40. *Kinetics of the Reaction between Ethyl Iodomalonate and Iodide Ions.*

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The kinetics of the reversible reaction between ethyl iodomalonate and iodide ions have been studied with and without the addition of ascorbic acid to remove the iodine produced. By combining these results with equilibrium constants, values are deduced for the velocity constants of the very fast reactions of enol and enolate ion with iodine and tri-iodide ion. These velocity constants are compared with those for the corresponding reactions with bromine and tribromide ion.

THE halogenation of organic compounds containing activated methylene groups is commonly of zero order with respect to the halogenating agent. Under these conditions it is impossible to obtain information about the velocity of the actual halogenation reaction, or to distinguish the reactivity of different halogenating species; moreover, when the reaction is catalysed by bases there is ambiguity as to whether halogenation proceeds through the anion, the enol (or analogous uncharged species), or both. It has been shown recently [1] that the bromination of diethyl malonate at low bromine concentrations is no longer a zero-order reaction, and it was possible to deduce the velocities of the reactions of bromine and tribromide ion with the anion and enol of the ester. Since many halogenation reactions of this type are reversible, an alternative approach is to study the kinetics of the reverse reaction $RX + X^- + H^+ \longrightarrow RH + X_2$ between the halogenated derivative and halide ions. Information about the kinetics of halogenation can then be obtained by using the principle of detailed balancing together with equilibrium data, which are available for a number of reactions.[2] The problem is simplified if the halogen produced is removed by adding a suitable substance to the reacting system, thus rendering the reaction irreversible.

The present paper describes the kinetics of the reaction between ethyl iodomalonate and iodide ions, both with and without the removal of the iodine formed. This system has an equilibrium constant of such magnitude ($[RI][I^-][H^+]/[RH][I_2] \simeq 0{\cdot}05$) that iodine will react almost completely with a moderate excess of malonic ester in an acetate buffer, provided that there is no large excess of iodide ions. This method was used for preparing ethyl iodomalonate *in situ*, and the reaction was then reversed by adding an excess of iodide ions, or hydrogen ions, or both. The equilibrium measurements by Bell and Gelles [2] gave steady values of the redox potential over long periods, indicating that the iodo-ester is stable in aqueous solution, and the results of the same authors for the introduction of a second iodine atom show that not more than 0·02% of di-iodo-ester will be formed under our conditions.

A suitable substance for removing the iodine formed must react rapidly and irreversibly with iodine over the range pH = 1 to pH = 5, and must react slowly, if at all, with the iodo-ester. Sodium thiosulphate reacts rapidly with iodine, but also reacts with iodo-ester. Arsenious acid does not appear to react with iodo-ester, but its reaction with low concentrations of iodine is slow and incomplete especially in the more acid solutions. In most of our experiments the iodine was removed by reaction with (—)-ascorbic acid, which satisfies the necessary conditions.

Kinetic Analysis.—It is convenient first to consider the kinetic behaviour to be expected. Suppose that equilibrium between the ester RH and the iodo-ester RI can be effected through either the anion R^- or the enol HR, and that the only effective iodinating species are I_2 and I_3^-. The solution will contain in general a number of acid-base pairs A_i—B_i,

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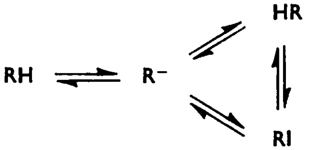
[1] Bell and Spiro, *J.*, 1953, 429.

[2] Bell and Gelles, *Proc. Roy. Soc.*, 1952, *A*, **210**, 310.

including the solvent pairs H_3O^+–H_2O and H_2O–OH^-. The general reaction scheme can then be written as follows:



The iodination of the enol will no doubt take place through the species $-\mathrm{C}(:\overset{+}{\mathrm{O}}\mathrm{H})\cdot\mathrm{CI}<$, but it can safely be assumed that this species never attains an appreciable concentration, being in mobile equilibrium with a much larger concentration of RI at all relevant hydrogen-ion concentrations. It will also be assumed that there is mobile equilibrium between the hydrogen ions and each acid–base pair A_i–B_i, between the species I_2, I^-, and I_3^-, and also between R^-, H^+, and HR (enol), but not between RH (ester) and the ions R^-, H^+. The remaining reactions can then be described by the following rate expressions:

Reaction	Velocity
$RH \longrightarrow R^-$	$[RH]\sum_i k_1^i[B_i]$
$R^- \longrightarrow RH$	$[R^-]\sum_i k_{-1}^i[A_i]$
$R^- \longrightarrow RI$	$[R^-]\{k_2[I_2] + k_2'[I_3^-]\}$
$RI \longrightarrow R^-$	$[RI]\{k_{-2}[I^-] + k_{-2}'[I^-]^2\}$
$HR \longrightarrow RI$	$[HR]\{k_3[I_2] + k_3'[I_3^-]\}$
$RI \longrightarrow HR$	$[H^+][RI]\{k_{-3}[I^-] + k_{-3}'[I^-]^2\}$

The concentration [HR] and some of the velocity constants can be eliminated by using the following equilibrium expressions, together with the principle of detailed balancing:

$$K_{RH} = \frac{[H^+][R^-]_e}{[RH]_e} = \frac{[H^+]k_1^i[B_i]}{k_{-1}^i[A_i]}$$

$$K = \frac{[RI]_e[I^-][H^+]}{[RH]_e[I_2]_e} = K_{RH}\frac{k_2}{k_{-2}}$$

$$K_I = \frac{[I_3^-]}{[I_2][I^-]} = \frac{k_2}{k_{-2}}\Big/\frac{k_2'}{k_{-2}'} = \frac{k_3}{k_{-3}}\Big/\frac{k_3'}{k_{-3}'}$$

$$K_E = \frac{[HR]_e}{[RH]_e} = K_{RH}\frac{[HR]}{[R^-][H^+]}$$

In these expressions the suffix *e* is used to denote equilibrium concentrations of species which are not in mobile equilibrium during the course of the reaction. The complete expression for the net rate of the reaction is then obtained by applying the steady-state conditions to the concentrations of R^-, and HR, with the following result:

$$\frac{d[RI]}{dt} = ([RH][I_2] - [H^+][I^-][RI]/K) \times \frac{\sum_i k_1^i[B_i]\{K_E(k_3 + k_3'K_I[I^-]) + K_{RH}(k_2 + k_2'K_I[I^-])/[H^+]\}}{\sum_i k_1^i[B_i] + [I_2]\{K_E(k_3 + k_3'K_I[I^-]) + K_{RH}(k_2 + k_2'K_I[I^-])/[H^+]\}} \qquad (1)$$

In applying this equation to the reversible iodination of malonic ester, the thermodynamic value of *K* can be taken from the electrometric measurements of Bell and Gelles [2] and a colorimetric determination of the same constant is described in the present paper. K_I is known accurately as 714 (Jones and Kaplan [3]), and the values of k_1^i for a number of basic catalysts were measured by Bell, Everett, and Longuet-Higgins: [4] this investigation deals

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[3] Jones and Kaplan, *J. Amer. Chem. Soc.*, 1928, **50**, 1845.

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

with the irreversible bromination of ethyl malonate at relatively high bromine concentrations, where the reaction rate is independent of the concentration and nature of the halogen, being determined by the first step in our reaction scheme. K_{RH} was given as 5×10^{-14} by Pearson and Mills,[5] and Bell and Spiro [1] estimated that K_{E} is in the range 10^{-4}—10^{-6}, though there is no direct determination of this quantity. The uncertainties in K_{RH} and K_{E} produce corresponding uncertainties in the numerical values of the velocity constants k_2, k_2', k_3, and k_3', but they do not affect the comparisons of velocity constants for iodination with those previously obtained for bromination by Bell and Spiro,[1] since the same equilibrium constants are involved in both cases.

If $K \longrightarrow \infty$ (corresponding to complete halogenation at equilibrium) equation (1) reduces to the expression derived by Bell and Spiro [1] for the irreversible bromination reaction. On the other hand, if $[\text{I}_2]$ is kept at zero, as in our experiments with added ascorbic acid, equation (1) becomes

$$-\frac{1}{[\text{RI}]} \cdot \frac{d[\text{RI}]}{dt} = [\text{I}^-]\{K_{\text{E}}[\text{H}^+](k_3 + k_3' K_{\text{I}}[\text{I}^-]) + k_{\text{RH}}(k_2 + k_2'K_{\text{I}}[\text{I}^-])\}/K \quad (2)$$

Provided that $[\text{H}^+]$ and $[\text{I}^-]$ are kept constant during an experiment this represents a first-order reaction with a velocity constant given by the right hand side of the equation and this type of experiment is therefore specially suitable for determining the separate velocity constants.

