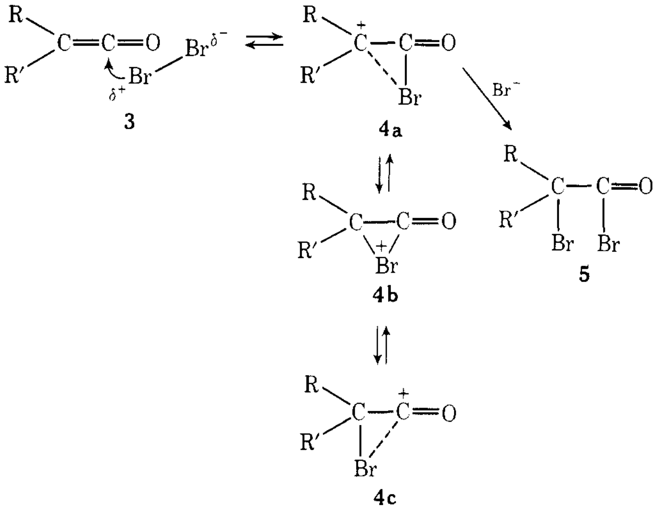


Figure 2. Plot of log k_{rel} vs. summation of Taft's σ^* value.



Lower aliphatic acids show less reactivity than that expected from Taft's equation;[19] this tendency is remarkable with acetic acid. This may be due to the higher association or lower solubility of ketene $RR'CHC(OH)_2^+$ and $RR'CHCO^+$ formed from acetic acid in 1,2-dichloroethane compared with those of the other acids which have larger alkyl groups.

In conclusion, the rates of reaction increase in the following order.

$$CH_3CO_2H \ll CH_3CH_2CO_2H < CH_3CH_2CH_2CO_2H < (CH_3)_2CHCH_2CO_2H < (CH_3)_2CHCO_2H < (CH_3CH_2)_2CHCO_2H$$

Experimental Section

Materials. Commercial first-grade acetic [bp 118 °C], propionic [bp 73–75 °C (53 mm)], n-butyric [bp 163 °C], isovaleric [bp 175–177 °C], isobutyric [bp 86–88 °C (48 mm)], diethylacetic [bp 124 °C (38 mm)], hexahydrobenzoic [bp 86–87 °C (1.3 mm)], and chlorosulfonic [bp 86–88 °C (33 mm)] acids were distilled before use.

Kinetics. 1,2-Dichloroethane (100 mL) containing a mixture of aliphatic acid (5 mmol), bromine (5 mmol), and chlorosulfonic acid (5 mmol) was thermostated at 60 °C. The concentration of bromine was estimated by iodometry, i.e., each 5 mL of the mixture was pipetted out at appropriate intervals of time and poured into an excess amount of aqueous KI. Liberated iodine was titrated with 0.02 N $Na_2S_2O_3$. The second-order rate constants were calculated by ordinary means.

Analysis of Products. A mixture of aliphatic acid (10 mmol), bromine (10 mmol), chlorosulfonic acid (0.5 mL), and 1,2-dichloroethane (50 mL) was heated at 85 °C for 2 h.

After unreacted bromine and 20 mL of 1,2-dichloroethane were distilled off, methanol (30 mL) was added to the mixture and the solution was refluxed for 10 h. The resulting ester of the α-bromo acid was identified and estimated by means of GLC using a Yanagimoto GCG 550 gas chromatograph equipped with a copper column packed with PEG 20 M 10% on Chromosorb WAW 60–80 mesh by employing methyl caprate as an internal standard.

After removal of methanol by distillation from the ester solution the residual mixture was washed with water, dried (Na_2SO_4), and distilled in vacuo. The isolated ester of α-bromo acid was identified by NMR and IR spectroscopies. NMR and IR spectra were measured with a 60 MHz Hitachi R-24B NMR spectrometer at 35 °C and a Perkin-Elmer Model 337 spectrophotometer, respectively.

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Registry No.—Chlorosulfonic acid, 7790-94-5.

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(16) Dimethylketene was mixed with a solution of Cl_2 in 1,2-dichloroethane and then esterified by methanol:

$$(CH_3)_2CHCO_2H \xrightarrow{P,\ Br_2} (CH_3)_2CBrCOBr \xrightarrow{Zn} (CH_3)_2C{=}C{=}O$$
$$\xrightarrow[EDC]{Cl_2} (CH_3)_2CClCOCl \xrightarrow{CH_3OH} (CH_3)_2CClCO_2CH_3$$

Resulting methyl α-chloroisobutyrate was analyzed by GLC (12%). The analogous reaction was observed with the reaction of dimethylketene with Br_2.

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Carbanion Halogenations with Carbon Tetrahalides. α-Halo Esters

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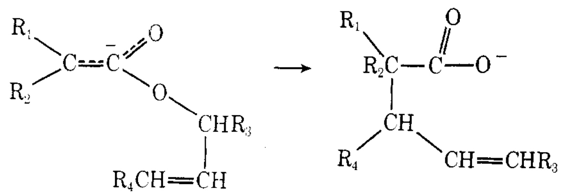
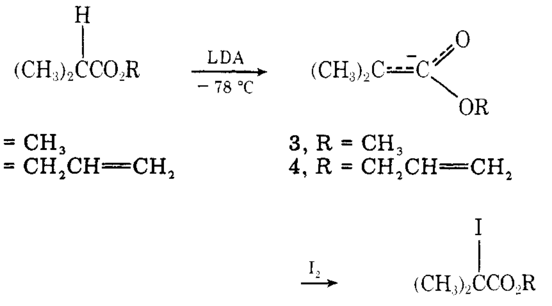
Carbanions generated by treatment of saturated or unsaturated esters with lithium diisopropylamide in THF at −78 °C react rapidly with carbon tetrahalides to produce α-halo esters in high yields (75–95%). Competitive bromination and chlorination of these carbanions with bromotrichloromethane are also described. These halogenations can be rationalized in terms of a radical anion–radical pair mechanism recently proposed for similar halogenations of carbanions derived from ketones or sulfones.

The regiospecific thermal rearrangement of enolate carbanions derived from allylic esters (eq 1), which we first described many years ago,[1] has proven to be of general synthetic usefulness. In certain cases, it is advantageous to convert the enolate anion into its *O*-trialkylsilyloxy derivative prior to rearrangement.[2]


(1)

During the course of a recent study relating to this symmetry-allowed [3.3] sigmatropic rearrangement, we required a quantitative method for determining the amount of carbanion formed when allylic esters of isobutyric acid were treated with 1 equiv of lithium diisopropylamide (LDA) in THF at −78 °C.

The quantitative iodination of ester carbanions with elemental iodine, which may be used with saturated or unsatu-



1, R = CH_3
2, R = $CH_2CH{=}CH_2$
3, R = CH_3
4, R = $CH_2CH{=}CH_2$
5, R = CH_3
6, R = $CH_2CH{=}CH_2$

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