362. *Kinetics of the Chlorination of Acetone in Aqueous Solution.*

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The kinetics of chlorination of acetone have been studied with chlorine concentrations in the range 10^{-2}M to 10^{-8}M. At the higher concentrations the reaction is of zero order with respect to halogen, both in solutions of strong acids and in acetate buffer solutions, and the rate is the same as for bromination and iodination, being determined by the rate of enolization or ionization of the acetone. At low chlorine concentrations the velocity in acid solutions becomes proportional to the chlorine concentration, and the results lead to a velocity constant of $7 \cdot 3 \times 10^5$ l. mole^{-1} sec.$^{-1}$ for the reaction between chlorine and the enol form of acetone. In hypochlorous acid solutions there is some reaction with the keto-form of acetone, possibly involving H_2OCl^+, but the major part of the reaction involves enolization, followed by reaction with the small amount of chlorine present in these solutions. Bromine reacts with the enol at least five times faster than chlorine.

THE halogenation of acetone is the classical example of a reaction which is kinetically of zero order with respect to halogen, its velocity being determined by the rate of enolization or ionization of the ketone in the presence of acid or basic catalysts. In Lapworth's original work [1] chlorine was found to differ somewhat from bromine and iodine in its behaviour, though Rice and Fryling [2] subsequently reported, without details, that chlorine, bromine, and iodine reacted at identical rates with acetone in acid solution. It seemed

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[1] Lapworth, *J.*, 1904, **85**, 30.

[2] Rice and Fryling, *J. Amer. Chem. Soc.*, 1925, **47**, 382.

desirable to investigate this further, and to extend measurements to very low concentrations of chlorine, so as to measure the rate of chlorination of the very reactive intermediate enol or enolate ion, as has been done for the bromination of ethyl malonate [3,4] and of methyl methanetricarboxylate.[4]

Most of our measurements were made in solutions of strong acids. Under these conditions, and on the assumption that only one chlorine atom is introduced, the reaction scheme for chlorination is:

$$\mathrm{SH} + \mathrm{H}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{HS} + \mathrm{H}^+$$

$$\mathrm{HS} + \mathrm{Cl}_2 \xrightarrow{k_2} \mathrm{SCl} + \mathrm{H}^+ + \mathrm{Cl}^-$$

where SH and HS are, respectively, the keto- and the enol form of acetone. (The formation of the enol is actually believed to involve the rapid reversible addition of a proton to oxygen, followed by the transfer of a proton from carbon to a water molecule, but these two steps can be represented as one for present purposes.) The steady-state assumption gives for the reaction velocity

$$v = -\frac{1}{[\mathrm{SH}]}\cdot\frac{\mathrm{d}[\mathrm{SH}]}{\mathrm{d}t} = -\frac{1}{[\mathrm{SH}]}\cdot\frac{\mathrm{d}[\mathrm{Cl}_2]}{\mathrm{d}t} = \frac{k_2k_1[\mathrm{H}^+][\mathrm{Cl}_2]}{k_{-1}[\mathrm{H}^+] + k_2[\mathrm{Cl}_2]}. \qquad (1)$$

At sufficiently high halogen concentrations this reduces to $v = k_1[\mathrm{H}^+]$, the usual expression for acid-catalyzed enolization (zero order in halogen), but if $[\mathrm{Cl}_2]$ is small and $[\mathrm{H}^+]$ large the rate will depend upon halogen concentration, becoming eventually $v = k_2K_{\mathrm{E}}[\mathrm{Cl}_2]$, where $K_{\mathrm{E}} = k_1/k_{-1}$ is the keto–enol equilibrium constant, equal to $2{\cdot}5 \times 10^{-6}$ for acetone in aqueous solution.[5] Archer and Bell [6] did in fact find some dependence on bromine concentration in the bromination of acetone in aqueous hydrochloric acid up to 8M. The velocity constant k_2 in the above treatment does not discriminate between the different halogenating species which may be present in aqueous chlorine, but it will be shown later that molecular chlorine is the only one of importance under our conditions.

EXPERIMENTAL

" AnalaR " acetone was used without purification. Its density indicated a water content of less than 0·5%. Drying over potassium carbonate and subsequent distillation produced small quantities of an impurity which reacted rapidly with chlorine. Chlorine was prepared from " AnalaR " potassium permanganate and hydrochloric acid, washed with aqueous potassium permanganate, and absorbed in conductivity water. Chlorine solutions were stored in blackened vessels.

