137. *The Elimination of Chlorine from Sodium Chloroacetate by the Salts of Weak Acids.*

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The elimination of chlorine from the chloroacetate ion is brought about by water and by basic anions. The reactivity of 34 anions has been examined, and the bimolecular velocity coefficients measured at 45° in solutions of unit ionic strength. The velocity coefficient increases with the basic strength of the participating base.

In previous papers (J., **1933**, 49, 1133; **1934**, 778; **1936**, 153, 487; *Proc. Leeds Phil. Soc.*, **1934**, **2**, 544; **1935**, **3**, 135, 293) kinetic measurements on the removal of halogen from the $CH_2X\cdot\overline{CO}_2$ group ($X = Cl$ or Br) in neutral, acid, and alkaline solutions were reported. By restricting the measurements of velocity to the very early stages of the reaction, complications arising from the intervention of reaction products are largely avoided, and in these circumstances it was found that the velocity of reaction could be represented as the sum of five independent processes, as follows :

$$(1)\quad CH_2X\cdot\overline{CO}_2 + H_2O \longrightarrow CH_2(OH)\cdot CO_2H + \overline{X}$$

$$(2)\quad CH_2X\cdot\overline{CO}_2 + \overline{OH} \longrightarrow CH_2(OH)\cdot\overline{CO}_2 + \overline{X}$$

$$(3)\quad CH_2X\cdot\overline{CO}_2 + CH_2X\cdot\overline{CO}_2 \longrightarrow CH_2X\cdot CO_2CH_2\cdot\overline{CO}_2 + \overline{X}$$

$$(4)\quad CH_2X\cdot\overline{CO}_2 + CH_2X\cdot CO_2H \longrightarrow CH_2X\cdot CO_2CH_2\cdot CO_2H + \overline{X}$$

$$(5)\quad CH_2X\cdot CO_2H + H_2O \longrightarrow CH_2(OH)\cdot CO_2H + H^+ + \overline{X}$$

If attention is confined to alkaline or neutral solutions containing initially the salt $CH_2X\cdot CO_2Na$, then in the virtual absence of the acid $CH_2X\cdot CO_2H$, account need be taken of reactions (1)—(3) only. Each of these reactions involves the interaction of the ion $CH_2X\cdot\overline{CO}_2$ with a substance which on present views is a base, and it might therefore be anticipated that these are but special cases of a general reaction involving $CH_2X\cdot\overline{CO}_2$ and any base of sufficient strength. Evidence for this view has already been given in the case of sodium bromoacetate, where it was shown that the weakly basic anions chloroacetate, glycollate, formate, and acetate all undergo reaction in accord with the general equation

$$(6)\ CH_2X{\cdot}\bar{C}O_2 + \bar{B} \longrightarrow CH_2B{\cdot}\bar{C}O_2 + \bar{X}$$

where $\bar{B}$ stands for the basic anion.

TABLE I.

Initial velocities for 0·2M-$CH_2Cl{\cdot}CO_2Na$ + xM-NaB + (0·8 − x)M-$NaNO_3$ *at* 45°.

$\bar{B}$ = Formate; 10^6k_6 = 20·3.

x	0	0·0791	0·10	0·158	0·237	0·30	0·316	0·396	0·50
$10^6V_{\text{obs.}}$	0·560	0·864	0·958	1·19	1·53	1·78	1·84	2·18	2·61
$10^6V_{\text{calc.}}$	0·558	0·879	0·965	1·20	1·52	1·78	1·84	2·17	2·59

$\bar{B}$ = Acetate; 10^6k_6 = 15·5.

x	0	0·10	0·20	0·30	0·40	0·50
$10^6V_{\text{obs.}}$	0·562	0·857	1·16	1·44	1·82	2·15
$10^6V_{\text{calc.}}$	0·558	0·868	1·18	1·49	1·80	2·11

$\bar{B}$ = Propionate; 10^6k_6 = 15·0.

x	0	0·10	0·30	0·50
$10^6V_{\text{obs.}}$	0·561	0·842	1·46	2·08
$10^6V_{\text{calc.}}$	0·558	0·858	1·46	2·06

$\bar{B}$ = *n*-Butyrate; 10^6k_6 = 13·8.

x	0	0·10	0·20	0·30
$10^6V_{\text{obs.}}$	0·557	0·820	1·12	1·41
$10^6V_{\text{calc.}}$	0·558	0·834	1·11	1·39

$\bar{B}$ = Glycollate; 10^6k_6 = 10·8.

