87. *The Mechanism of the Bromination of Ethyl Malonate.*

By R. P. BELL and M. SPIRO.

The kinetics of the base-catalysed bromination of ethyl malonate have been studied in aqueous solutions at 25° over the pH range 1·7—4·5 and with bromine concentrations of 10^{-4}—10^{-3}M. In this range the velocity varies with bromine concentration, and is thus no longer determined solely by the rate of ionization or enolization of the ester. The variation of rate with bromine concentration and with pH can be accounted for quantitatively by supposing that both the anion and the enol react with bromine. The main brominating species is molecular bromine, but there is a small contribution from the less active species Br_3^- and HOBr. At pH >3 most of the bromination takes place through the anion, while at pH <3 the enol is more important. Absolute rate constants are estimated for the bromination reactions. Bartlett and Vincent's results for the chlorination of ketones in alkaline hypochlorite have been re-interpreted, and estimates made of the velocity constants involved.

THE halogenation of compounds containing a reactive $\geqslant$CH group, *e.g.*, ketones and keto-esters, is usually kinetically of zero order with respect to halogen. The rate-determining step must therefore be the formation of a reactive intermediate, but there is still some doubt whether this intermediate is the enol or the anion of the original substance. Lapworth (*J.*, 1904, **85**, 30) supposed that halogenation involved the formation of enol, and this view has been widely accepted. The usual modern interpretation (see, *e.g.*, Bell, " Acid-Base Catalysis," Oxford, 1941, p. 135) distinguishes between catalysis by acids and by bases. In acid catalysis the formation of enol is believed to be rate-determining, but in basic catalysis the anion is thought to be the species which is halogenated, since it is an intermediate in the formation of the enol and would be expected to halogenate even more rapidly. Thus Hammett ("Physical Organic Chemistry," New York, 1940, p. 231) writes : " There is no reason to suppose that the formation of an electrically neutral enol form represents anything more than an unimportant by-path into which a portion of the reacting substance may transiently stray." However, this view does not depend on direct kinetic evidence, and cannot be tested as long as the reaction remains of zero order with respect to halogen; it is also impossible to obtain evidence by studying directly the halogenation of pure enols or anions of ketonic substances, since these reactions are much too fast to follow by ordinary methods.

A test is possible in principle if a reaction can be found in which the enolization or ionization is not wholly rate-determining. West (*J.*, 1924, **125**, 1277) showed that in the bromination of malonic acid the rate of introduction of the first bromine atom is independent of bromine concentration, but that the subsequent bromination of monobromomalonic acid is of first-order with respect to bromine. He concludes that the reactive species concerned are the enols, but the interpretation is complicated by the two stages of dissociation of the acids concerned. Further information comes from the work of Bartlett (*J. Amer. Chem. Soc.*, 1934, **56**, 967) and of Bartlett and Vincent (*ibid.*, 1935, **57**, 1596) on the halogenation of acetone and other ketones in alkaline hypochlorite solutions. In these solutions the rate of ionization and enolization is increased by the high value of $[OH^-]$, and the halogenating power of the solution is decreased by the conversion of Cl_2 into HOCl and OCl^- : correspondingly it was found that in the neighbourhood of pH 10 the reaction became of first order with respect to halogen. The variation of rate with pH should give information about the nature of the reacting species, but does not provide an unambiguous answer, since the two reactions enol + OCl^- and anion + HOCl are kinetically indistinguishable. Bartlett's results are reconsidered on p. 434.

It would be of interest to discover which species react with the more usual halogenating species Br_2 and I_2, and this is possible in principle if measurements can be made at sufficiently low halogen concentrations. With most ketonic substances the reaction velocity remains independent of halogen concentration down to very low values of the latter, but it has been observed (Bell, Everett, and Longuet-Higgins, *Proc. Roy. Soc.*, 1946, *A*, **186**, 443) that in the bromination of ethyl malonate the velocity falls off noticeably with bromine concentrations less than about 0·01M. Preliminary work in this laboratory by Mr. D. R. Mayne showed that the reaction in dilute bromine solutions could be interpreted in terms of two consecutive steps, and the present paper reports a quantitative study of the effect of bromine concentration and pH.

