# 183. *Mechanism of Substitution at a Saturated Carbon Atom. Part XVIII. Polar Effect of the Carboxylate Ion Group as illustrated by the Hydrolysis of the Bromomalonate and α-Bromomethylmalonate Ions.*

By Edward D. Hughes and Nazeer Ahmed Ṭaher.

In this paper we show that the hydrolysis, with moderately dilute alkali, of the anions named in the title proceeds by the unimolecular mechanism ($S_N1$), and we thereby complete the evidence establishing a duplexity of mechanism in a series of halides involving an accumulation of carboxylate-ion groups at the seat of substitution, *e.g.*, $\mathrm{R{\cdot}CH_2Br}$, $\mathrm{R{\cdot}CH(C\bar{O}_2)Br}$, $\mathrm{R{\cdot}C(C\bar{O}_2)_2Br}$ (R = H or Me). The position of the mechanistic transition point is dependent on R: when R = H, it occurs between the second and the third member, but when R = Me it is located between the first and the second member, consistently with the known facilitation of the unimolecular mechanism by a methyl substituent.

The main evidence of a unimolecular mechanism for the hydrolysis of the bromomalonate and bromomethylmalonate ions is the insensitivity of their rates to alkali, but there are other indications. Thus the *B*-factors in the equation $k = Be^{-E/RT}$ are of the order $10^{16}$—$10^{17}$ sec.$^{-1}$, and, while this is readily interpretable for a unimolecular reaction, corresponding *B*-values are unusual for bimolecular reactions. The *E*-values are also abnormally large for reactions of this type and recall similar results for the unimolecular decompositions of sulphonium salts (von Halban).

Comparative rates for the unimolecular hydrolysis of the α-bromomethylmalonate, α-bromomalonate, and α-bromopropionate ions show that the methyl and carboxylate-ion substituents increase the rate by factors of about 200 and 30, respectively. The former effect is correlated mainly with a decrease in *E*.

In their discussion of the Walden inversion, Cowdrey, Hughes, Ingold, Masterman, and Scott (J., 1937, 1252) stated that the electron-repelling $C\bar{O}_2$-substituent should (like alkyl substituents) operate against the bimolecular mechanism of hydrolysis (or alcoholysis) of a C-halogen compound,

$$\left.\begin{array}{ll} & \mathrm{H_2O + Alk{\cdot}Hal \longrightarrow H^+ + Alk{\cdot}OH + Hal^-} \\ \text{or} & \mathrm{OH^- + Alk{\cdot}Hal \longrightarrow Alk{\cdot}OH + Hal^-} \end{array}\right\} (S_N2)$$

and favour the incursion of the unimolecular mechanism:

$$\left.\begin{array}{lll} & & \mathrm{Alk{\cdot}Hal \xrightarrow{\text{slow}} Alk^+ + Hal^-} \\ \text{followed by} & \left\{\begin{array}{l} \text{either} \\ \text{or} \end{array}\right. & \begin{array}{l} \mathrm{Alk^+ + H_2O \xrightarrow{\text{fast}} Alk{\cdot}OH + H^+} \\ \mathrm{Alk^+ + OH^- \xrightarrow{\text{fast}} Alk{\cdot}OH} \end{array} \end{array}\right\} (S_N1)$$

In series (1) and (2), for example, the accumulation of carboxylate-ion groups would be expected to lead to a change of mechanism in the sense $S_N2 \longrightarrow S_N1$ :

$$\mathrm{CH_3,\ \ CH_2(C\bar{O}_2),\ \ CH(C\bar{O}_2)_2} \quad . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

$$\mathrm{CH_2Me,\ \ CHMe(C\bar{O}_2),\ \ CMe(C\bar{O}_2)_2} \quad . \ . \ . \ . \ . \ . \ . \quad (2)$$