Hypochlorous acid was prepared by Cady's method.[7] Chlorine monoxide was prepared by shaking mercuric oxide with a solution of chlorine in carbon tetrachloride, and was extracted into water. The aqueous hypochlorous acid was distilled and stored in a blackened vessel at 0°. The pH of this solution was initially 2·55 (glass electrode). If it is assumed that $[\mathrm{H}^+] = [\mathrm{Cl}^-]$, the value of the hydrolysis constant [8,9,10] $[\mathrm{HOCl}][\mathrm{H}^+][\mathrm{Cl}^-]/[\mathrm{Cl}_2] = 3{\cdot}9 \times 10^{-4}$ leads to the ratio $[\mathrm{Cl}_2]/[\mathrm{HOCl}] = 0{\cdot}02$. During the period of the experiments pH changed to 2·36, corresponding $[\mathrm{Cl}_2]/[\mathrm{HOCl}] = 0{\cdot}04$. These figures represent an upper limit to the chlorine content, since the solutions probably contain chlorate as well as chloride ions.

Sodium iodide and perchlorate were of Laboratory Reagent grade, and all other materials

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[3] Bell and Spiro, *J.*, 1953, 429.
[4] Bell and Rawlinson, *J.*, 1961, 726.
[5] Schwarzenbach and Wittwer, *Helv. Chim. Acta*, 1947, **30**, 669.
[6] Archer and Bell, *J.*, 1959, 3228.
[7] Cady, *Inorg. Synth.*, 1957, **5**, 160.
[8] Jakowkin, *Z. phys. Chem.*, 1899, **29**, 613.
[9] Zimmerman and Strong, *J. Amer. Chem. Soc.*, 1957, **79**, 2063.
[10] Connick and Yuan-tsan Chia, *J. Amer. Chem. Soc.*, 1959, **81**, 1280.

of " AnalaR " grade. In measurements with dilute solutions of chlorine or hypochlorous acid water had been re-distilled from alkaline permanganate in an all-glass still.

All kinetic measurements were at 25°. With the more concentrated chlorine solutions (initial $[Cl_2] > 10^{-3}$) the reaction could be followed by titration. The reaction vessel was a blackened 20-ml. glass syringe without air space, as used by Bell and Spiro.[3] Samples were expelled at intervals into weighed flasks containing 10 ml. of 0·1M-sodium iodide in an acetate buffer ([HOAc] = [NaOAc] = 0·2), the tip of the syringe being held just below the surface of the liquid. The iodine liberated was titrated (starch–glycollate indicator) against 0·002N-sodium thiosulphate, stabilized by the addition of chloroform and standardized against potassium iodate at frequent intervals. Control experiments showed that there was no detectable loss of chlorine from the syringe, and that the monochloroacetone formed does not liberate iodine from iodide at an appreciable rate under our experimental conditions. Chlorination by hypochlorous acid solutions was also followed by titration.

A more convenient kinetic method for the same range of chlorine concentrations was to follow the decrease in the absorption of chlorine at 324 mμ. Measurements were made in a 1-cm. stoppered quartz cell, which was filled completely with solution, a Unicam SP 500 spectrophotometer with a cell compartment controlled at 25° ± 0·05° being used. The scale of the instrument was shown to be linear at 373 and 273 mμ over the range of optical densities 0·02—0·3 by calibrating it with alkaline solutions of potassium chromate.[11] Because of hydrolysis and the formation of Cl_3^- the apparent extinction coefficient of chlorine varies with the concentration of hydrogen ions and chloride ions, and calibrations were therefore carried out over a range of conditions, so that the appropriate extinction coefficient could be used in each kinetic experiment. Since it is impossible to transfer chlorine solutions without loss to the optical cells, in the calibration experiments the cell was opened under the surface of 0·05M-sodium iodide, and the iodine liberated titrated with sodium arsenite solution. Our results resemble those of Zimmerman and Strong,[9] but the value which we deduce for the maximum extinction coefficient of the species Cl_2 ($\varepsilon = 79 \pm 1$ at 324 mμ) is considerably greater than theirs ($\varepsilon = 75{\cdot}3 \pm 0{\cdot}3$ at 325 mμ).*