x	0	0·10	0·20	0·30	0·40
$10^6V_{\text{obs.}}$	0·560	0·777	0·984	1·20	1·43
$10^6V_{\text{calc.}}$	0·558	0·775	0·990	1·21	1·43

$\bar{B}$ = Phenylacetate; 10^6k_6 = 11·6.

x	0	0·099	0·198	0·297
$10^6V_{\text{obs.}}$	0·560	0·788	1·02	1·25
$10^6V_{\text{calc.}}$	0·558	0·788	1·02	1·25

$\bar{B}$ = Phenylpropionate; 10^6k_6 = 13·3.

x	0	0·1	0·2	0·3
$10^6V_{\text{obs.}}$	0·560	0·821	1·09	1·37
$10^6V_{\text{calc.}}$	0·558	0·824	1·09	1·36

$\bar{B}$ = *p*-Nitrophenylacetate; 10^6k_6 = 9·8.

x	0	0·05	0·1	0·2
$10^6V_{\text{obs.}}$	0·556	0·649	0·760	0·966
$10^6V_{\text{calc.}}$	0·558	0·656	0·754	0·952

$\bar{B}$ = Benzoate; 10^6k_6 = 9·5.

x	0	0·1	0·3	0·5
$10^6V_{\text{obs.}}$	0·557	0·740	1·11	1·52
$10^6V_{\text{calc.}}$	0·558	0·748	1·13	1·51

$\bar{B}$ = Mandelate; 10^6k_6 = 8·2.

x	0	0·1	0·2	0·3
$10^6V_{\text{obs.}}$	0·561	0·715	0·893	1·07
$10^6V_{\text{calc.}}$	0·558	0·722	0·886	1·05

$\bar{B}$ = *o*-Toluate; 10^6k_6 = 12·3.

x	0	0·1	0·2	0·3
$10^6V_{\text{obs.}}$	0·560	0·802	1·04	1·30
$10^6V_{\text{calc.}}$	0·558	0·804	1·05	1·30

$\bar{B}$ = *m*-Toluate; 10^6k_6 = 9·8.

x	0	0·1	0·2	0·3
$10^6V_{\text{obs.}}$	0·557	0·750	0·947	1·16
$10^6V_{\text{calc.}}$	0·558	0·754	0·950	1·15

$\bar{B}$ = *p*-Toluate; 10^6k_6 = 10·2.

x	0	0·1	0·2	0·3
$10^6V_{\text{obs.}}$	0·561	0·757	0·963	1·18
$10^6V_{\text{calc.}}$	0·558	0·764	0·968	1·17

$\bar{B}$ = *o*-Hydroxybenzoate; 10^6k_6 = 4·4.

x	0	0·1	0·2	0·3
$10^6V_{\text{obs.}}$	0·557	0·648	0·737	0·831
$10^6V_{\text{calc.}}$	0·558	0·648	0·736	0·824

$\bar{B}$ = *m*-Hydroxybenzoate; 10^6k_6 = 11·1.

x	0	0·1	0·2	0·3
$10^6V_{\text{obs.}}$	0·560	0·780	1·02	1·21
$10^6V_{\text{calc.}}$	0·558	0·780	1·00	1·21

$\bar{B}$ = *p*-Hydroxybenzoate; 10^6k_6 = 12·6.

x	0	0·1	0·2	0·3
$10^6V_{\text{obs.}}$	0·556	0·818	1·06	1·31
$10^6V_{\text{calc.}}$	0·558	0·812	1·06	1·32

$\bar{B}$ = *o*-Nitrobenzoate; 10^6k_6 = 4·5.

x	0	0·1	0·2	0·3
$10^6V_{\text{obs.}}$	0·561	0·643	0·740	0·837
$10^6V_{\text{calc.}}$	0·558	0·648	0·738	0·828

$\bar{B}$ = *m*-Nitrobenzoate; 10^6k_6 = 6·6.

x	0	0·1	0·2	0·3
$10^6V_{\text{obs.}}$	0·563	0·692	0·823	0·966
$10^6V_{\text{calc.}}$	0·558	0·690	0·822	0·954

$\bar{B}$ = *p*-Nitrobenzoate; 10^6k_6 = 7·3.

x	0	0·1	0·2	0·3
$10^6V_{\text{obs.}}$	0·557	0·704	0·859	1·00
$10^6V_{\text{calc.}}$	0·558	0·706	0·852	0·998

$\bar{B}$ = *o*-Chlorobenzoate; 10^6k_6 = 6·1.

x	0	0·1	0·2	0·3
$10^6V_{\text{obs.}}$	0·560	0·681	0·821	0·924
$10^6V_{\text{calc.}}$	0·558	0·682	0·805	0·926

