# 53. *Kinetics of the Bromination of Some Enols and Their Anions.*

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The bromination reactions of the enols and enolate ions of dimedone, 2-bromodimedone, 3-methyltetronic acid, 3-bromotetronic acid, methylacetylacetone, and 2-acetylcyclohexanone have been studied kinetically in aqueous solution at 25°. The equilibrium enol contents of these aqueous solutions have been measured, and acid dissociation constants determined for dimedone, 3-methyltetronic acid, and 3-ethyltetronic acid. All the velocity constants measured fall in the range $5 \times 10^6$—$2 \times 10^7$ l. mole$^{-1}$ sec.$^{-1}$, and for four of the compounds there appears to be little difference between the reactivities of the enols and their anions. An explanation is suggested for the abnormally low reactivity of these anions.

The rate of halogenation of keto-compounds in aqueous solutions is commonly of zero order with respect to the halogen, being determined by the rate of enolization or ionization of the keto-compound. Work in this laboratory [1-4] has shown that, if very low halogen concentrations (down to $10^{-7}$M) are employed, the reactions become first order in halogen, and the velocity constants for the reaction of halogens with enol or enolate ion can be deduced, provided that the equilibrium constants for enolization and ionization are known; these were such that only a very small fraction of the keto-compound was present as the enol or enolate ion under experimental conditions. The velocity constants obtained were in the range $10^4$—$10^6$ and $10^9$—$10^{11}$ l. mole$^{-1}$ sec.$^{-1}$ for the halogenation of enols and enolate ions, respectively, and similar values were obtained [5,6] by indirect methods involving reversible halogenations. The main uncertainties in these values arise from the equilibrium constants for enolization or ionization, which are often difficult to estimate.

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[1] Bell and Spiro, *J.*, 1953, 429.
[2] Bell and Rawlinson, *J.*, 1961, 726.
[3] Bell and Yates, *J.*, 1962, 2285; Yates and Wright, *Canad. J. Chem.*, 1963, **41**, 2882.
[4] Bell and Davis, *J.*, 1964, 902.
[5] Bell and Engel, *J.*, 1957, 247.
[6] Bell and Vogelsong, *J.*, 1958, 243.

Recent developments in the determination of low halogen concentrations by measurement of redox potentials [7] have made it possible to determine directly velocity constants as high as $10^7$ l. mole$^{-1}$ sec.$^{-1}$. It should therefore be possible to make kinetic measurements on compounds whose solutions contain a considerable and accurately known proportion of enol or enolate ion, thus avoiding uncertainties connected with the equilibrium constants. The present Paper reports measurements on the bromination of six compounds of this kind, together with results for the bromination of 2,4-dinitrophenol and methyl methanetricarboxylate, which serve to test the experimental method and to confirm and extend earlier work.[2,8]

## EXPERIMENTAL

Dimedone (5,5-dimethylcyclohexane-1,3-dione), twice recrystallized from water, had m. p. 149°. 2-Bromodimedone, prepared [9] from dimedone and bromine, and recrystallized twice from 5% ethanol–water, had m. p. 174°. 3-Bromotetronic acid (3-bromofuran-2,4-dione), prepared [10] from acetoacetic ester and bromine, and recrystallized from ethyl acetate (charcoal), formed fine white crystals, m. p. 182—183°. 3-Methyltetronic acid, prepared [11] from α-methylacetoacetic ester and bromine, and recrystallized several times from water, had m. p. 189°. To obtain 3-ethyltetronic acid, α-ethylacetoacetic ester was brominated [11] and the crude ethyl 4-bromo-2-ethyl-3-oxobutanoate cyclized; [12] m. p. 126—126·5° after two recrystallizations from water. Methylacetylacetone (3-methylpentane-2,4-dione) was prepared [13] from acetylacetone and methyl iodide. 2-Acetylcyclohexanone was redistilled, b. p. 105—106°/17 mm. Methyl methanetricarboxylate [13] had m. p. 43°. Inorganic reagents were of AnalaR quality, and water was redistilled from potassium permanganate in a glass still.

*Measurements of Enol Content.*—The equilibrium enol contents of dilute aqueous solutions of dimedone, 2-bromodimedone, 3-methyltetronic acid, 3-bromotetronic acid, and methylacetylacetone were determined by adding a small volume of the solution to a dilute aqueous bromine solution and measuring the initial rapid disappearance of bromine by observing the change in redox potential at a platinum gauze electrode. The solutions used were 0·1M in perchloric acid, to avoid the presence of appreciable amounts of enolate ion, and errors due to the conversion of the keto-form into enol (relevant only for methylacetylacetone) were avoided by keeping the duration of an experiment to less than 5 sec.