Chlorination by dilute chlorine solutions (initial $[Cl_2] < 10^{-5}$M) was followed by the potential of a platinum-gauze redox electrode, as previously applied to bromination reactions.[12,13] The reference electrode was a saturated calomel electrode, the side-arm of which was drawn out to a fine tip and immersed directly in the reacting solution. Tests showed that no significant quantities of chloride diffused into the solution. The e.m.f. was measured with a conventional potentiometer, and the solution was stirred at about 600 r.p.m. The cell was filled with all the solutions except acetone, and after the initial potential had been noted the reaction was started by squirting in the acetone solution. Readings were taken by repeatedly unbalancing the potentiometer by an arbitrary amount (usually 5 mv) and speaking into a tape recorder the times at which the galvanometer spot passed through zero. The initial chlorine concentration was usually 10^{-5}—10^{-4}M, and its value was calculated from the initial e.m.f. (E_i) by the equation $\log [Cl_2]_0 = \{(E_i - 1{\cdot}148)/0{\cdot}0295\} + 2 \log [Cl^-]$, where 1·148 is the standard redox potential of the chlorine–chloride system relative to saturated calomel. This procedure neglects activity coefficients and liquid-junction potentials, so that the concentrations obtained are only approximate: however, it will be seen later that they do not enter into the derivation of velocity constants. The fall in chlorine concentration was followed until it reached 10^{-8}—10^{-9}M, when it ceased to poise the electrode. A typical experiment lasted for a few minutes, and readings were taken every 10—20 sec.

RESULTS AND DISCUSSION

A series of experiments was carried out (by titration or spectrophotometry) with perchloric acid in the range 0·05—0·2M, and initial $[Cl_2]$ between 0·001 and 0·005M. In

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* It has been pointed out by Connick and Yuan-tsan Chia [10] that the discrepancy between Zimmerman and Strong's value for the hydrolysis constant of chlorine and other values can be reduced by assuming a higher value for ε (Cl_2).

[11] Vandenbelt, Forsyth, and Garrett, *Ind. Eng. Chem., Analyt.*, 1945, **17**, 235.
[12] Bell and Ramsden, *J.*, 1958, 161.
[13] Bell and Rawlinson, *J.*, 1961, 63.

every case the chlorine concentration decreased linearly with time, corresponding to a zero-order reaction. According to equation (1), the kinetics can then be described by $-d[Cl_2]/dt = k_1[H^+][SH]$, where k_1 is the catalytic constant for the enolization of acetone by hydrogen ions. The constancy of k_1 is shown by the last line of Table 1.

TABLE 1.

Chlorination of acetone at higher chlorine concentrations.

$[Cl^-] = 0{\cdot}20$ throughout. Spectrophotometric method, except for values marked *, which are by titration. k_1 in l. mole^{-1} sec.$^{-1}$.

$[HClO_4]_0 = 0{\cdot}050$, $[SH]_0 = 0{\cdot}248$

$10^5[Cl_2]_0$	151	159	168	305	343	358
10^7k_1	288	292	296	274	271	276

$[HClO_4]_0 = 0{\cdot}100$, $[SH]_0 = 0{\cdot}300$

$10^5[Cl_2]_0$	138	139	178	180	215	220	271	331	340	395	520
10^7k_1	280	281	286	284	288	293	281 *	299 *	295 *	290 *	285 *

$[HClO_4]_0 = 0{\cdot}200$

$10^5[Cl_2]_0$	111	115	116	127	187	191
$10^3[SH]_0$ ...	300	300	300	300	248	248
10^7k_1	283	288	277	287	293	290

Table 2 compares our value of k_1 with those derived from the kinetics of the iodination or bromination of acetone. The agreement is excellent, showing that with all three halogens the rate is determined by the enolization of the ketone. In all cases it has been assumed that the substitution of more than one halogen can be neglected. This is justifiable, since not more than 1% of the acetone was halogenated, and the introduction of one or two halogen atoms produces only a small increase in the rate of acid-catalyzed enolization.[14] The anomalous behaviour found by Lapworth [1] for chlorination was not observed: it will be shown later that this is because his solutions contained a considerable proportion of hypochlorous acid.

TABLE 2.

Catalytic constants for the acid-catalyzed halogenation of acetone at 25°.