Although there was a certain amount of evidence of this at the time, it was fragmentary: in particular, little was known of the third members of the two series. It was known that methyl and ethyl halides, the first members of the series, undergo reactions with alkali in alcohol or aqueous alcohol by the bimolecular mechanism, and there was some indirect evidence (which is reinforced in an accompanying paper—this vol., p. 925) that their solvolysis in neutral and acidic solutions proceeds essentially by the same mechanism. The position with regard to the middle members of the series was as follows. The bromoacetate ion (series 1) undergoes hydrolysis in alkaline solution by the bimolecular mechanism, but Dawson's work led to the suggestion that in acid aqueous solution there is a partial incursion of the unimolecular mechanism. [This argument, which is later corrected, was not conclusive, because it was based on a small enhancement of rate, such as is sometimes observed slightly earlier in a series than the point at which actual change of mechanism sets in (Hughes, Ingold, and Shapiro, J., 1936, 225); and also because the rates themselves are too critically sensitive to the approximations implicit in the method of analysis used by Dawson.] The α-bromopropionate ion (series 2) was shown by Cowdrey, Hughes, and Ingold to undergo hydrolysis by a mixture of mechanisms, the bimolecular mechanism predominating in strongly alkaline, and the unimolecular in dilute alkaline, solution.

In order to complete the evidence, and, in particular, to establish the expected change of mechanism in series (1) and (2), we have now undertaken a kinetic examination of the hydrolysis of sodium bromomalonate and of sodium α-bromomethylmalonate in aqueous alkaline solution.

The hydrolysis of sodium bromomalonate has been previously examined by Madsen (*Z. physikal. Chem.*, 1914, **86**, 538), who obtained good first-order rate constants in alkaline aqueous solution at 25·2°. He did not study the effect of variation in the initial concentration of alkali, however, and the evidence relating to the order and mechanism of the reaction was thereby weakened; for the constancy of an integrated velocity constant in one experiment is an insensitive test for purity of kinetic form. The hydrolysis of the α-bromomethylmalonate ion does not appear to have been previously studied.

We found the rate of reaction to be inconveniently slow at 25°, but, by working at two higher temperatures, we have determined the temperature coefficients and can therefore compare our data with those of Madsen. The results are summarised in Table I.

TABLE I.

*Summary of the First-order Rate Constants of the Hydrolysis of Sodium Bromomalonate* (NaBM) *and Sodium α-Bromomethylmalonate* (NaBMeM) *in Aqueous Solution.* (*[Halide]* $\sim$ 0·05M; $k_1$ *in* sec.$^{-1}$.)

| Expt. | Halide. | Initial [NaOH]. | [NaBr]. | Temp. | $10^5k_1$. |
|---|---|---|---|---|---|
| 1 | NaBM* | 0·116 | — | 100·0° | 202 |
| 2 | ,, | 0·243 | — | ,, | 199 |
| 3 | ,, | 1·02 | — | ,, | 370 |
| 4 | ,, | 0·0549 | 0·200 | ,, | 132 |
| 5 | ,, | ,, | 0·500 | ,, | 81·4 |
| 6 | NaBM | 0·0549 | — | 65·3 | 2·22 |
| 7 | NaBMeM | 0·0514 | — | ,, | 435 |
| 8 | ,, | 0·148 | — | ,, | 418 |
| 9 | ,, | 1·01 | — | ,, | 450 |
| 10 | ,, | 0·0514 | — | 35·0 | 5·17 |

* Madsen's result for sodium bromomalonate at 25·2° was $10^5k_1 = 0·00363$; from our results at 65·3° and 100·0° we calculate, for 25·2°, $10^5k_1 = 0·00330$ sec.$^{-1}$.

In each experiment we obtained good first-order constants (cf. experimental section), and, except in the hydrolysis of the bromomalonate ion in concentrated alkaline solution (Expt. 3), the rate is practically the same when the initial alkaline concentration is widely varied (Expts. 1, 2 and 7, 8, 9). The results with added sodium bromide (Expts. 4 and 5) may indicate that an even more marked dependence on the concentration of hydroxide ions than Expt. 3 exhibits is partly masked by a negative salt effect.* It is, however, clear that hydroxide ions in moderately small concentrations take no significant part in controlling the rate of these reactions, and we therefore conclude that they are of the unimolecular type ($S_N1$). We ascribe the substantial increase in the rate of hydrolysis of the bromomalonate ion in the presence of high concentrations of alkali to the incursion of a bimolecular reaction with hydroxide ions ($S_N2$).† The absence of any appreciable increase in the rate of hydrolysis of the α-bromomethylmalonate ion, even under these conditions, is in harmony with our knowledge that alkyl groups stabilise the unimolecular mechanism.