The apparatus used was that employed previously [14] for kinetic measurements, with a glass electrode as reference electrode, and the potentials were measured with a Radiometer valve potentiometer. The solutions of carbonyl compounds were allowed to stand overnight at 25° to ensure equilibrium. All solutions were 0·1M in both perchloric acid and sodium bromide in order to simplify the interpretation of the observed potentials. The bromine concentrations

TABLE 1.

Enol content of carbonyl compounds in aqueous solution at 25°.

| Compound | No. of expts. | % Enol (this work) | % Enol (previous work) |
|---|---|---|---|
| Dimedone | 3 | 93 | 95 (ref. 15) |
| 2-Bromodimedone | 3 | 98 | 80 (ref. 17) |
| 3-Methyltetronic acid | 2 | 98 | 100 (ref. 18) |
| 3-Bromotetronic acid | 4 | 98 | — — |
| Methylacetylacetone | 6 | 4·1 | 3·6, 3·1 (refs. 19—21) |

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[7] Atkinson and Bell, *J.*, 1963, 3260.
[8] Bell and Rawlinson, *J.*, 1961, 63.
[9] Voitila, *Ann. Acad. Sci. Fennicae*, 1938, *A*, **49**, No. 1, 110.
[10] Kumler, *J. Amer. Chem. Soc.*, 1938, **60**, 859.
[11] Wolff, *Annalen*, 1895, **288**, 1.
[12] Reid, Fortenbaugh, and Paterson, *J. Org. Chem.*, 1950, **15**, 572.
[13] *Org. Synth.*, 1933, **13**, 100.
[14] Bell and Robinson, *Proc. Roy. Soc.*, 1962, *A*, **270**, 411.
[15] Schwarzenbach and Felder, *Helv. Chim. Acta*, 1944, **27**, 1044, 1071.
[16] Crossley and Le Sueur, *J.*, 1903, **83**, 110.
[17] Arndt, Loewe, and Ginkok, *Rev. Fac. Sci. Univ. Istanbul*, 1946, *A*, **11**, 147.
[18] Henecka, quoted in ref. 26.
[19] Nachod, *Z. phys. Chem.*, 1938, *A*, **182**, 193.
[20] Long and Watson, *J.*, 1958, 2019.
[21] Pearson and Mills, *J. Amer. Chem. Soc.*, 1950, **72**, 1692.

were in the range $10^{-5}$—$10^{-6}$M, and the kinetic measurements described below show that under these conditions the reaction with enol is virtually complete in less than 1 sec. After recording of the potential before and after the addition of the enol solution, the electrode system was calibrated by adding a drop of pure bromine to the solution and measuring the potential once more, after which the bromine concentration (usually about $10^{-3}$M) is determined by adding potassium iodide and titrating the liberated iodine with thiosulphate solution. Since the concentrations of hydrogen and bromide ions have been kept constant, the last two measurements serve to determine $E_0'$ in the equation $E = E_0' + 0{\cdot}02958 \log [\mathrm{Br_2}^*]$, where $[\mathrm{Br_2}^*]$ is the sum of the concentrations of molecular bromine and tribromide ion. The amount of bromine consumed by the enol can then be calculated from the first two measured potentials.

The results are given in Table 1. It has been shown [15] that the initial product in the bromination of dimedone, the keto-form of 2-bromodimedone, is converted rapidly into the enol form, which then reacts rapidly with a second molecule of bromine; the enol content of dimedone has therefore been calculated by halving the bromine consumption. Crystals of 2-bromodimedone dried in air (as in the present work) have been reported [16] to consist of the monohydrate, and the percentage of enol has been calculated on this basis.

*Measurements of Dissociation Constants.*—The acid dissociation constants of the keto-compounds studied have all been measured previously, in most instances by a pH-titration method. Since compounds of this class readily undergo cleavage in alkaline solution,[10,22] it was thought desirable to check some of the values by conductivity measurements.

Conductivity measurements were made at 25 ± 0·01° with a Tinsley bridge (type 4896) at 1000 c./sec. and were reproducible to better than 0·1%. The thermodynamic dissociation constant $K_a$ was derived [23] from the observed value of $\Lambda/\Lambda_0$. The limiting equivalent conductance of each anion was taken as 30 ohm$^{-1}$ eq.$^{-1}$ cm.$^2$; reasonable variations in this value have little effect on the value of p$K_a$ obtained, and do not remove the slight trend of p$K_a$ with concentration observed with all three substances. The values of p$K_a$ extrapolated to infinite dilution are in good agreement with the most reliable previous values. The results are given in Table 2.

TABLE 2.