EXPERIMENTAL

Ethyl malonate was redistilled *in vacuo* (85—86°/14 mm.) and its aqueous solutions were not kept for more than a day before use. Samples of (—)-ascorbic acid from B.D.H. and from Messrs. Boots were used with identical results. The atmospheric oxidation of ascorbic acid is catalysed by traces of copper,[6] and the water used was therefore redistilled in glass. About 0·2M-potassium chloride was added to the solutions of ascorbic acid as a stabilizer, but the use of potassium cyanide for the same purpose [8] had to be abandoned, since it was found that concentrations as low as 10^{-5}M had a powerful catalytic effect on the de-iodination reaction. Solutions of ascorbic acid were protected from light and used on the day of their preparation. Titration with standard iodine solution showed that they were stable under these conditions. Iodine, potassium iodide, potassium chloride, and hydrochloric acid were all " AnalaR " materials. Hydrochloric acid solutions were standardized against recrystallized borax, and sodium hydroxide solutions were prepared from washed sticks and standardized against hydrochloric acid. Acetate buffer solutions were made up by weight from " AnalaR " acetic acid and sodium acetate, the water contents of which had been determined by titration with sodium hydroxide and hydrochloric acid, respectively. Monochloroacetate buffer solutions were freshly prepared from solutions of monochloroacetic acid and sodium hydroxide which had been titrated against one another.

The following procedure was used in most of the kinetic measurements. A solution containing a known concentration of iodo-ester was prepared by the partial iodination of a solution of ethyl malonate in an acetate buffer. A second solution contained potassium iodide, an amount of ascorbic acid equivalent to a part of the iodo-ester and either a buffer solution or hydrochloric acid. The solutions were mixed, and the time noted at which free iodine first appeared in the solution. By repeating the experiment with varying quantities of ascorbic acid a number of points on the reaction curve could be obtained.

The appearance of free iodine was detected by the depolarization method of Foulk and Bawden,[9] in which a platinum cathode in a stirred solution is depolarized by free halogen, thus allowing a current to flow. In our experiments an e.m.f. of 30 mv was applied between two platinum wire electrodes, and the current detected by a Cambridge spot galvanometer (resistance 450 ohms, sensitivity 170 mm./μA). Calibration experiments showed that 1 cm. deflection corresponded to an iodine concentration of about 3×10^{-7}M. The time recorded was always

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[5] Mills and Pearson, *J. Amer. Chem. Soc.*, 1950, **72**, 1694.
[6] Hess and Unger, *Proc. Soc. Exptl. Biol. Med.*, 1921, **19**, 119.
[7] Kellie and Zilva, *Biochem. J.*, 1935, **29**, 1028.
[8] Szent-Györgyi, *ibid.*, 1928, **22**, 1402.
[9] Foulk and Bawden, *J. Amer. Chem. Soc.*, 1926, **48**, 2045.

that for a deflection of 3 cm. In most of the experiments the rise of galvanometer reading was very sharp, but it was less so in hydrochloric acid solutions, probably because the ascorbic acid is here almost entirely in the less reactive undissociated form, and there is a small steady concentration of iodine ($\sim 10^{-7}$M) even before all the ascorbic acid has reacted.

In a typical experiment the composition of the iodo-ester solution was $[RH] = 0{\cdot}04$, $[RI] = 0{\cdot}004$, $[I^-] = 0{\cdot}014$, $[HOAc] = [OAc^-] = 0{\cdot}008$—$0{\cdot}16$. The time necessary for all the iodine to react can be calculated from the previous kinetic measurements,[4] and the iodo-ester solution was used within 30 min. of its preparation. 10 ml. of this solution were added to 70 ml. of a solution containing 0·02—0·1M-potassium iodide, ascorbic acid equivalent to 10—80% of the iodo-ester, and enough potassium chloride to make the final ionic strength of the mixture $I = 0{\cdot}2$. The reaction was carried out at 25°, and the pipette used for adding the iodo-ester solution was warmed slightly above this temperature to counteract cooling. For experiments under more acid conditions the potassium iodide solution contained either hydrochloric acid or monochloroacetate buffer, and the concentration of acetate buffer in the iodo-ester solution was reduced to 0·01—0·02M. Under these conditions all the acetate is converted into acetic acid in the mixture, and the appropriate correction to $[H^+]$ is easily applied.