$\bar{B}$ = *m*-Chlorobenzoate; 10^6k_6 = 8·2.

x	0	0·1	0·2	0·3
$10^6V_{\text{obs.}}$	0·556	0·718	0·897	1·06
$10^6V_{\text{calc.}}$	0·558	0·722	0·886	1·05

$\bar{B}$ = *p*-Bromobenzoate; 10^6k_6 = 9·3.

x	0	0·1	0·15	0·2
$10^6V_{\text{obs.}}$	0·560	0·747	0·839	0·929
$10^6V_{\text{calc.}}$	0·558	0·746	0·839	0·933

$\bar{B}$ = *p*-Chlorobenzoate; 10^6k_6 = 8·7.

x	0	0·1	0·2	0·3	0·4
$10^6V_{\text{obs.}}$	0·563	0·729	0·905	1·09	1·26
$10^6V_{\text{calc.}}$	0·558	0·734	0·908	1·08	1·26

The experiments to be described show that analogous processes are effective in the elimination of chlorine from $\mathrm{CH_2Cl{\cdot}\overline{C}O_2}$. The evidence for this is provided chiefly by measurements at 45° of the initial velocities in aqueous solutions containing sodium chloroacetate and the sodium salts of various weak acids under controlled conditions of total salt concentration. Under the experimental conditions reaction (2) may be neglected, and the reaction velocity will be given by the equation

$$V_{\text{obs.}} = V_1 + V_3 + V_6 = k_1[\mathrm{A}^-] + k_3[\mathrm{A}^-]^2 + k_6[\mathrm{A}^-][\mathrm{B}^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

where V_6 and k_6 relate to reaction (6) and $[\mathrm{A}^-]$ and $[\mathrm{B}^-]$ represent respectively the concentration of chloroacetate and the basic anion. Measurement of the initial rate of production of chloride, together with a knowledge of k_1 and k_3, allows of the evaluation of k_6. In this paper the same units are employed as in the previous papers of the series; time is given in minutes, and concentration in g -mols./l.

A. *Salts of Monocarboxylic Acids.*—The reaction mixtures were of compositions given by the general formula $0{\cdot}2\text{M-}\mathrm{CH_2Cl{\cdot}CO_2Na} + x\text{M-NaB} + (0{\cdot}8 - x)\text{M-}\mathrm{NaNO_3}$. Since the salts involved are uni-univalent, the ionic strength of the solutions is unity and hence, provided specific salt effects be negligible, no differential inert-salt effect should occur on varying x. In Table I are given the kinetic data for the salts of aliphatic and aromatic acids. The values of $V_{\text{calc.}}$ are in each case those obtained by means of equation (*a*), the values of k_6 being those given in the table, and it being assumed that $10^6k_1 = 1{\cdot}65$ and $10^6k_3 = 5{\cdot}7$. The close agreement obtained in each case between observed and calculated velocities indicates that the inert-salt effects due to the nitrate and the basic anions cannot differ to any marked extent.

B. *Salts of Polycarboxylic Acids.*—The reaction mixtures had the composition $0{\cdot}2\text{M-}\mathrm{CH_2Cl{\cdot}CO_2Na} + x\text{M-}\mathrm{Na_zB} + (0{\cdot}8 - zx)\text{M-}\mathrm{NaNO_3}$, where z is the valency of the anion derived from the salt $\mathrm{Na_zB}$. In such a series of solutions the change in ionic strength with variation of x may bring about corresponding changes in the various velocity coefficients, and account must be taken of this in order to evaluate k_6 under salt conditions comparable to those obtaining in section A ($\mu = 1$). Examination of the experimental material shows that for all the solutions the observed velocities are closely accounted for by equation (*a*) on taking constant values for the coefficients k_1 and k_3, and by assuming that the value of the coefficient k_6 is related to the ionic strength by the empirical equation

$$\log k_6' = \log k_6 + \alpha(\mu - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

where k_6' and k_6 refer respectively to ionic strengths of μ and of unity, and α is a constant specific to the salt $\mathrm{Na_zB}$. This is shown by the data in Table II, which relate to the reaction between malonate and chloroacetate ions. The values of $V_{\text{calc.}}$ given in the last line are obtained by means of equations (*a*) and (*b*), the various constants being assigned the values $10^6k_1 = 1{\cdot}65$; $10^6k_3 = 5{\cdot}7$; $10^6k_6 = 31{\cdot}1$; $\alpha = 0{\cdot}200$.

TABLE II.