Conductivities and dissociation constants at 25°.

| | *Dimedone* | | | | | 3-*Methyltetronic acid* | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | p$K_a$ (extrap.) = 5·27 (lit.,[24] 5·25) | | | | | p$K_a$ (extrap.) = 4·15 (lit., 3·6,[25] 4·1 [26]) | | | | |
| $10^6$m ... | 65·0 | 133 | 300 | 649 | 1662 | 76·6 | 146 | 327 | 532 | 950 |
| $10/\Lambda/\Lambda_0$ | 869 | 621 | 430 | 301 | 184 | 2692 | 2040 | 1437 | 1145 | 887 |
| p$K_a$ ...... | 5·27 | 5·27 | 5·24 | 5·23 | 5·23 | 4·15 | 4·13 | 4·12 | 4·11 | 4·11 |

3-*Ethyltetronic acid* p$K_a$ (extrap.) = 4·15 (previous value,[25] 4·1)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $10^6$m ... | 67·2 | 76·8 | 123 | 124 | 217 | 253 | 539 | 1305 | 1454 |
| $10/\Lambda/\Lambda_0$ | 2790 | 2664 | 2186 | 2191 | 1753 | 1617 | 1157 | 797 | 740 |
| p$K_a$ ... | 4·15 | 4·15 | 4·13 | 4·13 | 4·12 | 4·12 | 4·11 | 4·07 | 4·09 |

*Kinetic Measurements.*—The experimental method was essentially that of Atkinson and Bell.[7] The bromide ion concentration was 0·1M unless otherwise stated. In experiments with enols no attempt was made to distinguish between the reactivities of molecular bromine and tribromide ion, since the experiments with 3-methyltetronic acid at different bromide ion concentrations (cf. Table 5) revealed no difference between these two species; the velocity constants reported refer to the sum of the concentrations $[\mathrm{Br_2}] + [\mathrm{Br_3}^-]$.

In order to test the method, the bromination of 2,4-dinitrophenol was studied over a wide range of acidity; previous measurements had been made [8] over a narrower range. At the two highest acidities a large excess of the phenol could be used, and the reactions followed a first-order course. At pH 3 a small excess of bromine was used and second-order kinetics were obeyed; the exact phenol concentration was calculated from the initial and final potentials.[7] The experiments at pH 5 required a special procedure. The platinum electrode was replaced by a calomel electrode, and dilute perchloric acid solution was added to 0·1M-sodium bromide solution in the reaction vessel until a pH of *ca.* 5 was recorded. The platinum electrode

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[22] Pearson and Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

[23] Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 1955, p. 332.

[24] Schwarzenbach and Lutz, *Helv. Chim. Acta*, 1940, **23**, 1147, 1162.

[25] Chopra, Cocker, Cross, Edward, Hayes, and Hutchinson, *J.*, 1955, 588.

[26] Eistert and Reiss, *Chem. Ber.*, 1954, **87**, 108.

was replaced, and bromine solution added until the redox potential indicated the desired bromine concentration. The pH of this solution was recorded, and the kinetic experiment carried out as usual; pH measurements at the conclusion of the experiment showed that there had been no appreciable change of acidity during the reaction. There was, however, a significant decrease of pH when liquid bromine was added to the system in order to determine $E_0'$, and dilute sodium hydroxide solution was therefore added at this stage until the pH was close to the value obtaining in the kinetic experiment. Any small difference remaining was allowed for in calculating $E_0'$.

The results are given in Table 3. It had been found [8] that only the dinitrophenoxide ion showed any detectable reactivity towards bromine and tribromide ion, and the velocity constants [8] yield the following expression for the observed second-order velocity constant $k$ when $[\mathrm{Br}^-] = 0{\cdot}1$:

$$k = 4{\cdot}0 \times 10^5 K_a/(K_a + f_\pm^2[\mathrm{H}^+]), \qquad (1)$$

where $K_a$ is the thermodynamic dissociation constant of 2,4-dinitrophenol ($8{\cdot}4 \times 10^{-5}$).[27] In the experiments with $[\mathrm{H}^+] = 0{\cdot}1$, the ionic strength $I = 0{\cdot}2$, and we have taken $f_\pm = 0{\cdot}778$, the value for 0·2M-perchloric acid. In the remaining experiments $I = 0{\cdot}1$, and we have taken $f_\pm = 0{\cdot}805$ (the value for 0·1M-hydrogen bromide); the same value was used in converting the observed pH to hydrogen ion concentration in the solutions of lowest acidity. The last column in Table 3 gives the velocity constants calculated from eqn. (1). The agreement with experiment is good, showing that the experimental method is valid over a wide range of conditions.

TABLE 3.

Bromination of 2,4-dinitrophenol at 25°.