Four points were normally taken on each reaction curve; the reaction followed strictly first-order kinetics over the range investigated (up to about 80% reaction). The first-order velocity constants were obtained graphically by plotting $\log_{10}$ [RI] against t. In some of the early experiments in acetate buffer solutions irreproducible results were obtained, involving velocity constants up to 20% higher than those finally adopted. It was eventually found that these abnormally high reaction rates occurred when a freshly prepared iodine solution was used in preparing the iodo-ester solution. These abnormalities were reduced to a minimum if the iodine solutions were kept for at least three days before use, and they did not appear when the kinetic experiments were carried out in hydrochloric acid or monochloroacetate buffer solutions. It appears that the iodine used (B.D.H. " AnalaR," or Harrington's " pure ") contained a small quantity of a catalyst which is slowly destroyed in aqueous solution, and which is inactive in moderately acid solutions. This catalyst was not identified, but its behaviour is reminiscent of the catalytic effect (already mentioned) of traces of cyanide, which is also repressed by hydrogen ions.

The use of ascorbic acid for following the reaction involves the assumption that any direct reaction between iodo-ester and ascorbic acid can be neglected. This assumption is supported by the fact that the reactions follow a strictly first-order course, but separate experiments were also made to test the point. The direct reaction will be relatively more important at low iodide concentrations, and experiments were carried out in an acetate buffer with $[I] = 0{\cdot}02$, and an initial iodo-ester concentration of 2×10^{-4}. In some experiments the ascorbic acid was added in one portion, and in others it was added in two halves, the second being added shortly before the first had been used up. The reaction times were longer by a few units % in the second set of experiments, suggesting that a small amount of direct reaction between ascorbic acid and iodine had taken place: however, it can be estimated that under normal conditions the error involved cannot exceed 2% in the most unfavourable circumstances.

The velocity constants obtained in the presence of ascorbic acid are given in Table 1. The calculated values are from the expression

$$k = [I^-](A + B[I^-] + C[H^+] + D[H^+][I^-]) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

with the values $A = 5{\cdot}3 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$, $C = 2{\cdot}40$ l.^{2} mole^{-2} sec.$^{-1}$, $B = 0{\cdot}35$ l.^{2} mole^{-2} sec.$^{-1}$, $D = 6{\cdot}_0$ l.^{3} mole^{-3} sec.$^{-1}$. Of these constants B and C are well defined by the experimental data, while the value of A is subject to more uncertainty, and D is still less certain: it never contributes more than 10% of the observed velocity constant, and the experimental data can be reproduced with moderate accuracy even if the term involving D is omitted from equation 3. We consider, however, that the presence of a term proportional to $[H^+][I^-]^2$ is established with fair certainty.

The concentrations given in Table 1 refer in all cases to the final reaction mixture. The values of $[H^+]$ in the buffer mixtures were calculated by using the thermodynamic dissociation constants of acetic and monochloroacetic acid, together with the value 0·60 for the activity coefficient factor in a solution of ionic strength $I = 0{\cdot}2$.[10]

[10] Larsson and Adell, *Z. phys. Chem.*, 1931, **156**, 352.

Some experiments were carried out on the same reaction in the absence of ascorbic acid, the concentration of iodine formed being determined colorimetrically by means of a Hilger " Spekker " photoelectric colorimeter, the mercury line 4360 Å being used. The colorimeter was calibrated with iodine solutions of known concentration, the total iodide concentration ($[I^-] + [I_3^-]$) being kept at the value used in the kinetic experiments. Reactions were started as in the experiments already described, and samples extracted at intervals for colorimetric estimation. Some mixtures in acetate buffer solutions were left for about an hour, after which the iodine concentration remained constant for at least another hour: these measurements were used for calculating the equilibrium constant of the reaction. The initial concentrations were throughout $[RH] = 1{\cdot}4 \times 10^{-3}$—$3{\cdot}3 \times 10^{-3}$, $[RI] = 0{\cdot}2 \times 10^{-3}$—$0{\cdot}3 \times 10^{-3}$.

TABLE 1. *Velocities in presence of ascorbic acid.*

k = first-order velocity constant, sec.$^{-1}$.

