439. *Kinetics of the Chlorination of Diethyl Malonate in Aqueous Solution.*

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The kinetics of the chlorination of diethyl malonate have been studied in aqueous solution with chlorine concentrations between 10^{-2}M and 10^{-5}M. At the higher concentrations the rate is the same as for bromination under the same conditions, being determined by the rate of ionization of the ester. At low concentrations the rate becomes dependent upon chlorine concentration, and results over a range of acidities lead to velocity constants for the reaction of chlorine with both the enol and the enolate ion. Chlorine is somewhat less reactive than bromine and iodine towards both species.

In a previous paper, on the chlorination of acetone,[1] it was shown that the rate at high halogen concentrations was the same as the rate of bromination or iodination, and hence equal to the rate of enolization or ionization of the ketone, while measurements at very low concentrations of chlorine gave information about the rate of chlorination of the enol.

[1] Bell and Yates, *J.*, 1962, 1927.

The present paper describes similar work on the chlorination of diethyl malonate. Previous work on the bromination of this substance at relatively high bromine concentrations [2] showed that under these conditions the reaction was of zero order with respect to halogen, its velocity being determined by the rate of ionization of the ester in presence of base. Later measurements with lower concentrations of bromine [3] showed that halogenation took place through either the enol or the enolate ion, according to the acidity of the solution, and yielded rate constants for the reaction of both species with various brominating agents. Analogous information for iodination has been obtained indirectly from a study of the reaction of diethyl iodomalonate with iodide ions.[4]

EXPERIMENTAL

Diethyl malonate was redistilled (b. p. 54·5—55·0°/2 mm., n_D^{25} 1·4125; lit.,[5] 55°/2 mm., 1·4136). Diethyl monochloromalonate was of Laboratory Reagent grade (n_D^{25} 1·4317; lit.,[6] 1·4327). Chlorine was prepared from " AnalaR " potassium permanganate and concentrated hydrochloric acid, and was passed through potassium permanganate solution before being absorbed in water, to give solutions which were kept in blackened bottles. Other reagents were of " AnalaR " grade, and solutions were made up with water re-distilled from an all-glass still. Solutions of ester were freshly prepared every few days so as to minimize hydrolysis.

Since chlorine is extensively hydrolyzed in the buffer solutions used in some of the kinetic measurements, the e.m.f. method previously used [1] is not suitable for measuring total concentrations of chlorine, and all reactions were followed by chemical analysis. The reactions were carried out in a glass syringe without air space (cf. Bell and Spiro [3]), and samples were expelled into a weighed quantity of 0·1N-potassium iodide in a 1 : 1 acetate buffer. The iodine liberated was titrated against 10^{-3}—10^{-4}N-sodium thiosulphate, the end-point being detected by the dead-stop method with platinum electrodes.[7,8] Titrations were reproducible to about 0·02 ml. of thiosulphate solution.

RESULTS AND DISCUSSION

One series of experiments was carried out with relatively high initial chlorine concentrations (10^{-3}—10^{-2}M). In order to interpret the experiments with diethyl malonate, it was necessary to make some measurements with diethyl monochloromalonate, and the results of these are given in Table 1. Over the first 50%, the reaction proved to be zero-order in halogen and first-order in ester, and the velocity constants in the Table refer to this part of the reaction. The subsequent slowing down probably indicates that the reaction is no longer of zero order in halogen at the low concentrations involved. Because of the low solubility of the ester it was not practicable to work with initial chlorine concentrations greater than about $1·5 \times 10^{-3}$M.

In Table 1 (and subsequent Tables) [OAc⁻] represents the mean concentration, corrected for the hydrolysis of chlorine and for the acid produced during the reaction. The observed values of v^1 are represented with sufficient accuracy by $v^1 = 3·4 \times 10^{-4} + 0·20[\mathrm{OAc}^-]$.

It is easily shown [9,10] that if both stages of the chlorination of diethyl malonate are of zero order in halogen but of first order in ester (with velocity constants v and v^1), then y, the fall in chlorine concentration after time t, is given by

$$0·434vt = \log \frac{c_0}{c_0 - \frac{1}{2}y} + \log \left\{ 1 + \frac{1 - e^{-(j-1)vt}}{2(j-1)} \right\} = \phi(t), \qquad (1)$$

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[2] Bell, Everett, and Longuet-Higgins, *Proc. Roy. Soc.*, 1946, *A*, **186**, 443.

[3] (*a*) Bell and Spiro, *J.*, 1953, 429; (*b*) Bell and Rawlinson, *J.*, 1961, 726.

[4] Bell and Engel, *J.*, 1957, 247.

[5] Brühl, *J. prakt. Chem.*, 1894, **50**, 141.