Initial velocities for $0{\cdot}2\text{M-}\mathrm{CH_2Cl{\cdot}CO_2Na} + x\text{M-}\mathrm{CH_2(CO_2Na)_2} + (0{\cdot}8 - 2x)\text{M-}\mathrm{NaNO_3}$ *at* 45°.

x	0	0·05	0·10	0·15	0·20	0·30
μ	1·0	1·05	1·1	1·15	1·2	1·3
$10^6V_{\text{obs.}}$	0·557	0·870	1·20	1·51	1·89	2·66
$10^6V_{\text{calc.}}$	0·558	0·875	1·21	1·56	1·92	2·70

The method described above for the evaluation of the limiting value of $k_6(\mu = 1)$ will be valid provided that, as μ increases, the contributions to the total velocity made by V_1 and V_3 progressively decrease to an appropriate extent. Inspection of numbers in Table II shows that this condition is likely to obtain; *e.g.*, when $x = 0{\cdot}30$ and $\mu = 1{\cdot}3$, then V_1 and V_3 together account for only about 21% of the total velocity, so that considerable uncertainty as to the precise magnitudes of V_1 and V_3 can no longer be of importance.

The results given above are typical of those obtained for this group of anions, and the remainder of the observations are therefore given in summarised form. In cols. 2 and 3 of Table III are given respectively the range of x values employed and the values of α in equation (*b*), and in col. 4 are the values for $k_6(\mu = 1)$ derived by means of (*a*) and (*b*).

TABLE III.

Reactant.	x.	α.	10^6k_6.	Reactant.	x.	α.	10^6k_6.
Oxalate	0—0·15	0·210	26·4	Malate	0—0·40	0·130	26·3
Malonate	0—0·30	0·200	31·1	Tartrate	0—0·30	0·140	21·3
Succinate	0—0·30	0·147	29·9	Phthalate	0—0·15	0	31·8
Adipate	0—0·15	0·135	26·3	Citrate	0—0·25	0	55

C. *Sodium Carbonate.*—The experimental procedure described in sections A and B is no longer applicable when the basic reactant is derived from sodium carbonate, since the hydrolysis of this salt is by no means negligible in dilute aqueous solution. It is therefore necessary to repress the hydrolysis by the addition of free alkali. Measurements of initial velocity were made for mixtures of the type $a\text{M-}\mathrm{CH_2Cl{\cdot}CO_2Na} + b\text{N-NaOH} + c\text{M-}\mathrm{Na_2CO_3} + (1 - a - b - 2c)\text{M-}\mathrm{NaNO_3}$, where a and b had values 0·2 and 0·01 respectively, and c ranged from 0·1 to 0·3. If x is the concentration of chloride ions at time t, then the rate of reaction is given by

$$\mathrm{d}x/\mathrm{d}t = k_1[\mathrm{A}^-] + k_3[\mathrm{A}^-]^2 + k_6[\mathrm{A}^-][\mathrm{CO_3}^=] + k_2[\mathrm{A}^-][\mathrm{OH}^-]$$

Now in the presence of free alkali the production of acid keeps pace with the production of halogen, since the compounds formed by reactions (3) and (6) undergo very rapid hydrolysis thus :

$$(6a)\ \mathrm{CH_2B{\cdot}\bar{C}O_2 + H_2O \longrightarrow CH_2(OH){\cdot}CO_2 + HB}$$

Hence the above velocity equation may be written

$$\mathrm{d}x/\mathrm{d}t = k_1a + k_3a^2 + k_6ac + k_2a(b - x)$$

or

$$\mathrm{d}x/\mathrm{d}t = m + k_2a(b - x)$$

where $m = k_1a + k_3a^2 + k_6ac$. Integration of this equation, m being treated as a constant, gives

$$\mathrm{e}^{tk_2a} = (m + k_2ab)/[m + k_2a(b - x)]$$

Consequently, if x_0 and x refer respectively to times t_0 and t, then

$$\mathrm{e}^{(t - t_0)k_2a} = [m + k_2a(b - x_0)]/[m + k_2a(b - x)]$$

which gives

$$m = k_2a\left[\frac{x\mathrm{e}^{(t - t_0)k_2a} - x_0}{\mathrm{e}^{(t - t_0)k_2a} - 1} - b\right] = k_1a + k_3a^2 + k_6ac$$

whence

$$k_6 = k_2\left[\frac{x\mathrm{e}^{(t - t_0)k_2a} - x_0}{\mathrm{e}^{(t - t_0)k_2a} - 1} - b\right] - k_1 - k_3a/c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

The experimental results are in Table IV, where t_0 relates to the first titration in each experiment and x_0 is the value of x when $t - t_0 = 0$. The values of k_6 have been calculated from (c) with the previous values for k_1 and k_3 and with $10^6k_2 = 1040$ (for the evaluation of k_1, k_2, and k_3, see papers cited on p. 517).