Hydrochloric acid solutions

		10^5k,				10^5k,	
10^4[HCl]	$10^4[I^-]$	obs.	calc.	10^4[HCl]	$10^4[I^-]$	obs	calc
200	200	119	125	200	400	287	288
400	200	223	226	300	400	394	394
600	200	332	327	270	600	611	606
780	200	429	419	380	600	784	787

Monochloroacetate buffer solutions

				10^5k,	
$10^4[CH_2Cl{\cdot}CO_2H]$	$10^4[CH_2Cl{\cdot}CO_2^-]$	$10^5[H^+]$	$10^4[I^-]$	obs.	calc.
400	400	207	200	32	35
400	800	397	200	40	44
400	400	207	400	93	99
400	800	397	400	115	119
400	1400	655	400	144	147
400	2300	1005	400	184	183
400	400	207	600	192	192
400	800	397	600	222	224
400	1350	635	600	264	263
400	2000	895	600	316	306
800	400	110	1000	448	436
400	400	207	1000	465	465
400	809	401	1000	541	523

Acetate buffer solutions

				10^5k,	
$10^7[MeCO_2H]$	$10^4[MeCO_2^-]$	$10^7[H^+]$	$10^4[I^-]$	obs.	calc.
200	200	288	391	74	75
300	100	865	391	70	75
300	100	865	400	73	77
200	200	288	591	155	154
300	100	865	591	150	155
200	200	288	798	267	266
300	100	865	798	260	268
200	200	288	1000	395	404
300	100	865	1000	398	405
200	200	288	1200	566	568
300	100	865	1200	555	570
200	200	288	1400	751	761

In order to interpret these kinetic experiments it is necessary to use equation (1), which can be integrated if we assume that [RH], $[I^-]$, and $[H^+]$ are constant during the course of a reaction, as is approximately the case in our experiments. Introducing the abbreviations $x = [I_2] + [I_3^-]$, $q = 1/(1 + K_I[I^-])$, $r = [H^+][I^-]$, $K/1/F = K_E(k_3 + k_3'K_1[I^-]) + K_{RH}(k_2 + k_2'K_I[I^-])/[H^+]$, we find on integration

$$\sum k_1{}^i[B_i]t + qx/(q[RH] + r) = \frac{F\sum_i k_1{}^i[B_i](q[RH] + r) + qr[RI]_0}{(q[RH] + r)^2} \ln\left\{1 - \frac{(q[RH] + r)x}{r[RI]_0}\right\} \quad (4)$$

where $[RI]_0$ is the initial iodo-ester concentration. The quantity F has the same significance as in the paper by Bell and Spiro [1] on the bromination reaction. All the quantities in equation (4) are known except F: the value of K was taken from the final readings in the experiments in acetate buffer solutions, and those of $k_1{}^i$ from the results of Bell and Spiro.[1] By plotting the left-hand side of equation (4) against the logarithm on the right-hand side a fairly straight line was obtained in each experiment, from the slope of which F could be calculated. The values thus obtained are given in Table 2. By comparison with eqn. (3), $1/F = K(A + B[I^-] + C[H^+] + D[H^+][I^-])/[H^+]$, and values of F can therefore be calculated by using the values of A, B, C, and D derived from the experiments made in presence of ascorbic acid. These are given in Table 2 for comparison with the observed values. There is moderate agreement, and the fact that the calculated values are all somewhat greater than the observed ones is probably attributable to the approximations made in deriving equation (4). We may conclude that the same kinetic scheme is valid both in presence and in absence of ascorbic acid.

TABLE 2. *Velocities without addition of ascorbic acid.*

Acetate buffers. $[MeCO_2H]$ and $[MeCO_2^-]$ are initial stoicheiometric concentrations. $[RH]_0 = 1·4 \times 10^{-3}$ $[RI]_0 = 2 \times 10^{-4}$, $[I^-] = 0·0707$, and the ionic strength is 0·2 throughout.