[6] Fritsch, *Annalen*, 1897, **297**, 319.

[7] Foulk and Bawden, *J. Amer. Chem. Soc.*, 1926, **48**, 2045.

[8] Furman and Wilson, *J. Amer. Chem. Soc.*, 1928, **50**, 277.

[8] Pedersen, *J. Phys. Chem.*, 1933, **37**, 751.

[10] Bell, Gelles, and Möller, *Proc. Roy. Soc.*, 1949, *A*, **198**, 308.

where c_0 is the initial ester concentration and $j = v^1/v$. Since $j > 10$ the second term in equation (1) rapidly becomes much smaller than the first, and then v can be determined directly from a plot of $\log \{c_0/(c_0 - \frac{1}{2}y)\}$ against t, as in the bromination experiments of Bell, Everett, and Longuet-Higgins.[2] However, in many of our experiments (especially those with low chlorine concentrations) this approximation is not justified, and the full equation (1) has been used to obtain v. This involves assuming trial values of v (and hence of j) until the plot of $\phi(t)$ against t has a slope of $0{\cdot}434v$. These plots were linear in the experiments with high chlorine concentrations, and the velocity constants are given in Table 2. Our mean value for v in acid solution (corresponding to basic catalysis by water molecules) is $2{\cdot}8 \times 10^{-5}$ sec.$^{-1}$, which lies between previous values of $2{\cdot}4 \times 10^{-5}$ (refs. 2 and 10) and $3{\cdot}0 \times 10^{-5}$ (ref. 11). The last two values were obtained by indirect methods, and we regard our value as more reliable.

TABLE 1.

Chlorination of diethyl monochloromalonate at 25°.

$[Cl^-] = 0{\cdot}2$M. $I = 0{\cdot}41$ ($NaNO_3$ added). $r = [HOAc]/[OAc^-]$. v^1 = first-order velocity constant (sec.$^{-1}$). [Ester] $= 6 \times 10^{-4}$M.

$10^4[HCl]$ (M)	42	122	—	—	—
$10^4[OAc^-]$ (M)	—	—	28·6	23·6	18·6
r	—	—	4·8	3·2	1·7
10^5v^1	34	35	94	77	71

TABLE 2.

Chlorination of diethyl malonate at 25° at high chlorine concentrations.

$[Cl^-] = 0{\cdot}16$M. v = First-order velocity constant (sec.$^{-1}$).

$10^4[HCl]$ (M)	200	200	100	100	50	50
10^4[Ester] (M)	41	41	67	67	67	67
$10^4[Cl_2]_0$ (M)	227	216	360	362	186	180
10^6v	29	29	27	28	28	28

It is difficult to make reliable measurements with moderate concentrations of chlorine in acetate buffer solutions, since the hydrolysis of chlorine disturbs the buffer ratio, which thus varies during the experiment. A single experiment gave 0·0232 l. mole^{-1} sec.$^{-1}$ for the catalytic constant of the acetate ion, in good agreement with 0·0235 given by Bell and Spiro.[3] It is therefore clear that the reaction of diethyl malonate with chlorine at moderately high concentrations follows the same mechanism as its bromination, the velocity being determined by the rate of formation of the enol or enolate ion. In treating the results at low chlorine concentrations we have assumed $v_\infty = 2{\cdot}8 \times 10^{-5} + 0{\cdot}0235[OAc^-]$, the subscript ∞ indicating that the velocity corresponds to an effectively infinite halogen concentration.

In the experiments with dilute chlorine solutions the initial halogen concentration was between 2×10^{-4} and 5×10^{-4}M, and the reactions were followed to about 90% completion. The reaction scheme is

$$SH + B_i \rightleftharpoons S^- + A_i \rightleftharpoons HS + B_i$$

$$S^- + Cl_2 \xrightarrow{k_2} SCl + Cl^-$$

$$HS + Cl_2 \xrightarrow{k_3} SCl + Cl^-$$

where SH and HS are the keto and the enol form, and A_i and B_i are acids and bases, respectively. It was shown by Bell and Spiro [3] that, if the reaction velocity is defined as $v = -[SH]^{-1}\,d[Cl_2]/dt$, then for a given composition of catalyst solution the dependence of reaction velocity on halogen concentration is represented by

$$\frac{1}{F} = \frac{vv_\infty}{[Cl_2](v_\infty - v)} = k_3K_E + \frac{k_2K_{SH}}{[H^+]}, \qquad (2)$$