It is convenient to consider first the kinetic behaviour expected. Suppose that the substance RH can be brominated to RBr through either the anion R^- or the enol HR, and that the only reactive bromine species is Br_2. (It will be shown later that in the bromination of malonic ester the observed rate is determined mainly by the substitution of the first bromine atom, though a small correction is necessary to allow for the fact that the rate of bromination of the monobromo-ester is not infinitely great: similarly, a small correction is necessary for bromination by the species Br_3^- and HOBr.) If the solution contains a number of acid–base pairs A_i–B_i, the kinetic scheme for basic catalysis is

$$\left.\begin{array}{l} \mathrm{RH} + \Sigma \mathrm{B}_i \underset{k^i_{-1}}{\overset{k^i_1}{\rightleftharpoons}} \mathrm{R}^- + \Sigma \mathrm{A}_i \underset{k^i_{-2}}{\overset{k^i_2}{\rightleftharpoons}} \mathrm{HR} + \Sigma \mathrm{B}_i \\ \mathrm{R}^- + \mathrm{Br}_2 \xrightarrow{k_3} \mathrm{RBr} + \mathrm{Br}^- \\ \mathrm{HR} + \mathrm{Br}_2 \xrightarrow{k_4} \mathrm{RBr} + \mathrm{Br}^- + \mathrm{H}^+ \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the k's are all second-order velocity constants. We shall assume initially that the second step in the above scheme is effectively in equilibrium, *i.e.*, that the dissociation equilibrium between the enol HR and the ion R^- is set up very rapidly and is not disturbed by the removal of HR or R^- by bromination. This is reasonable, since the ionization of the enol involves no electronic rearrangement (cf. Bell and Higginson, *Proc. Roy. Soc.*, 1949, *A*, **197**, 141). Making this assumption, we have throughout the reaction $[R^-]/[HR] = K_{HR}/[H^+]$, where K_{HR} is the acid dissociation constant of the enol. Applying the steady state conditions $d[R^-]/dt = d[HR]/dt = 0$ (since for malonic ester $[R^-]$ and $[HR]$ are throughout vanishingly small) we find for the observed velocity constant v

$$v = \frac{1}{[\mathrm{RH}]}\frac{d[\mathrm{RBr}]}{dt} = \{k_3[\mathrm{R}^-][\mathrm{Br}_2] + k_4[\mathrm{HR}][\mathrm{Br}_2]\}/[\mathrm{RH}]$$

$$= \frac{[\mathrm{Br}_2]\sum\limits_i k^i{}_1[\mathrm{B}_i]\{k_3 + k_4[\mathrm{H}^+]/k_{\mathrm{HR}}\}}{[\mathrm{Br}_2]\{k_3 + k_4[\mathrm{H}^+]/K_{\mathrm{HR}}\} + \sum\limits_i k^i{}_{-1}[\mathrm{A}_i]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

At high bromine concentrations the observed velocity becomes $v_\infty = \sum\limits_i k^i{}_1[B_i]$. We have for each acid–base pair $k^i{}_{-1}/k^i{}_1 = [B_i][H^+]/[A_i]K_{RH}$, where K_{RH} is the dissociation constant of the substance RH, and we can also write $K_{RH}/K_{HR} = K_E$, where K_E is the equilibrium enol : keto ratio. If we define a quantity $F = [Br_2](v_\infty - v)/vv_\infty$, equation (2) becomes

$$1/F = vv_\infty/[\mathrm{Br}_2](v_\infty - v) = k_4K_E + k_3K_{\mathrm{RH}}/[\mathrm{H}^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The above reaction scheme can therefore be tested by investigating the dependence of the experimental quantity F on $[H^+]$.