$[\mathrm{Br}^-] = 0{\cdot}1$ throughout; $k$ = observed velocity constant (l. mole$^{-1}$ sec.$^{-1}$).

| $[\mathrm{H}^+]$ | $10^8[\mathrm{Br}_2^*]$ | $10^7$[phenol] | $k$ (obs.) | $k$ (calc.) |
|---|---|---|---|---|
| $10^{-1}$ | 24·0 | 173 | $6{\cdot}6 \times 10^2$ | $6{\cdot}7 \times 10^2$ |
| $10^{-1}$ | 10·6 | 173 | $6{\cdot}9 \times 10^2$ | $6{\cdot}7 \times 10^2$ |
| $10^{-2}$ | 24·9 | 234 | $5{\cdot}4 \times 10^3$ | $6{\cdot}3 \times 10^3$ |
| $10^{-2}$ | 16·0 | 243 | $5{\cdot}3 \times 10^3$ | $6{\cdot}3 \times 10^3$ |
| $10^{-3}$ | 559 | 35·5 | $5{\cdot}5 \times 10^4$ | $5{\cdot}6 \times 10^4$ |
| $10^{-3}$ | 414 | 29·1 | $5{\cdot}8 \times 10^4$ | $5{\cdot}6 \times 10^4$ |
| $10^{-3}$ | 554 | 33·5 | $5{\cdot}6 \times 10^4$ | $5{\cdot}6 \times 10^4$ |
| $1{\cdot}3 \times 10^{-5}$ | 22·7 | 1·44 | $4{\cdot}1 \times 10^5$ | $4{\cdot}5 \times 10^5$ |
| $1{\cdot}3 \times 10^{-5}$ | 26·4 | 1·44 | $4{\cdot}5 \times 10^5$ | $4{\cdot}5 \times 10^5$ |

2-Bromodimedone, 3-bromotetronic acid, and 3-methyltetronic acid exist almost entirely in the enol form in aqueous solution and were studied by the usual second-order procedure. The initial reactant concentrations were in the range $7 \times 10^{-9}$ to $4 \times 10^{-8}$M, and a small excess of bromine was used. It was sometimes necessary to adjust the final e.m.f. slightly to obtain a linear second-order plot, but this adjustment never exceeded 0·4 mv. The velocity constants obtained are given in Table 5.

The bromination of dimedone involves two consecutive stages, and was analysed kinetically according to the scheme:

$$\text{Dimedone } (a - x) + \text{bromine } (b - x - y) \xrightarrow{k_1} \text{2-bromodimedone } (x - y)$$

$$\text{2-Bromodimedone } (x - y) + \text{bromine } (b - x - y) \xrightarrow{k_2} \text{dibromodimedone } (y)$$

where the 2-bromodimedone, initially formed in the keto-form, is transformed very rapidly into the enol form. The experimental data were treated by the method developed by Widequist.[28] By introducing the substitutions,

$$z = x + y, \quad \phi = \int_0^t (b - z)\,\mathrm{d}t, \qquad (2)$$

the differential equations representing the above scheme can be solved, to give

$$x/a = 1 - \mathrm{e}^{-k_1\theta}$$
$$z/a = \{2(k_1 - k_2) + (2k_2 - k_1)\mathrm{e}^{-k_1\theta} - k_1\mathrm{e}^{-k_2\theta}\}/(k_1 - k_2). \qquad (3)$$

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[27] Bale and Monk, *Trans. Faraday Soc.*, 1957, **53**, 450.

[28] Widequist, *Arkiv Kemi*, 1955, **8**, 545.

Since $b - z$ is the bromine concentration at any instant, the values of $\phi$ corresponding to particular values of $t$ (and hence of $z$) in a given experiment can be obtained by graphical integration. For selected values of $\phi$ the quantity $z/a$ was calculated from eqn. (3), using a trial value of $k_1$ and, as a first approximation, the value of $k_2$ (appropriate to the experimental conditions) obtained from the measurements on the bromination of 2-bromodimedone. The calculated values of $z/a$ were compared with the experimental ones; the deviations were used to select a new value of $k_1$ and the calculations repeated. After several iterations the calculated and observed values of $z/a$ showed fair agreement, and at this point both $k_1$ and $k_2$ were treated as adjustable constants and the curve-fitting procedure repeated until concordant values of $z/a$ were obtained. The degree of concordance finally attained is illustrated (Table 4) for a typical experiment.

TABLE 4.

Bromination of dimedone at 25°.