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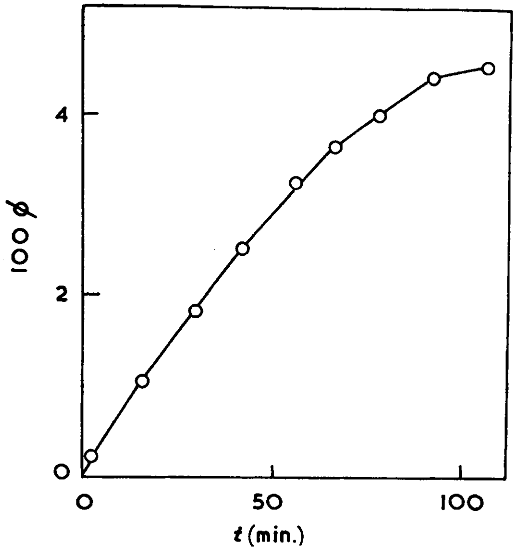
[11] Pearson and Mills, *J. Amer. Chem. Soc.*, 1950, **72**, 1692.

where v_∞ is the velocity at infinite halogen concentration, K_E is the keto–enol equilibrium constant [HS]/[SH], and K_{SH} is the acid dissociation constant of the keto-form. The derivation of this equation assumes that there is complete equilibration between enol and enolate ion: if this is not so, the right-hand side of equation (2) is replaced by an expression involving $[Cl_2]$ and the catalyst concentration, so that the validity of this assumption can be tested experimentally.

The integrated form of equation (2) is clumsy to use, and the position is complicated by the two successive chlorinations. We have therefore plotted $\phi(t)$ of equation (1) against t, using for j the ratio of the two consecutive velocity constants derived from the experiments at high chlorine concentrations. A typical plot of this kind is shown in the Figure. The values of v at different chlorine concentrations were then obtained by taking the best straight lines through groups of three adjacent points and calculating the mean chlorine concentration over this part of the reaction. This procedure is not strictly justifiable, since we are no longer dealing with two consecutive reactions which are of the first order in ester and of zero order in chlorine. However, no appreciable error will be involved provided that v/v_∞ has similar values for diethyl malonate and diethyl monochloromalonate, as was found by Bell and Spiro [3] to be the case for the monobromo-ester.



Plot used for determination of v.

The results are given in Tables 3 and 4. The values of $[H^+]$ and $[OAc^-]$ are mean values corrected both for the hydrolysis of chlorine and for the acid produced during the reaction. In calculating $[H^+]$ for the buffer solutions it was assumed that $f_\pm = 0{\cdot}71$ at $I = 0{\cdot}41$. The values of F obtained show fairly large random variations, which is not surprising since they depend on small differences between v and v_∞ and on approximate chlorine concentrations. However, F shows no systematic variation with chlorine concentration, and it is also independent of acetate concentration at constant $[H^+]$, as may be seen by comparing experiments 11 and 12, 15 and 17, or 16 and 18: the validity of equation (2) is thus confirmed. Although F is approximately constant in the acid solutions, it shows a large pH-dependence in buffer solutions. The calculated values in the Tables are from the equation

$$\frac{1}{F} = 0{\cdot}155 + \frac{6{\cdot}3 \times 10^{-5}}{[H^+]}, \qquad (3)$$

which reproduces the results within experimental error.

TABLE 3.

Chlorination of diethyl malonate in hydrochloric acid solution at low chlorine concentrations.

$I = 0·41$ ($NaNO_3$ added). $10^6 v_\infty = 28$ sec.$^{-1}$. $j = 12·3$. Concentrations are in molar units.

Expt.	$10^4[H^+]$	$[Cl^-]$	$10^5[SH]_0$	$10^6[Cl_2]$	$10^6 v$	F		
						obs.	av.	calc.
1	42	0·2	477	557	21·5	5·9	6·4	5·9
				293	17·0	6·7		
				187	14·0	6·6		
2	42	0·4	431	322	18·3	6·0	5·9	5·9
				140	13·0	5·8		
3	82	0·2	477	298	17·7	6·2	6·1	6·1
				103	10·3	6·3		
4	82	0·2	431	378	19·5	5·8		
				129	11·9	6·2		
5	162	0·1	477	391	19·0	6·5	6·3	6·3
				158	12·5	7·0		
6	162	0·1	431	419	20·5	5·4		
				239	16·0	6·4		
				105	10·5	6·2		
7	162	0·2	477	316	17·3	6·5	6·2	6·3
				134	12·2	6·2		
8	162	0·2	431	472	20·5	6·1		
				261	17·0	6·0		
				129	16·0	6·3		

TABLE 4.

Chlorination of diethyl malonate in buffer solutions at low chlorine concentrations.

$I = 0·41$ ($NaNO_3$ added). $j = 8·8$. $10^6 v_\infty = 240$ sec.$^{-1}$, except in experiments marked * ($10^6 v_\infty = 350$) or † ($10^6 v_\infty = 480$). $r = [HOAc]/[OAc^-]$. Concentrations in molar units.