If we do not make the simplifying assumption that the second step in (1) is at equilibrium, we obtain instead of (3) the equation

$$\frac{1}{F} = \frac{k_4K_E}{1 + k_4[\mathrm{Br}_2]/\sum\limits_i k^i{}_{-2}[\mathrm{B}_i]} + \frac{k_3K_{\mathrm{RH}}}{[\mathrm{H}^+]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

so that in this case the observed value of F will depend not only on $[H^+]$, but also on the concentration of bromine and of the bases present. It should thus be easy to test whether the assumption involved in (3) is justified.

EXPERIMENTAL

Ethyl malonate was redistilled (b. p. 104·5°/30 mm.) Ethyl monobromomalonate, prepared as described in *Org. Synth.*, Coll. Vol. I, 1st edn., p. 240, was redistilled (b. p. 109—110°/7·5 mm.). Acetic acid, monochloroacetic acid, and the inorganic reagents used were of " AnalaR " quality, and all solutions were made up with conductivity water. Enough potassium nitrate was added to each reaction mixture to bring the total ionic strength up to 0·1. Stock solutions of the esters were not kept for more than a few days, in order to avoid hydrolysis. Solutions of acids and of sodium hydroxide were standardized, constant-boiling hydrochloric acid being used as the primary standard. Sodium thiosulphate solution was periodically standardized against potassium iodate.

In order to avoid loss of bromine by evaporation, the kinetic measurements were carried out in a 20-ml. all-glass Pyrex syringe, with a suitably bent capillary fused to the nozzle. The arrangement of the syringe in the thermostat (25° ± 0·02°) is indicated in Fig. 1. Only a minute air bubble remained in the syringe after filling, and tests showed that no detectable amount of bromine was lost during an experiment. Samples for analysis were expelled into a weighed flask containing 1 ml. of a 1M-acetate buffer (1 : 1) and at least a three-fold excess of allyl alcohol to remove free bromine. A few crystals of potassium iodide were added from a weighed dish, and after the flask had been re-weighed the iodine liberated by the bromo-esters was titrated at 30-min. intervals with N/500-thiosulphate, as described by Bell, Everett, and Longuet-Higgins (*loc. cit.*). The same results were obtained by using Bell, Smith, and Woodward's iodate titration method (*Proc. Roy. Soc.*, 1948, *A*, **192**, 479).

In each experiment at least one sample was analysed without the addition of allyl alcohol in order to determine the total oxidizing power, which should be equivalent to the amount of bromine initially present. Identical results were obtained with samples taken near the beginning and near the end of an experiment, showing that no bromine had been lost by evaporation.

We shall describe first the experiments with relatively high concentrations of bromine ($\sim$0·02M) which give the value of v_∞ in equation (3). When monobromomalonic ester is the starting material there are no complications arising from successive stages of bromination, and the reactions should therefore be of first order with respect to the ester. This was found to be so for the earlier part of the reaction, though the rate fell off towards the end of each reaction. However, only very dilute solutions of ester could be used ($\sim 4 \times 10^{-4}$M), so the accuracy is not high. The chief purpose of the experiments with monobromomalonic ester was to obtain a correction to apply to the results for malonic ester, and the accuracy is ample for this purpose. The results obtained are given in Table 1. In this, and in all subsequent tables, the symbols have the following meanings : r = stoicheiometric buffer ratio, [acid]/[anion] ; $[B^-]$ = mean concentration of anion, corrected for the acid produced during the reaction; v = first-order velocity constant, min.$^{-1}$; v_0 = velocity constant of water-catalysed reaction; k_{B^-} = catalytic constant of anion.

TABLE 1. *Bromination of monobromomalonic ester at high bromine concentrations.*

[Ester] $\sim 4 \times 10^{-4}$M, [bromine] $\sim$0·02M.