Initial concentrations: [Dimedone] $= 7\cdot05 \times 10^{-9}$, $[\mathrm{Br}_2] = 2\cdot31 \times 10^{-8}$, $[\mathrm{H}^+] = 10^{-3}$, $[\mathrm{Br}^-] = 0\cdot10$.
Calculated values of $z/a$ from eqn. (3), with $k_1 = 1\cdot0 \times 10^{-7}$ l. mole$^{-1}$ sec.$^{-1}$, $k_2 = 6\cdot5 \times 10^6$ l. mole$^{-1}$ sec.$^{-1}$; $\phi$ is in mole l.$^{-1}$ sec.

| $10^7\phi$ | 0·2 | 0·4 | 0·6 | 0·8 | 1·0 | 1·2 | 1·4 | 1·6 |
|---|---|---|---|---|---|---|---|---|
| $z/a$ obs. | 0·202 | 0·374 | 0·535 | 0·688 | 0·820 | 0·942 | 1·058 | 1·161 |
| $z/a$ calc. | 0·193 | 0·372 | 0·536 | 0·686 | 0·824 | 0·948 | 1·061 | 1·163 |

| $10^7\phi$ | 1·8 | 2·0 | 2·2 | 2·4 | 2·6 | 2·8 | 3·0 |
|---|---|---|---|---|---|---|---|
| $z/a$ obs. | 1·255 | 1·331 | 1·404 | 1·471 | 1·531 | 1·581 | 1·629 |
| $z/a$ calc. | 1·255 | 1·337 | 1·411 | 1·477 | 1·536 | 1·589 | 1·636 |

Aqueous solutions of methylacetylacetone and 2-acetylcyclohexanone contain considerable quantities of the keto-form, and it is necessary to take into account its slow transformation into the enol. In the acid solutions used in these experiments the concentration of enolate ion is negligible, and the kinetic scheme is:

$$\text{Keto } (a - x) \xrightarrow{k_1} \text{enol } (b + x - y)$$

$$\text{Enol } (b + x - y) + \text{bromine } (c - y) \xrightarrow{k} \text{product } (y)$$

where $a$, $b$, and $c$ are the initial concentrations of keto, enol, and bromine, respectively. For the time intervals studied $a \gg x$, and hence $x = k_1at$. Introducing a function $\theta$ defined by

$$\theta = \int_0^t (b + x - y)\,\mathrm{d}t = \int_0^t (b + k_1at - y)\,\mathrm{d}t = bt + \tfrac{1}{2}k_1at^2 - \int_0^t y\,\mathrm{d}t \qquad (4)$$

the reaction scheme gives the equation

$$\ln (c - y) = -k\theta + \text{constant}. \qquad (5)$$

The values of $a$ and $b$ are given by the initial concentration of ketone and the equilibrium percentage of enol; the latter is 4·1% for methylacetylacetone (Table 1) and 29% for 2-acetylcyclohexanone.[15,29] Earlier measurements at higher bromine concentrations gave $k_1 = 9\cdot60 \times 10^{-5}$ sec.$^{-1}$ for methylacetylacetone [20] and $3\cdot96 \times 10^{-4}$ sec.$^{-1}$ for 2-acetylcyclohexanone.[29] Since the bromine concentration $c - y$ can be derived from the observed e.m.f. as before, $\theta$ can be evaluated (the last term by graphical integration), and $k$ determined from a plot of $\ln (c - y)$ against $\theta$. The values obtained are given in Table 5.

The bromination of methyl methanetricarboxylate has been previously studied [8] over a range of concentrations of hydrogen ion and bromide ion with initial bromine concentrations of about $10^{-5}$M. It was concluded that the halogenation step was completely rate-determining, and velocity constants were given for the reactions of enol and enolate ion with molecular bromine and tribromide. The conclusion was based on the observation that the reactions appeared to be strictly first-order in halogen, and on an estimate of the rate of ionization of the ester derived from its p$K$. Since the latter estimate appears to have been incorrect, we have re-investigated the reaction at both high and low bromine concentrations.

At the higher bromine concentrations (about $10^{-3}$M) it is inconvenient to follow the reaction by measuring the redox potential, since changes in the concentrations of hydrogen and bromide

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[29] Long and Riley, *J. Amer. Chem. Soc.*, 1962, **84**, 522.

TABLE 5.

Summary of kinetic results.