Halogen	Method	10^7k_1	Ref.	Halogen	Method	10^7k_1	Ref.
Iodine	Chemical analysis	285	15	Chlorine	Chemical analysis	285	2
Iodine	,, ,,	283	16	Chlorine	,, ,,	292	Present paper
Iodine	Spectrophotometric	288	17				
Bromine	Chemical analysis	283	18	Chlorine	Spectrophotometric	285	,,
Bromine	,, ,,	287	19				
Bromine	Spectrophotometric	283	20				

A brief study was made of chlorination in acetate buffer solutions at chlorine concentrations of about 10^{-3}, the titration method being used. The plots of chlorine concentration against time showed an appreciable acceleration in the early part of the reaction. Bell and Lidwell,[14] studying the corresponding iodination, had assumed that the second and the third stage of halogenation were very fast compared with the first, so that the observed rate of consumption of halogen was three times the rate of ionization or enolization of acetone. This assumption is not valid in the early stages of the reaction,

[14] Bell and Lidwell, *Proc. Roy. Soc.*, 1940, *A*, **176**, 88.
[15] Rice and Kilpatrick, *J. Amer. Chem. Soc.*, 1923, **45**, 1401.
[16] Dawson, *Trans. Faraday Soc.*, 1928, **24**, 640.
[17] Bamford and Bell, unpublished measurements.
[18] Dawson and Key, *J.*, 1928, 2154.
[19] Smith, *J.*, 1934, 744.
[20] Reitz, *Z. phys. Chem.*, 1937, *A*, **179**, 119.

and it is easily shown that the correct expression for the variation of chlorine concentration with time is

$$[\mathrm{Cl_2}] = [\mathrm{Cl_2}]_0 - [\mathrm{SH}]_0 \left\{ \frac{3rs - 2r - s + 1}{(r-1)(s-1)} (1 - e^{-v_1 t}) - \frac{2s - r}{(r-1)(s-r)} (1 - e^{-v_2 t}) + \frac{r}{(s-1)(s-r)} (1 - e^{-v_3 t}) \right\}, \qquad (2)$$

where $r = v_2/v_1$, $s = v_3/v_1$; v_1, v_2, and v_3 are the first-order rate constants for the ionization or enolization of acetone, monochloroacetone, and 1,1-dichloroacetone, respectively. v_2 and v_3 are known to involve only basic catalysis by water and by acetate ions,[14] but v_1 also contains contributions from acid-catalysis by hydrogen ions and acetic acid molecules. By using the values of v_2 and v_3 obtained by Bell and Lidwell [14] from rates of bromination it is possible by trial and error to derive the correct value of v_1 for each of our experiments. This was done for two series of experiments with buffer ratios of 1 : 3 and 3 : 1 and concentrations of acetate ion between 0·05M and 0·15M (0·273M-acetone and ionic strength $I = 0{\cdot}2$ throughout). The resulting values of v_1 were then treated in the usual way to derive catalytic constants for acetic acid and acetate ion in the enolization or ionization of acetone, giving finally $k(\mathrm{HOAc}) = 3{\cdot}8 \times 10^{-8}$ l. mole^{-1} sec.$^{-1}$, $k(\mathrm{OAc})^- = 8{\cdot}3 \times 10^{-8}$ l. mole^{-1} sec.$^{-1}$. The corresponding values obtained by Bell and Lidwell [14] from the iodination of acetone are (converted into the present units) $k(\mathrm{HOAc}) = 3{\cdot}4 \times 10^{-8}$, $k(\mathrm{OAc^-}) = 8{\cdot}1 \times 10^{-8}$. Considering the approximate treatment employed by Bell and Lidwell the agreement is satisfactory, and there can be no doubt that in this range of halogen concentration chlorination in buffer solutions follows the same mechanism as bromination and iodination.

The experiments with low chlorine concentrations ($<10^{-5}$M) were carried out at high concentrations of hydrogen ion and chloride ion, so as to minimize hydrolysis to hypochlorous acid and to favour a rate-determining halogenation step (cf. equation 1). The e.m.f. decreased linearly with time, except for an occasional more rapid initial decrease, which was probably due to a trace of impurity in the acetone. This linearity shows that the reaction is of the first order with respect to halogen, and experiments with acetone concentrations varying from 0·003M to 0·015M showed that it was also of the first-order in acetone. The second-order velocity constant for the reaction between chlorine and enol was calculated from the equation $k_2 = -78{\cdot}1(\mathrm{d}E/\mathrm{d}t)/K_\mathrm{E}[\mathrm{SH}]$, where E is in mv and $K_\mathrm{E} = 2{\cdot}5 \times 10^{-6}$.[5] The values obtained are given in Table 3.

TABLE 3.