In 0·0011N-$HClO_4$, 10^4v = 161, 161, 145; mean 10^4v = 156.

	r	$10^4[B^-]$	10^4v	k_{B^-}	Mean		r	$10^4[B^-]$	10^4v	k_{B^-}	Mean
Monochloroacetate buffers	1·02	519	366	0·405	0·415	Acetate buffers	1·12	19·5	364	10·7	10·1
	1·02	519	373	0·418			1·07	38·6	532	9·5	
	1·74	536	382	0·422							

The value obtained for v_0 agrees much better with that given by Bell, Gelles, and Möller (*Proc. Roy. Soc.*, 1949, *A*, **198**, 308; $v_0 = 181 \times 10^{-4}$ in our units) than with that of Pearson and Mills (*J. Amer. Chem. Soc.*, 1950, **72**, 1692), *viz.*, $v_0 = 86 \times 10^{-4}$. The latter workers prepared the monobromo-ester *in situ* by adding less than one equivalent of bromine and allowing the solution to stand " until equilibrium was reached," after which the rate of further bromination was measured. However, it is likely that equilibrium was not attained, since the first addition of bromine will initially form dibromo-ester, which then reverts slowly to monobromo-ester. If the solution contained less monobromo-ester than was believed the observed rate would be too low.

In the bromination of malonic ester the rate is mainly determined by the first stage of the reaction, but a small correction is necessary for the finite rate of bromination of the monobromo-ester. The method of estimation used gives the total oxidizing power of the monobromo- and dibromo-ester. If this is x equiv./l. and the initial ester concentration is c, the course of the reaction is given by

$$2(R - 1)(c - \tfrac{1}{2}x)/c = (2R - 1)\,e^{-vt} - e^{-v't} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

(cf. Pedersen, *J. Phys. Chem.*, 1933, **37**, 751 ; Bell, Gelles, and Möller, *loc. cit.*), where v and v'

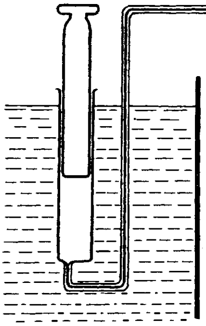
are the first-order constants for the two stages of bromination (at high bromine concentrations), and $R = v'/v$. Equation (5) can be re-written in the form

$$vt = Q + \Delta Q, \quad Q = \ln(1 - \tfrac{1}{4}x/c)$$
$$\Delta Q = \ln\{1 + (1 - e^{-(R-1)vt})/2(R - 1)\} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

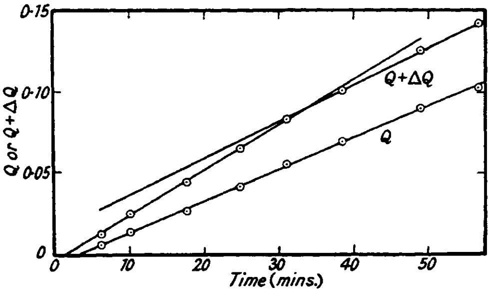
ΔQ is a correction term to allow for the fact that v' is not infinite. As t increases, ΔQ approaches the constant value $\ln\{1 + 1/2(R - 1)\}$, and a plot of Q against t thus approaches a slope v.

The values of v in Table 2 were obtained by plotting $Q + \Delta Q$ against t; ΔQ was calculated by successive approximations, using first an approximate value of v and a value of v' from Table 1. These plots were linear, but had a small negative intercept (0·002—0·005) at $t = 0$ (cf. Fig. 2). This was due to the fact that at the end-point of the titration a small amount of iodine remained combined with the malonic ester and the allyl alcohol. The magnitude of the intercept agrees with that calculated from the known equilibrium constants for these iodinations (Bell and Gelles, *Proc. Roy. Soc.*, 1951, *A*, **210**, 310; Berthoud and Mosset, *J. Chim. physique*, 1936, **33**, 272), and does not affect the slope of the plot since it remains approximately constant throughout the reaction.

Fig. 1.



Fio. 2.



The data in Table 2 show good agreement with the earlier results of Bell, Everett, and Longuet-Higgins (*loc. cit.*), who followed the reaction up to about two-thirds completion, and neglected the correction ΔQ, whereas the present work deals chiefly with the first few units % of the reaction, where this correction is important. The agreement between the two sets of results justifies the method of applying the correction.

TABLE 2. *Bromination of malonic ester at high bromine concentrations.*

[Bromine] ~ 0·02M. Values of v in parentheses are calculated from the catalytic constants given by Bell, Everett, and Longuet-Higgins (*loc. cit.*).