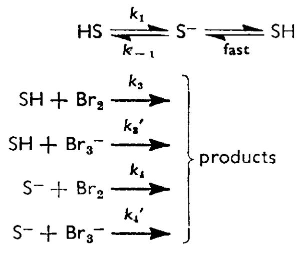
$k$ = second-order velocity constant (l. mole$^{-1}$ sec.$^{-1}$).
$[Br^-]$ = 0·10 unless otherwise stated. The errors given represent the standard deviation of a single experiment.

| | Expts. | $[H^+]$ | $10^{-6}k$ |
|---|---|---|---|
| *Dimedone* (p$K$ = 5·27) | 15 | 0·100 | 22 ± 2 |
| | 10 | 0·050 | 20 ± 3 |
| | 15 | 0·020 | 22 ± 4 |
| | 29 | 0·001 | 11 ± 1 |
| *2-Bromodimedone* (p$K$ = 3·2) | 25 * | 0·100 | 8·5 ± 0·5 |
| | 15 † | 0·100 | 8·5 ± 0·6 |
| | 10 † | 0·050 | 11·5 ± 0·7 |
| | 15 † | 0·020 | 14·0 ± 3·0 |
| | 28 * | 0·010 | 11·5 ± 0·7 |
| | 33 * | 0·005 | 7·0 ± 0·9 |
| | 23 * | 0·002 | 6·5 ± 0·4 |
| | 29 * | 0·001 | 5·8 ± 0·4 |
| | 29 † | 0·001 | 6·5 ± 1·3 |
| *3-Methyltetronic acid* (p$K$ = 4·15) | 15 | 0·100 | 6·9 ± 0·6 |
| | 17 ‡ | 0·100 | 6·2 ± 0·4 |
| | 6 § | 0·100 | 6·3 ± 0·4 |
| | 13 | 0·010 | 9·2 ± 0·7 |
| | 12 | 0·001 | 6·8 ± 0·5 |
| | 5 | $1·2 \times 10^{-5}$ | 5·9 ± 0·3 |
| *3-Bromotetronic acid* (p$K$ = 2·23) | 9 | 0·100 | 7·2 ± 0·4 |
| | 4 | 0·010 | 7·1 ± 0·2 |
| *Methylacetylacetone* (p$K$ = 11·0) | 7 | 0·100 | 5·0 ± 0·5 |
| *2-Acetylcyclohexanone* (p$K$ = 10·0) | 8 | 0·100 | 8·3 ± 0·9 |

* From direct measurements. † From measurements on dimedone. ‡ $[Br^-]$ = 0·20. § $[Br^-]$ = 0·30.

ions affect the potentials of the glass and platinum electrodes. The method used was to follow the pH with the glass electrode, a calomel electrode being used as reference electrode. Typical initial concentrations were $10^{-3}$M-bromine, 0·1M-bromide, $10^{-3}$M-perchloric acid, and $10^{-3}$M-ester. The measured pH was converted to hydrogen ion concentration by assuming $f_{\pm}$ = 0·805, the value for 0·1M-hydrobromic acid. If the reaction is of zero order with respect to bromine, the increase in hydrogen ion concentration (which is equivalent to the decrease in ester concentration) should follow a first-order law. This was found to be the case, and three experiments under similar conditions gave $k_1$ = 0·109, 0·109, and 0·108 sec.$^{-1}$. This is consistent with p$K$ = 7·84 for methyl methanetricarboxylate [8] on the basis of the approximate relationship previously pointed out [22,30] between the acidity of ketonic substances and their rates of ionization. It is about a hundred times smaller than the value estimated by Bell and Rawlinson,[8] who probably confused log $k_1$ = −1 with log $k_1$ = +1.

Measurements were made by the usual redox potentiometric method, at low bromine concentrations ($10^{-6}$—$10^{-7}$M), in solutions $10^{-1}$, $10^{-2}$, and $10^{-3}$M in perchloric aid, and in a buffer solution 0·008M in acetic acid and 0·002M in sodium acetate, in which $[H^+] = 1·1 \times 10^{-4}$. The kinetic scheme is



where HS and SH represent the keto and enol forms, respectively. The equilibrium proportion of enol in aqueous solutions of methyl methanetricarboxylate is only about 0·5 %, and the

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[30] Bell, " The Proton in Chemistry," Methuen, London, 1959, p. 140.

proportion of enolate ion even smaller at the acidities investigated. The above reaction scheme then leads to the equation

$$-\frac{1}{[\mathrm{HS}]}\frac{\mathrm{d}[\mathrm{HS}]}{\mathrm{d}t} = -\frac{1}{[\mathrm{HS}]}\cdot\frac{\mathrm{d}[\mathrm{Br}_2^*]}{\mathrm{d}t} = \frac{k_1k'[\mathrm{Br}_2^*]}{k'[\mathrm{Br}_2^*] + k_1}, \qquad (6)$$

where $[\mathrm{Br}_2^*] = [\mathrm{Br}_2] + [\mathrm{Br}_3^-]$, and $k'$ is given by