The following is a comparison of rates, and of the parameters of the equation $k = Be^{-E/RT}$:

| | $10^5 k_{65\cdot3°}$ (sec.$^{-1}$). | $E$ (kg.-cals.). | $B$ (sec.$^{-1}$). |
|---|---|---|---|
| Sodium bromomalonate ........................ | 2·22 | 32·54 | $2{\cdot}46 \times 10^{16}$ |
| Sodium α-bromomethylmalonate ............ | 435 | 30·27 | $16{\cdot}2 \times 10^{16}$ |

(If we combine Madsen's rate for sodium bromomalonate at 25·2° with our rate for this substance at 100°, we obtain an $E$-value, 32·30 kg.-cals., in close agreement with that tabulated.)

There are several points of interest in these figures. First, the 200-fold increase of rate produced by the methyl group in the second compound is correlated mainly with a decrease in $E$, but partly also with an increase in $B$. We should expect an idealised energy of activation to be reduced by the electron-releasing methyl group. Secondly the $E$-values, taken together, are considerably greater than those previously found for simple alkyl halides (Hughes, Ingold, and Shapiro, *loc. cit.*; Hughes and Shapiro, J., 1937, 1177; Cooper and Hughes, *ibid.*, p. 1183). Similarly large values have been found by von Halban for the unimolecular, non-solvolytic decompositions of sulphonium salts (*Z. physikal. Chem.*, 1909, **67**, 129), and by workers in these laboratories for corresponding solvolytic reactions of these substances; and now that we have obtained such values for the unimolecular solvolytic reactions of anions, the suggestion presents itself that they may be characteristic for unimolecular decompositions of ionic reactants (concerning the mechanistic similarity of solvolytic and non-solvolytic reactions, cf. the last three papers of this consecutive series). Finally, the $B$-values are abnormally large. Hinshelwood has asserted (*Trans. Faraday Soc.*, 1938, **34**, 105) that correspondingly large values are theoretically improbable for bimolecular reactions, but that large $B$-values are readily interpretable for unimolecular reactions: the distinction will be of interest as an auxiliary indication of mechanism to those who attach such significance to analysis in terms of Arrhenius parameters. The slightly larger $B$-value of the methyl compound fits in with the idea of associating high values with the storage of energy in many degrees of freedom (Hinshelwood, *loc. cit.*; cf. Lewis and Smith, *J. Amer. Chem. Soc.*, 1925, **47**, 1508).

Returning now to a consideration of the carboxylate-ion series discussed on p. 957, we conclude that, for hydrolysis in dilute alkaline solution, a duplexity of mechanism is established in both series (1) and (2) as follows:

$$\begin{array}{cccccc}
\multicolumn{3}{c}{\underbrace{CH_3 \qquad\qquad\qquad CH_2(C\bar{O}_2)}_{S_N2}} & \vdots & \begin{array}{c} CH(C\bar{O}_2)_2 \\ S_N1 \end{array} & (1) \\
\begin{array}{c} CH_2Me \\ S_N2 \end{array} & \vdots & \multicolumn{3}{c}{\underbrace{CHMe(C\bar{O}_2) \qquad\qquad\qquad CMe(C\bar{O}_2)_2}_{S_N1}} & (2)
\end{array}$$

The earlier location of the point of mechanistic change in the second series is consistent with the known facilitation of the unimolecular mechanism by methyl substituents.

---

* Further experiments are needed to show whether the influence of sodium bromide is, at least in part, due to the operation of a mass-law effect (cf. this vol., pp. 960, 979).

† A good first-order rate constant is found in this case because the hydroxide-ion concentration is buffered.