In 0·02M-$HClO_4$: 10^4 [ester] = 29·7, 44·0, 63·8; 10^4v = 13·9, 14·3, 14·5; mean 14·2 (14·3).

	10^4[ester]	r	$10^4[B^-]$	10^4v	Mean	
Monochloroacetate buffers...	10·0	1·03	515	35·2	36·1	(36·8)
	49·0	1·03	515	36·2		
	50·0	1·03	515	36·9		
	50·0	1·03	219	23·7	23·7	(23·9)
Acetate buffers	3·46	6·18	200	290	290	(285)
	3·94	6·18	200	291		

The remaining experiments are concerned with the bromination of the malonic ester at low bromine concentrations where v and v_∞ differ appreciably. The experimental method is the same as before, and the values of v have again been obtained by plotting $Q + \Delta Q$ against t, the data in Tables 1 and 2 being used for calculating R. This procedure is not strictly justified, since we are no longer dealing with consecutive first-order reactions. However, the correction ΔQ is not large, except in the very early stages of the reaction, and some rough experiments showed that the ratio v/v_∞ has similar values for malonic ester and monobromomalonic ester under the same conditions. The values of v should therefore not be subject to any appreciable error.

Fig. 2 shows typical plots of Q and of $Q + \Delta Q$ against time. The former is fortuitously linear, but the slope of the latter decreases with time because of the decreasing bromine concentration. It is possible to integrate equation (2) to represent the course of the reaction, but the expression obtained is cumbrous, and we have preferred to obtain v for different bromine concentrations by measuring the slope of the plot over a range of points. In this way two (and sometimes three) values of v were obtained from each experiment. Examples of the results obtained are given in Table 3. In the buffer solutions the values of $[H^+]$ are calculated from the thermodynamic dissociation constants $K(CH_3{\cdot}CO_2H) = 1{\cdot}751 \times 10^{-5}$, $K(CH_2Cl{\cdot}CO_2H) = 1{\cdot}385 \times 10^{-3}$, $f_{\pm}$ being taken as 0·76; v_{∞} is obtained from Table 2 by a small extrapolation ($<2\%$) to infinite bromine concentration. In calculating v for the most strongly acid solutions we have applied a small correction ($\sim 2\%$) for the acid hydrolysis of the malonic ester. This followed the treatment of Bell, Everett, and Longuet-Higgins (*loc. cit.*) except that the rate of hydrolysis of the dibromo-ester was assumed to be much smaller than that of the unsubstituted ester.

The values of F in the table are calculated from $F = [Br_2](v_{\infty} - v)/vv_{\infty}$. In each series a few experiments were done with much higher concentrations of bromide ion. This produces a slight decrease of velocity because of the conversion of Br_2 into the less reactive Br_3^-. In addition, in the series with acetate buffers a few experiments were done with very low values of $[Br^-]$, thus favouring the formation of HOBr, which was also found to be less reactive than Br_2. These experiments do not provide any accurate measurement of the reactivity of Br_3^- or HOBr, but they are sufficient to correct for the small amounts of these species present in the remaining experiments. (No evidence was found for bromination by any other species, such as H_2OBr^+ or $CH_3{\cdot}CO_2Br$.) The column headed F(corr.) in Table 3 represents the values which would have been obtained if all the bromine had remained in the form of Br_2 : it will be seen that they differ little from the values directly observed.

TABLE 3. (*Typical results.*) *Bromination of malonic ester at low bromine concentrations.*

c = initial ester concentration; other concentrations are mean values.