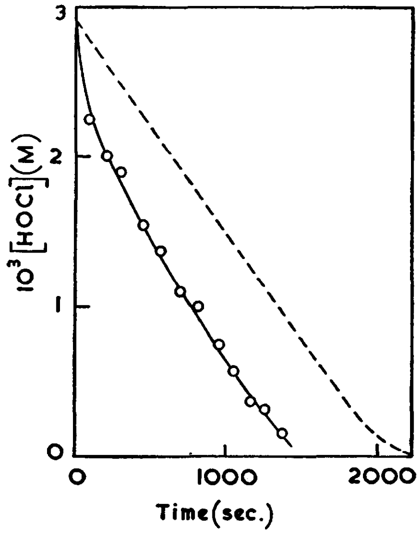
Chlorination of acetone at low chlorine concentrations.

Acetone concn. ~0·007M throughout. Ionic strength made up to $I = 1{\cdot}5$ with sodium nitrate. k_2 in l. mole^{-1} sec.$^{-1}$.

$10^6[\mathrm{Cl_2}]_0$ ...	8·5	1·5	1·7	1·5	1·1	0·9	1·8	1·6	6·4	4·4
$[\mathrm{H^+}]$	0·86	0·86	0·95	0·95	1·04	1·04	1·12	1·12	1·21	1·21
$[\mathrm{Cl^-}]$	1·21	1·21	1·21	1·21	1·21	1·21	1·21	1·21	1·21	1·21
$10^{-5}k_2$	7·3	7·4	7·2	7·3	7·1	7·1	7·6	7·2	8·0	7·9
$10^6[\mathrm{Cl_2}]_0$ ...	2·0	1·2	1·5	1·9	1·9	1·4	5·0	1·9	1·6	1·8
$[\mathrm{H^+}]$	1·10	1·10	1·01	1·01	0·93	0·93	0·86	0·86	0·81	0·81
$[\mathrm{Cl^-}]$	1·10	1·10	1·20	1·20	1·30	1·30	1·40	1·40	1·50	1·50
$10^{-5}k_2$ ...	7·5	7·4	7·1	7·2	7·2	7·2	7·3	7·0	7·2	7·2

Table 3 reveals no significant variation of k_2 with the concentrations of chlorine, hydrogen ions, or chloride ions. This suggests strongly that the main chlorinating species is the chlorine molecule. Under our experimental conditions less than 0·1% of the chlorine is present as hypochlorous acid, which would therefore not contribute appreciably to the observed velocity unless it were a much more effective chlorinating agent than molecular chlorine: this is improbable, and is shown not to be the case by the experiments with hypochlorous acid solutions described in the next section. At the high concentrations of chloride ion employed an appreciable proportion of the chlorine is probably present as Cl_3^-, the equilibrium constant $[Cl_3^-]/[Cl_2][Cl^-]$ having been estimated as 0·2.[21] The constancy of k_2 in Table 3 suggests that the reactivity of Cl_3^- differs little from that of Cl_2, though this is not a firm conclusion since the range of chloride ion concentrations is small and specific salt effects may be important at these high concentrations.

The results at high and low chlorine concentrations are mutually consistent, since if we insert in equation (1) the values $k_1 = 2{\cdot}9 \times 10^{-7}$ (Table 2), $k_1/k_{-1} = 2{\cdot}5 \times 10^{-6}$,[5] and $k_2 = 7{\cdot}3 \times 10^5$ (Table 3) we find that with $[H^+] = 0{\cdot}05$—$0{\cdot}2$ the reaction should be effectively of zero-order with respect to halogen provided that $[Cl_2] > 10^{-4}$, as was in fact observed. The same equation predicts that in this range of acid concentrations an order between zero and unity should be observed for $[Cl_2] \approx 10^{-5}$; this agrees with the fact that in the spectrophotometric measurements and (less reliably) in the titration method the last point or two showed some falling off from the zero-order rate.



Rate of disappearance of hypochlorous acid in presence of acetone in water at 25°. For broken line see text.