$$k'(1 + K[\mathrm{Br}^-]) = k_3K_{\mathrm{E}} + k_3'K_{\mathrm{E}}K[\mathrm{Br}^-] + k_4K_{\mathrm{HS}}/[\mathrm{H}^+] + k_4'K_{\mathrm{HS}}K[\mathrm{Br}^-]/[\mathrm{H}^+], \qquad (7)$$

in which $K_{\mathrm{E}}$ is the equilibrium proportion of enol, $K_{\mathrm{HS}}$ the acid dissociation constant of the keto-form, and $K$ the equilibrium constant $[\mathrm{Br}_3^-]/[\mathrm{Br}_2][\mathrm{Br}^-]$. If, as in the present experiments, the concentration of bromide ion is kept constant throughout, eqn. (7) can be written in the form

$$k' = k_3''K_{\mathrm{E}} + k_4''K_{\mathrm{HS}}/[\mathrm{H}^+] \qquad (8)$$

where $k_3''$ and $k_4''$ are average velocity constants for the reaction of $Br_2$ and $Br_3^-$ with the enol and with the enolate ion, respectively.

In the experiments with 0·1M- and 0·01M-perchloric acid (cf. Table 6) the ester was in large excess with respect to the bromine, and the e.m.f. decreased linearly with time, indicating that the reaction is of the first order with respect to bromine. This is consistent with the fact that the apparent second-order constant $k'$ for the reaction between bromine and ester (obtained from the slope of the e.m.f.–time plot) satisfies the relationship $k'[\mathrm{Br}_2^*] \ll k_1$, which is the condition that eqn. (6) should reduce to the simple second-order form.

The experiments at $[\mathrm{H}^+] = 10^{-3}$ and $10^{-4}$ involved similar initial concentrations of bromine ($a$) and of ester ($b$), and the plots of $\log\{(a - x)/(b - x)\}$ against time showed no marked deviations from linearity. However, the values of $k'$ thus obtained did not satisfy the condition $k'[\mathrm{Br}_2^*] \ll k_1$, and in order to obtain the true value of $k'$ it is necessary to use the integrated form of eqn. (6). This is

$$\log\{(a - x)/(b - x)\} = k'(a - b)\{0{\cdot}434t + (1/k_1)\log(b - x)\} + \text{const.}, \qquad (9)$$

and the value of $k'$ was determined from the linear plot of $\log\{(a - x)/(b - x)\}$ against $0{\cdot}434t + (1/k_1)\log(b - x)$. In the experiments in $10^{-3}$M-perchloric acid $k_1 = 0{\cdot}109$ sec.$^{-1}$, from the results at higher bromine concentrations. In the acetate buffer solution $k_1$ will be somewhat higher because of proton-transfer to acetate ions. No experimental data are available for the rate of the latter process, but we have estimated $k_1 = 0{\cdot}13$ sec.$^{-1}$ in 0·002M-sodium acetate by analogy with the relative effectiveness of acetate ion and water as bases in the ionization of methylacetylacetone [20] and 2-acetylcyclohexanone.[29] Partly because of this uncertainty, and partly because of the high velocities involved, the value obtained for $k'$ in this solution is less certain than those for the perchloric acid solutions.

The calculated values of $k'$ in Table 6 are from eqn. (8) with $k_3'' = 1{\cdot}4 \times 10^4$ l. mole$^{-1}$ sec.$^{-1}$, $k_4'' = 3{\cdot}0 \times 10^9$ l. mole$^{-1}$ sec.$^{-1}$. The values calculated from the constants given by Bell and Rawlinson [8] are $3{\cdot}0 \times 10^4$ and $4{\cdot}0 \times 10^9$, respectively.

TABLE 6.

Bromination of methyl methanetricarboxylate.

p$K$ = 7·84; $k'$ = apparent second-order velocity constant (l. mole$^{-1}$ sec.$^{-1}$); concentrations are initial ones.

| $[\mathrm{H}^+]$ | $10^7[\mathrm{Br}_2^*]$ | $10^7$[Ester] | $k'$(obs.) | $k'$(calc.) |
|---|---|---|---|---|
| 0·10 | 4·85 | 322 | $5{\cdot}0 \times 10^2$ | $4{\cdot}9 \times 10^2$ |
| 0·10 | 7·30 | 463 | $5{\cdot}1 \times 10^2$ | $4{\cdot}9 \times 10^2$ |
| 0·010 | 5·11 | 105 | $3{\cdot}9 \times 10^3$ | $4{\cdot}3 \times 10^3$ |
| 0·010 | 4·90 | 174 | $3{\cdot}7 \times 10^3$ | $4{\cdot}3 \times 10^3$ |
| 0·0010 | 29·0 | 20·1 | $3{\cdot}9 \times 10^4$ | $4{\cdot}2 \times 10^4$ |
| 0·0010 | 28·1 | 19·4 | $4{\cdot}3 \times 10^4$ | $4{\cdot}2 \times 10^4$ |
| 0·00011 | 10·9 | 7·24 | $5{\cdot}7 \times 10^5$ | $3{\cdot}8 \times 10^5$ |
| 0·00011 | 10·6 | 7·29 | $5{\cdot}4 \times 10^5$ | $3{\cdot}8 \times 10^5$ |