TABLE IV.

Initial velocities for $0{\cdot}2\mathrm{M}$-$\mathrm{CH_2Cl{\cdot}CO_2Na}$ + $0{\cdot}01\mathrm{M}$-NaOH + $c\mathrm{M}$-$\mathrm{Na_2CO_3}$ + $(0{\cdot}79 - c)\mathrm{M}$-$\mathrm{NaNO_3}$ at 45°.

	$c = 0{\cdot}100$.				$c = 0{\cdot}200$.				$c = 0{\cdot}300$.			
$t - t_0$	0	800	820	841	0	506	522	555	0	410	433	462
10^3x	0·140	4·152	4·251	4·361	0·279	4·251	4·391	4·591	0·359	4·900	5·140	5·389
10^6k_6	—	142	142	143	—	142	145	142	—	150	150	147

The change in the value of k_6 with increase in c is little more than the possible experimental error, and is in all probability due to the change in ionic strength from 1·1 ($c = 0{\cdot}1$) to 1·3 ($c = 0{\cdot}3$). The value adopted for $10^6k_6(\mu = 1)$ is 140 and is considered to be substantially correct.

For purpose of comparison the velocity coefficients referred to in the preceding pages are collected together in the following table. It is not proposed yet to discuss the implications of these results, but it may be remarked that consideration of the values of 10^6k_6 for water (1·65) and for the ions acetate (15·5), carbonate (140), hydroxyl (1040), indicates clearly that there exists a general relation connecting velocity coefficient and the basic strength of the participating base.

Velocity coefficients (k_6) *for the reaction between chloroacetate ions and bases at* 45°.

Base.	10^6k_6.	Base.	10^6k_6.	Base.	10^6k_6.
Water	1·65	*Univalent anions.*		*Univalent anions.*	
Bi- and ter-valent anions.		Formate	20·3	*m*-Toluate	9·8
Oxalate	$26{\cdot}_4$	Acetate	15·5	*p*-Toluate	10·2
Malonate	$31{\cdot}_1$	Propionate	15·0	*o*-Hydroxybenzoate	4·4
Succinate	$29{\cdot}_9$	Butyrate	13·8	*m*-Hydroxybenzoate	11·1
Adipate	$26{\cdot}_3$	Chloroacetate	5·7	*p*-Hydroxybenzoate	12·6
Malate	$26{\cdot}_3$	Glycollate	10·8	*o*-Nitrobenzoate	4·5
Tartrate	$21{\cdot}_3$	Phenylacetate	11·6	*m*-Nitrobenzoate	6·6
Phthalate	$31{\cdot}_8$	Phenylpropionate	13·3	*p*-Nitrobenzoate	7·3
Carbonate	140	*p*-Nitrophenylacetate	9·8	*o*-Chlorobenzoate	6·1
Citrate	55	Benzoate	9·5	*m*-Chlorobenzoate	8·2
		Mandelate	8·2	*p*-Chlorobenzoate	8·7
		o-Toluate	12·3	*p*-Bromobenzoate	9·3
				Hydroxyl	1040

EXPERIMENTAL.

The general procedure was as described in previous papers. The estimation of chloride was by Drechsel's method (*Z. anal. Chem.*, 1877, **16**, 351). The sample of reaction mixture was run into a measured volume of M/20-silver nitrate containing sufficient nitric acid to coagulate the silver chloride. This was filtered off, washed thoroughly, and the filtrate titrated with thiocyanate. In general, the accuracy of the method appears to be unimpaired by the presence of the organic acids which are liberated by the nitric acid from the corresponding salts. When, however, the organic acid is only sparingly soluble in water, it is necessary first to precipitate the acid by addition of nitric acid, followed by extraction with ether or benzene, before proceeding to the chloride estimation.

In the presence of oxalic acid Drechsel's method is not applicable, since this acid reacts with the ferric indicator, and Liebig's method of estimation (*Annalen*, 1851, **77**, 102) was adopted. The sample containing sodium oxalate was added to excess silver nitrate solution and the precipitated silver chloride filtered off, well washed, and then dissolved in ammonia. To the resulting solution was added slight excess of N/20-potassium cyanide, followed by 5 c.c. of 2% potassium iodide solution. This liquid was then titrated against N/100-silver nitrate until a permanent turbidity was produced on stirring.

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