It has been stated in previous papers of this series that a change of mechanism with change of structure may not only be associated with a change in the reaction kinetics, but should also be characterised by certain rather definite variations in the rates of reaction. In the region of the bimolecular mechanism the electron-repelling carboxylate-ion group (like alkyl groups) should decrease the rate of substitution (with possible exceptions, as already mentioned), whereas in the region of the unimolecular mechanism the effect should be an increase. The comparative rates required to test this statement fully are not yet available, but for the unimolecular hydrolysis of the α-bromopropionate and α-bromomethylmalonate ions it is now established that the second carboxylate-ion group in the latter produces a 30-fold increase of rate. The comparative figures ($k_1$ in sec.$^{-1}$) for the hydrolysis in aqueous solution at 64·0° are as follows, the figure for the α-bromopropionate ion being taken from Cowdrey, Hughes, and Ingold's results (J., 1937, 1208), and that for the α-bromomethylmalonate ion being calculated from our results at higher temperatures :

$$\mathrm{CHMe(C\bar{O}_2)Br},\ 10^4k_1 = 1{\cdot}18;\quad \mathrm{CMe(C\bar{O}_2)_2Br},\ 10^4k_1 = 36{\cdot}5.$$

For the hydrolysis of the bromoacetate and bromomalonate ions in aqueous solution at 25°, the following rates (sec.$^{-1}$) are available :

$$\mathrm{CH_2(C\bar{O}_2)Br},\ 10^8k_1 = 5{\cdot}66;\quad \mathrm{CH(C\bar{O}_2)_2Br},\ 10^8k_1 = 3{\cdot}63.$$

The first-order rate for the bromomalonate ion (Madsen, *loc. cit.*) is undoubtedly that of a unimolecular reaction, since we have demonstrated its insensitivity to alkali. The constant for the bromoacetate ion (Brooke and Dawson, J., 1936, 497) may not be accurate, since it emerges as a relatively small difference in a complicated analysis, wherein a completely satisfactory method of allowing for salt effects is difficult to devise; but it is probably of the right order of magnitude, and, on this account alone, having regard to the value for the bromomalonate ion, we draw the provisional conclusion that the solvolytic reaction of the bromoacetate ion is, at least largely, bimolecular.

## EXPERIMENTAL.

*Materials.*—Bromomalonic and α-bromomethylmalonic acids, prepared by well-known methods and crystallised from chloroform, had m. p. 113° (decomp.) and 145° (decomp.), respectively.

*Rate Measurements.*—The thermostats at 35·0°, 65·3°, and 100·0° could be set to within ±0·1°. Portions of 10 c.c. of the reaction mixture containing the halide (~0·05M) in the appropriate aqueous alkaline medium were enclosed in small, thin-walled, glass tubes, which were placed in the thermostat for known times, quickly cooled, and opened. The contents were estimated either by the change in alkalinity of the solution, or by titration with silver nitrate. In the former method, the tubes were broken under about 100 c.c. of ether, and the alkali was titrated with, *e.g.*, 0·1N-hydrochloric acid, phenolphthalein being used as indicator. In the latter method, the tubes were broken under ether as before, and to the contents were added excess of nitric acid, 10 or 20 c.c. (excess) of a standard solution of silver nitrate, and the ferric alum indicator. The excess of silver ions was determined by titration with standard ammonium thiocyanate solution. The first method is suitable for hydrolysis in dilute alkaline solutions in the presence of comparatively large concentrations of halide ions, and the second method is especially applicable to the reactions in concentrated alkaline solutions. For dilute alkaline solutions in the absence of added halide ions either method may be used, and in some experiments both were employed with concordant results. In order to eliminate error due to reaction before the mixtures, which were sealed up at 20°, had reached the temperature of the thermostat, an "initial" estimation was made on a sample which had been shaken in the thermostat for, *e.g.*, 1 minute. The samples used for the other estimations were similarly shaken in the thermostat for the same period, the end of which was taken as the zero of time.