## DISCUSSION

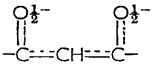
The bromination of methylacetylacetone and 2-acetylcyclohexanone was studied only in 0·1N-perchloric acid, and both of these compounds are such weak acids (p*K* 10—11) that no significant concentrations of anion can be present in these solutions. The velocity constants in Table 5 therefore refer to the enol, and are of the same order of magnitude as those found previously for the reaction of bromine and tribromide ion with the enols of acetone [3,4] and of diethyl malonate.[1,2] In the bromination of methyl methanetricarboxylate (Table 6) the rate increases rapidly with increasing pH, and can be mainly attributed to the anion. The rate constant for the enol is not well established, since it makes only a small contribution to the observed rate, and the equilibrium proportion of enol is not known accurately; however, it appears to be lower than those for the other enols.

The results for the first four compounds in Table 5 show some surprising features. Although the Papers quoted in the introduction (and our own results with methyl methanetricarboxylate) indicate that enolate ions react about $10^5$ times as fast as enols with halogenating agents, the rate constants in Table 5 show no systematic variation with pH, even in solutions which must contain a large proportion of anions. (There are some unexplained variations which are certainly greater than the experimental error, but no consistent increase of velocity with increasing pH.) This is particularly striking for 3-methyltetronic acid, where a change in the degree of dissociation from 0·07 to 86% has no effect upon the rate of reaction. It is also remarkable that the velocity constants for the six compounds in Table 5 all lie with the range $5 \times 10^6$ to $22 \times 10^6$, although they comprise both β-diketones and β-keto-lactones, two of them with bromo-substitution.

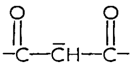
The simplest explanation of the above facts is that the reactions of both the enol and its anion with bromine are mainly controlled by the rate at which the reactants can diffuse together. This does not necessarily imply that the enol and the anion have fundamentally the same chemical reactivity, since, provided that they both react with bromine during the duration of an encounter (10—100 collisions), the observed reaction velocity will be the same. Moreover, since there is a highly mobile equilibrium between enol, solvents, and enolate ions, a given enol molecule (although less reactive itself) is extremely likely to become an enolate ion at some stage during its encounter with a bromine molecule, and hence to react. It has been shown[31] that even for the fastest conceivable reactions in solution the observed rate cannot depend solely on the rate of diffusion. This effect, together with differences in diffusion coefficients, might account for the minor variations in rate between different compounds in Table 5, and with hydrogen ion concentration.

There are, however, some difficulties connected with this interpretation. In the first place, the constants in Table 5, averaging $10^7$ l. mole$^{-1}$ sec.$^{-1}$, are about two powers of ten smaller than the value expected for a diffusion-controlled reaction between fairly large molecules in aqueous solution. This discrepancy seems too large to be explained by any steric requirements. A further serious difficulty is that a number of previous investigations,[1-6] including that of methyl methanetricarboxylate in the present Paper, have attributed to the reactions of enolate ions with halogens velocity constants in the range $10^9$—$10^{11}$ l. mole$^{-1}$ sec.$^{-1}$, *i.e.*, equal to or greater than the estimated value for diffusion control.

It therefore seems likely that the enolate ions which we have investigated do in fact have an abnormally low reactivity, differing little from that of the enol itself. The first four compounds in Table 5 all contain the β-diketone system as part of a ring, and their



$$-\overset{\overset{O^{\frac{1}{2}-}}{\|}}{C}\!\!\;{=}\!{=}\!{=}\;CH\;{=}\!{=}\!{=}\;\overset{\overset{O^{\frac{1}{2}-}}{\|}}{C}- \quad \text{(I)}$$



$$-\overset{\overset{O}{\|}}{C}-\overset{-}{C}H-\overset{\overset{O}{\|}}{C}- \quad \text{(II)}$$

high acidities compared with other β-diketones suggest that some special factor contributes

[31] Noyes, *Progr. Reaction Kinetics*, **1961**, **1**, 137.

to the stabilization of the enolate ion. The planar structure (I) will be particularly compatible with the ring, and by the same token the non-planar structure (II), which will be susceptible to electrophilic attack, will play a small part; thus, the anion may be similar in reactivity to the enol.

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