10^4c	$10^4[Br_2]$	$10^4[Br^-]$	10^4v	10^3F	10^3F (corr.)	10^4c	$10^4[Br_2]$	$10^4[Br^-]$	10^4v	10^3F	10^3F (corr.)
Series 2 : 0·0081M-$HClO_4$; 10^4v_{∞} = 14·3.											
71·8	6·39	27·6	12·8	52	51		1·49	33·8	9·0	61	60
	3·22	30·8	11·1	65	64	36·2	1·86	8·6	10·3	50	50
51·2 *	3·81	30·9	12·1	48	47		0·81	9·7	7·4	53	53
	1·63	33·1	9·7	54	53	52·0	3·93	731	11·7	61	—
50·5	3·72	31·1	12·0	50	49		1·88	733	9·1	75	—
										Mean	53 ± 2
Series 7 : Acetate buffer; r = 6·18, $10^4[B^-]$ = 200, $[H^+] = 1{\cdot}87 \times 10^{-4}$, 10^4v_{∞} = 296.											
5·51	6·65	51·3	193	12·0	11·4	4·97	2·00	18·6	113	10·9	10·6
	4·58	53·4	162	12·8	12·1		1·04	19·6	73	10·7	10·4
3·75	4·01	30·7	164	10·9	10·5	5·02	4·05	731	140	15·2	—
	2·90	31·8	130	12·5	12·1		2·78	732	104	17·3	—
										Mean	11·2 ± 0·3

* In these experiments HCl was used in place of $HClO_4$.

DISCUSSION

The data for monobromomalonic ester at high bromine concentrations (Table 1) can be compared with similar data for other substrates (cf. table given by Bell, Gelles, and Möller, *loc. cit.*, p. 321). The velocity of the anion-catalysed reaction is intermediate between those for ethyl malonate and ethyl acetoacetate, and the same is true for the exponent α, since the catalytic constants for the two anions can be represented by $k_{B^-} = 3{\cdot}40 \times 10^{-3} (1/K_{HB})^{0{\cdot}73}$.

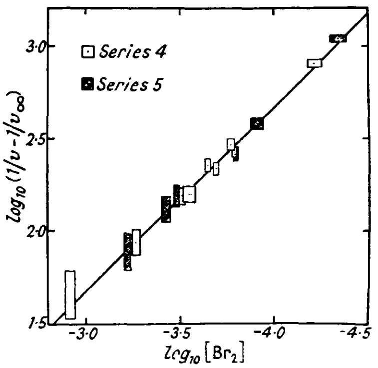
With regard to the data for low bromine concentrations, the first-order constants in Table 3 show the expected falling off, and are almost proportional to the bromine concentration at very low values of the latter. In Series 4 the ester concentration was varied by a factor of 15 without producing any change in the value of F. Fig. 3 shows a plot of $\log(1/v - 1/v_{\infty})$ against $\log[Br_2]$ for series 4 and 5. The size of the rectangles represents an error of $\pm 3\%$ in v and $\pm 1\%$ in $[Br_2]$. The agreement with a straight line of slope unity confirms that the kinetics involve two consecutive reactions [cf. equation (3)]. The same point is illustrated by the constancy of F within any one series. The individual variations in F appear rather large, but it must be remembered that errors in the velocity are magnified several times in F, especially when v is close to v_{∞}. The errors attached to the mean F values in Table 3 are standard deviations calculated by the usual methods.

Table 4 contains a summary of the mean F values. The variation of F with $[H^+]$ is of the type expressed by equation (3), and the values of F (calc.) in Table 4 are those given by

$$1/F = 15{\cdot}5 + 0{\cdot}0136/[H^+] \qquad (7)$$

where the best values of the constants have been obtained by applying the method of least squares to the weighted values of F (obs.) (cf. Birge, *Phys. Review*, 1932, **40**, 207). The comparison of series 4 and 5 in Table 4 and Fig. 3 shows that F is independent of the catalyst concentration: since we have already seen that it is independent of $[Br_2]$, the simplifying assumption made in deriving equation (3) is justified, and it is not necessary to use the more complicated equation (4).

Fig. 3.