The experiments with hypochlorous acid were less conclusive but are of interest in their bearing on the classical work of Lapworth.[1] Hypochlorous acid gives neither a reproducible redox potential nor a sufficiently characteristic absorption spectrum, and its reaction was therefore studied by titration. The course of a typical reaction is shown in the Figure. The occurrence of an initial fast reaction agrees with Lapworth's observations with solutions of chlorine; this is not unexpected, since his solutions contained no added chloride and must therefore have been extensively hydrolysed to hypochlorous acid. The nature of this fast reaction is, however, still unclear. It is faster than the rate of enolization, and rough experiments indicated that the initial rate is proportional to $[H^+][HOCl][acetone]$, with a third-order constant of about 10^{-1} $l.^2$ $mole^{-2}$ $sec.^{-1}$. This suggests that the reaction may involve the attack of the ion ^+H_2OCl on acetone, without the preliminary formation of enol, but further work is needed to establish this. After the fast initial portion the reaction curve shows a linear section of slope approximately equal to the rate of enolization, as deduced from reaction with iodine or bromine. It is difficult to decide whether the enol reacts with hypochlorous acid or with the small

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

amounts of free chlorine which the solution contains, since recent work on the kinetics of the hydrolysis of chlorine[22] shows that any chlorine removed would be regenerated fast enough to maintain its equilibrium concentration. This fact, together with our own results for the rate of reaction with chlorine, makes it possible to predict the course of the reaction on the assumption that free chlorine is the only effective halogenating agent, neglecting the initial fast reaction, which becomes less important as the concentration of hypochlorous acid decreases. The results of such a calculation are shown as a broken line in the Figure. The predicted rate is somewhat less than that observed, which may indicate that the reaction of enol with hypochlorous acid is of importance, though this is not a firm conclusion. Bell and Spiro[3] interpreted one term in the kinetic expression obtained by Bartlett and Vincent[23] for the chlorination of acetone in alkaline hypochlorite solution as being due to the reaction of the enol with hypochlorous acid, for which they estimated a velocity constant of 3×10^9 l. mole^{-1} sec.$^{-1}$. It is very unlikely that this reaction would be much faster than the reaction of enol with molecular chlorine, for which we find $k = 7 \times 10^5$ l. mole^{-1} sec.$^{-1}$, and it is possible that the term in question (which contributes only a small proportion of the observed velocity) is due to a salt effect.

It is of interest to carry out experiments with low concentrations of bromine and iodine, so as to compare their rate of reaction with the enol with that of chlorine. Bromination experiments were carried out by the potentiometric method, just as for chlorine. With 0·77M-sulphuric acid and initial bromine concentrations between 5×10^{-6} and 10^{-5}M the plots of e.m.f. against time were initially curved, indicating that the bromination of the enol is not wholly rate-determining: this shows that bromination must be faster than chlorination, which is wholly rate-determining under these conditions. Experiments with $[Br_2] = 0{\cdot}9 \times 10^{-6}$, $2{\cdot}7 \times 10^{-6}$, and $3{\cdot}8 \times 10^{-6}$M gave linear plots of e.m.f. against time, leading to velocity constants $k_2 = 3{\cdot}7 \times 10^6$, $3{\cdot}8 \times 10^6$ and $3{\cdot}6 \times 10^6$ l. mole^{-1} sec.$^{-1}$, compared with $7{\cdot}3 \times 10^5$ l. mole^{-1} sec.$^{-1}$ for chlorination. Since the solutions contained 0·1M-potassium bromide, the observed velocity constant is an average value for the species Br_2 and Br_3^-, and the value for molecular bromine is presumably somewhat higher. It can be concluded, however, that the reactivity of bromine towards the enol is at least five times as great as that of chlorine, in contrast to the reverse behaviour observed for the addition of these halogens to olefinic substances (for example, cinnamic acid) in acetic acid solution.[24]

It was not possible to carry out analogous experiments with very dilute solutions of iodine, since the iodination of acetone is appreciably reversible in strongly acid solutions.[25] This could be partly prevented by adding potassium iodate to the solution, but the observed potentials then became poorly reproducible at low iodine concentrations, and their interpretation was complicated by uncertainty as to the concentration of iodide ions. It appeared, however, that the reaction remained of zero-order with respect to iodine down to at least 5×10^{-5}M-halogen, from which it can be concluded that $k_2 > 10^6$ l. mole^{-1} sec.$^{-1}$; *i.e.* iodine is more reactive than chlorine towards the enol, and may well be more reactive than bromine.

Our thanks are offered to the National Research Council of Canada for a Fellowship awarded to K. Y.

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[22] Lifschitz and Perlmutter-Hayman, *J. Phys. Chem.*, 1960, **64**, 1663.
[23] Bartlett and Vincent, *J. Amer. Chem. Soc.*, 1935, **57**, 1596.
[24] de la Mare, *Quart. Rev.*, 1949, **3**, 126.
[25] Bell and Gelles, *Proc. Roy. Soc.*, 1951, *A*, **210**, 310.