Expt.	$10^4[OAc^-]$	r	$10^6[H^+]$	$[Cl^-]$	$10^6[SH]_0$	$10^6[Cl_2]$	$10^6 v$	F		
								obs.	av.	calc.
9	90	1·7	59	0·2	592	230	143	0·65	0·59	0·82
						90	100	0·53		
10	90	1·7	59	0·4	827	214	140	0·64	0·67	0·82
						96	88	0·69		
11	90	3·4	118	0·2	592	306	118	1·3	1·4	1·4
						160	75	1·4		
12 †	192	3·4	118	0·2	414	344	145	1·6	1·4	1·4
						151	102	1·1		
13	90	5·1	177	0·13	592	414	122	1·7	2·0	2·0
						251	85	1·9		
						148	52	2·2		
						70	27	2·3		
14	90	5·1	177	0·2	592	449	123	1·8	2·0	2·0
						254	80	2·1		
						152	58	2·0		
15	90	6·8	236	0·1	592	475	108	2·4	2·5	2·4
						328	88	2·3		
						193	53	2·8		
16	90	6·8	236	0·2	592	544	122	2·2	2·4	2·4
						336	85	2·5		
						238	70	2·4		
17 *	137	6·8	236	0·1	414	589	148	2·3	2·7	2·4
						355	92	2·9		
						263	70	3·0		
18 *	137	6·8	236	0·2	414	387	108	2·5	2·6	2·4
						249	72	2·8		

Tables 3 and 4 also show that the chloride ion concentration has no detectable effect upon the observed velocity (*e.g.*, by comparison of experiments 1 and 2, 6 and 8, 13 and 14, 15 and 16). In the acid solutions the only likely halogenating species are Cl_2 and Cl_3^-, of which the latter constitutes less than 10% of the chlorine present.[12] In the buffer solutions the degree of hydrolysis of the chlorine to hypochlorous acid varies between

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[12] Sherrill and Izard, *J. Amer. Chem. Soc.*, 1931, **53**, 1667.

89% and 97%, and the lack of dependence on [Cl^-] indicates that the reactivities of chlorine and hypochlorous acid towards the enol and enolate ion cannot differ much. The values of k_2 and k_3 in equation (2) can, therefore, be taken to refer to the species Cl_2: in particular, there is no evidence for halogenation by the species H_2OCl^+ or ClOAc, the concentrations of which will be inversely proportional to that of chloride ion.

TABLE 5.

Halogenation kinetics of diethyl malonate at 25°.

(Velocity constants in l. mole^{-1} sec.$^{-1}$.)

Halogen	Reference	k_2 (enolate ion)	k_3 (enol)
Chlorine	This paper	1×10^{11}	3×10^{5}
Bromine	3(*a*)	4×10^{11}	2×10^{6}
	3(*b*)	4×10^{11}	8×10^{6}
Iodine	4	1×10^{12}	4×10^{6}

Equations (2) and (3) will give absolute values of k_2 and k_3, provided that K_{SH} and K_E are known. In previous papers we have assumed $K_{SH} = 5 \times 10^{-14}$ for diethyl malonate, as reported by Pearson and Mills.[11] This is likely to be less reliable than a recent estimate of $K_{SH} = 6 \times 10^{-16}$, based on indicator measurements in propan-2-ol,[13] and the latter value has been used in Table 5 when calculating k_2 and k_3 from equation (3), and also from the results previously obtained for bromination and iodination. K_E is subject to more uncertainty: we have used $K_E = 6 \times 10^{-16}/10^{-9} = 6 \times 10^{-7}$, since Schwarzenbach and Felder [14] found that a wide variety of enols had pK between 8 and 10. There is thus considerable uncertainty about the absolute values of k_2 and k_3, though the relative values for the different halogens are unaffected by uncertainties in K_{SH} and K_E.

The values of k_2 are close to the calculated encounter numbers for species in aqueous solution,[15,16] and the reaction of all three halogens with the enolate ion can involve little activation energy. The reactions with the enol are considerably slower, and correspond to an activation energy of about 7 kcal./mole. Towards both species chlorine is rather less reactive than bromine and iodine: this is the same sequence as was found for the halogenation of the enol of acetone.[1]

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[13] Vermesse-Jacquinot, Schaal, and Rumpf, *Bull. Soc. chim. France*, 1960, 2030.
[14] Schwarzenbach and Felder, *Helv. Chim. Acta*, 1944, **27**, 1044.
[15] Onsager, *J. Chem. Phys.*, 1934, **2**, 599.
[16] Debye, *Trans. Electrochem. Soc.*, 1942, **82**, 265.