The presence of two terms in equation (7) shows that both the enol and the anion are involved as reactive intermediates in the base-catalysed bromination, their relative importance varying with pH. At pH >3 most of the bromination takes place through the anion, while at pH <3 the enol is more important. This conclusion will still be valid at high bromine concentrations, provided that the assumption underlying equation (3) still holds. By comparing equations (3) and (7) we can obtain some information about the absolute rates of bromination of the anion and the enol (k_3 and k_4). Pearson and Mills (*loc. cit.*) give $K_{RH} \sim 5 \times 10^{-14}$ for malonic ester, whence $k_3 \sim 3 \times 10^{11}$ l. mole^{-1} min.$^{-1}$. This represents an extremely fast reaction, being only some 50 times smaller than the gas collision number expressed in these units. There are no direct estimates of K_E for malonic ester, but we can estimate it tentatively at 10^{-6}—10^{-4} if we assume that the enol form has a dissociation constant in the range 10^{-10}—10^{-8} (cf. Schwarzenbach and Felder, *Helv. Chim. Acta*, 1944, **27**, 1044). This gives $k_4 \sim 10^5$—10^7 l. mole^{-1} min.$^{-1}$, *i.e.*, the reaction of bromine with the enol is much less efficient than with the anion, as might be expected. The data in Table 3 suggest that Br_3^- reacts about two-thirds as fast as Br_2 with the enol, and even less rapidly with the anion, while HOBr appears to react roughly half as fast as Br_2 with the anion. These conclusions are reasonable, but are subject to some uncertainty because of the small experimental differences involved.

TABLE 4. *Summary of data for bromination of malonic ester.*

Series	r	$10^4[B^-]$	$[H^+]$	$10^4 v_\infty$	No. of expts.	Mean of 10^3F (obs.)	10^3F (calc.)
Perchloric acid.							
1	—	—	$2{\cdot}00 \times 10^{-2}$	14·3	20	58 ± 3	62
2	—	—	$8{\cdot}10 \times 10^{-3}$	14·3	10	53 ± 2	58
Monochloroacetate buffers.							
3	3·56	278	$8{\cdot}10 \times 10^{-3}$	26·2	11	67 ± 3	58
4	1·03	515	$2{\cdot}46 \times 10^{-3}$	36·4	12	48 ± 1	48
5	1·03	219	$2{\cdot}46 \times 10^{-3}$	23·7	11	48 ± 1	48
6	0·352	503	$8{\cdot}43 \times 10^{-4}$	35·9	10	28 ± 1	32
Acetate buffers.							
7	6·18	200	$1{\cdot}87 \times 10^{-4}$	296	8	$11{\cdot}2 \pm 0{\cdot}3$	11·3
8	3·13	199	$9{\cdot}48 \times 10^{-5}$	296	10	$7{\cdot}0 \pm 0{\cdot}5$	6·3
9	1·07	198	$3{\cdot}24 \times 10^{-5}$	295	11	$2{\cdot}4 \pm 0{\cdot}2$	2·3

Bartlett and Vincent's data (*loc. cit.*) for the chlorination of ketones in alkaline hypochlorite solutions can be expressed in the form $k = a/[OH^-] + b + c[OH^-]$, where k is the observed second-order velocity constant. The authors attribute the second and third terms to the reactions enol + OCl^- and anion + OCl^- respectively, but do not give any interpretation of the term $a/[OH^-]$. This must be due to the reaction enol + HOCl, and if we accept Schwarzenbach and Wittwer's estimate (*Helv. Chim. Acta*, 1947, **30**, 669) for the enol content of acetone, we obtain $k \sim 10^{11}$ l. mole^{-1} min.$^{-1}$ for this reaction. Similarly, taking p$K = 19$ for acetophenone and p$K = 20$ for acetone (McEwen, *J. Amer. Chem. Soc.*, 1936, **58**, 1124; Bell, *Trans. Faraday Soc.*, 1943, **39**, 253), we find $k \sim 10^7$ l. mole^{-1} min.$^{-1}$ for the reaction of hypochlorite ion with the anion of either of these ketones. The interpretation of the second term *b* is ambiguous, since the reaction enol + OCl^- suggested by Bartlett and Vincent is kinetically indistinguishable from anion + HOCl. For acetone the velocity constants can be estimated as 10^6 and 10^{12} l. mole^{-1} min.$^{-1}$ respectively, so that either would be kinetically possible.

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