The rate constants, recorded in the tables, are all of the first order and are calculated from the formula $k_1 = (1/t)\log_e\{a/(a - x)\}$, where $a$ is the initial concentration of the halogeno-acid and $x$ the decrease in concentration; $a$ was determined by measuring the asymptotic value of $x$ at large times. The initial concentrations of sodium hydroxide in the various experiments were obtained by titration of the contents of "initial" tubes with standard acid, phenolphthalein being the indicator. The rate constants ($k_1$ in sec.$^{-1}$) are listed in Table I, and some individual runs are illustrated in Table II.

### TABLE II.

*Illustrating Determination of First-order Rate Constants.*

(1) Hydrolysis of sodium bromomalonate in dilute aqueous alkali at 100·0°. $[NaOH]_{t=0}$ = 0·116N. [NaBM] expressed in equivalent c.c. of 0·0500N-$NH_4CNS$ per 10 c.c. sample.

| $t$ (secs.) | 0 | 210 | 300 | 420 | 600 | 780 | 1020 | 1320 |
|---|---|---|---|---|---|---|---|---|
| [NaBM] | 10·10 | 6·75 | 5·50 | 4·25 | 2·95 | 2·15 | 1·22 | 0·70 |
| $10^5k_1$ | — | 192 | 202 | 206 | 205 | 198 | 207 | 202 |

(2) Salt effect in the hydrolysis of sodium bromomalonate in dilute aqueous alkali at 100·0°. $[NaOH]_{t=0}$ = 0·0549N. [NaBr] = 0·500N. [NaBM] expressed in equivalent c.c. of 0·0508N-HCl per 10 c.c. sample.

| $t$ (secs.) | 0 | 300 | 420 | 600 | 780 | 1380 |
|---|---|---|---|---|---|---|
| [NaBM] | 9·40 | 7·35 | 6·68 | 5·78 | 4·98 | 3·05 |
| $10^5k_1$ | — | 81·9 | 81·2 | 81·0 | 81·3 | 81·5 |

(3) Hydrolysis of sodium bromomalonate in concentrated aqueous alkali at 100·0°. $[NaOH]_{t=0}$ = 1·02N. [NaBM] expressed in equivalent c.c. of 0·0500N-$NH_4CNS$ per 10 c.c. sample.

| $t$ (secs.) | 0 | 90 | 210 | 300 | 420 | 600 | 780 | 1020 |
|---|---|---|---|---|---|---|---|---|
| [NaBM] | 10·20 | 7·30 | 4·70 | 3·40 | 2·10 | 1·10 | 0·55 | 0·25 |
| $10^5k_1$ | — | 371 | 368 | 366 | 376 | 371 | 374 | 363 |

(4) Hydrolysis of sodium α-bromomethylmalonate in dilute aqueous alkali at 65·3°. $[NaOH]_{=0}$ = 0·0514N. [NaBMeM] expressed in equivalent c.c. of 0·0466N-$NH_4CNS$ per 10 c.c. sample.

| $t$ (secs.) | 0 | 60 | 120 | 180 | 240 | 330 | 420 | 540 |
|---|---|---|---|---|---|---|---|---|
| [NaBMeM] | 8·70 | 6·70 | 5·12 | 3·95 | 3·05 | 2·10 | 1·40 | 0·85 |
| $10^5k_1$ | — | 435 | 441 | 438 | 436 | 430 | 435 | 430 |

(5) Hydrolysis of sodium α-bromomethylmalonate in concentrated aqueous alkali at 65·3°. $[NaOH]_{t=0}$ = 1·01N. [NaBMeM] expressed in equivalent c.c. of 0·0466N-$NH_4CNS$ per 10 c.c. sample.

| $t$ (secs.) | 0 | 120 | 240 | 330 | 420 | 540 |
|---|---|---|---|---|---|---|
| [NaBMeM] | 8·80 | 5·17 | 3·00 | 1·93 | 1·35 | 0·75 |
| $10^5k_1$ | — | 443 | 448 | 459 | 446 | 455 |

SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C. 1.

[*Received, April* 18*th*, 1940.]