			$1/F$,			
$10^3[MeCO_2H]$	$10^3[MeCO_2^-]$	$10^5[H^+]$	obs.	calc.	$10^4[RI]_e$	K_0
1	1	2·75	102	105	1·233	0·0560
2	2	2·75	—	—	1·186	0·0562
2	1	5·38	50	54	0·913	0·0558
3	1	8·13	34	36	0·727	0·0555
5	1	12·64	21	23	0·546	0·0563

Hydrochloric acid. $[I^-] = 0·01$, $[MeCO_2H] = 0·002$, $[RH] + [RI] = 0·0033$, Ionic strength $= 0·2$

		$1/F$,				$1/F$,	
$10^4[RI]_0$	$[H^+]$	obs.	calc.	$10^4[RI]_0$	$[H^+]$	obs.	calc.
2·99	0·004	0·35	0·42	1·99	0·014	0·24	0·29
3·00	0·006	0·32	0·37	1·99	0·020	0·24	0·27
3·00	0·010	0·29	0·31	2·00	0·030	0·23	0·25

The results of the equilibrium measurements are given in the last two columns of Table 2. If it is assumed that in any solution the value of $f_\pm$ is the same for H^+ and I^- as for H^+ and $MeCO_2^-$, then the thermodynamic equilibrium constant for the reaction $RH + I_2 \rightleftharpoons RI + H^+ + I^-$ is given by the expression $K_0 = K_a[RI][I^-][MeCO_2H]/[RH][I_2][MeCO_2^-]$, where K_a is the thermodynamic dissociation constant of acetic acid ($1·751 \times 10^{-5}$ at 25°). The mean value of K_0, 0·056, is in reasonable agreement with 0·052 found by Bell and Gelles [2] by electrometric measurements in solutions of ionic strength 0·1. The constant K in equations (1), (2), and (4) involves concentrations rather than activities, so that $K_0 = Kf_+f_-/f_0$. For $I = 0·2$ the value of the activity-coefficient factor is about 0·60,[10] giving $K = 0·093$. One equilibrium measurement was carried out in 0·004M-hydrochloric acid, giving $K = 0·095$ (independent of any assumptions about activity coefficients). The mean value $K = 0·094$ was used in computing the kinetic experiments.

DISCUSSION

By comparing equations (2) and (3) the observed values of the coefficients A, B, C, and D can be used to derive approximate second-order velocity constants for the reaction of enol and enolate ion with the species I_2 and I_3^-, taking $K_{RH} = 5 \times 10^{-14}$, $K = 0·094$, and $K_E = 10^{-5}$. These velocity constants can be compared with those for reaction with Br_2 and Br_3^-, derived by Bell and Spiro [1] from bromination experiments at low bromine concentrations, the same values of K_{RH} and K_E being used. Both sets of values are given in Table 3. All these constants represent fast reactions, and those for reactions with the

TABLE 3. *Velocity constants for halogenation of ethyl malonate at 25°* (*l. mole*$^{-1}$ *sec.*$^{-1}$).

	Br_2	I_2	Br_3^-	I_3^-
Enol	2×10^4	2×10^4	1×10^4	1×10^2
Enolate	5×10^9	1×10^{10}	1×10^9	1×10^9

enolate ion are not far below a collision number : it is therefore not surprising that there is little variation between the different halogenating agents. The enol gives slower reactions, and it is remarkable that the three species Br_2, Br_3^-, and I_2 react at approximately the same rate. The considerably lower reactivity of I_3^- is probably related to the higher stability of this ion.

The reverse reaction of halogenation by I_3^- is formally termolecular (*e.g.*, $RI + 2I^- \longrightarrow R^- + I_3^-$), but it is not necessary to assume that two iodide ions react simultaneously with the iodo-ester. It is unlikely that a species I_2^{2-} is formed, but it is reasonable to suppose that the covalently bound iodine in RI can add on an iodide ion to give RI_2^-, which then reacts with a second iodide ion.

As already mentioned, cyanide ions exert a powerful catalytic effect upon the de-iodination reaction. It was found that the acceleration observed did not involve the ascorbic acid, since similar results were obtained by using arsenious oxide for removing the iodine. No detailed study was made, but it was established that the rate of the catalysed reaction is directly proportional to the concentration of iodo-ester and of cyanide, inversely proportional to the hydrogen-ion concentration, and independent of iodide concentration. This is consistent with the mechanism

$$RI + CN^- \longrightarrow R^- + ICN; \qquad ICN + I^- \longrightarrow I_2 + CN^-$$

with the first step rate-determining and the second very fast. Our approximate measurements indicate a value of about 10^6 l. mole^{-1} sec.$^{-1}$ for the velocity constant of the reaction $RI + CN^-$.

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