50. *Kinetics of the Reaction between 2-Ethoxycarbonyl-2-iodo*cyclo*hexanone and Iodide Ions.*

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Measurements are reported of the rate of the reaction of 2-ethoxycarbonyl-2-iodo*cyclo*hexanone with iodide ions over a range of hydrogen-ion concentrations. The pK of 2-ethoxycarbonyl*cyclo*hexanone and the equilibrium percentage of enol in its aqueous solutions have also been determined. By combining these results with the equilibrium constant for the iodination of 2-ethoxycarbonyl*cyclo*hexanone, velocity constants are derived for the fast reactions of iodine and tri-iodide ions with the enol and the anion of the ester.

BELL and ENGEL[1] studied the kinetics of the reaction between ethyl iodomalonate and iodide ions, and showed that the results could be used to deduce the velocities of the very fast reactions of iodine and tri-iodide ion with the enol and anion of malonic ester. It was necessary to know the equilibrium constant for the iodination reaction, the acid dissociation constant of malonic ester, and the equilibrium percentage of enol in aqueous solution, of which the last two could only be estimated roughly. The present paper describes similar measurements with 2-ethoxycarbonyl*cyclo*hexanone. Although this compound is experimentally somewhat less convenient than malonic ester, it has the advantage that the acid dissociation constant and the percentage of enol can be measured directly, and hence reliable values can be obtained for the velocity constants of the iodination reactions. The reaction between the iodo-ester (RI) and iodide ions was studied in presence of ascorbic acid, which removes the iodine produced and renders the reaction irreversible. Bell and Engel[1] showed that under these conditions the kinetics are represented by

$$\frac{1}{[\mathrm{RI}]}\cdot\frac{\mathrm{d}[\mathrm{RI}]}{\mathrm{d}t}=[\mathrm{I}^-]\left\{K_{\mathrm{RH}}(k_2+k_2'K_{\mathrm{I}}[\mathrm{I}^-])+K_{\mathrm{E}}\,[\mathrm{H}^+](k_3+k_3'K_{\mathrm{I}}[\mathrm{I}^-])\right\}/K \quad . \quad (1)$$

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

where, if RH and HR represent the keto and enol form of the ester, the equilibrium constants are given by

$$K_{RH} = [H^+][R^-]/[RH], \qquad K_E = [HR]/[RH],$$
$$K = [RI][I^-][H^+]/[RH][I_2], \text{ and } K_I = [I_3^-]/[I_2][I^-],$$

and the second-order velocity constants correspond to the following reactions:

$$HR + I_2, k_2 \qquad HR + I_3^-, k_2' \qquad R^- + I_2, k_3 \qquad R^- + I_3^-, k_3'$$

If, as in our measurements, $[I^-]$ and $[H^+]$ are constant during an experiment, then the left-hand side of eqn. (1) represents a first-order velocity constant for that experiment.

EXPERIMENTAL

2-Ethoxycarbonyl*cyclo*hexanone (subsequently referred to as " ester ") was redistilled *in vacuo* (109°/12 mm.) and its aqueous solutions were not kept for more than a few hours before use. Solutions of ascorbic acid were made from B.D.H. (−)-ascorbic acid, protected from the light, and used on the day of preparation. All other solutions were prepared from AnalaR materials, and all water used had been re-distilled in glass.

The general procedure in the kinetic experiments followed that described by Bell and Engel, but the greater velocities and higher value of K limited the range of concentrations of iodide and of hydrogen ion which could be studied. A solution of ester *ca.* 0·002M was partly iodinated in an acetate buffer solution, and brought to 25°. To this was added rapidly a solution of potassium iodide containing sufficient ascorbic acid to react with part of the iodine produced, and the time for the first appearance of free iodine was detected by the depolarization method.[1] Because of the high value of K and the low solubility of the iodo-ester it was necessary to detect very low concentrations of iodine, and the sensitivity of the method was increased by using platinum gauze in place of wire electrodes. By repeating this procedure with varying quantities of ascorbic acid five points were obtained for each value of $[I^-]$ and $[H^+]$, and the first-order velocity constant obtained from the linear plot of log [RI] against time. These constants are listed in the Table.

In all the reaction mixtures the ionic strength was made up to 0·2 by the addition of potassium chloride. In calculating the hydrogen-ion concentration of the buffer solutions the value $f_{\pm}^2 = 0{\cdot}6$ was taken for the activity coefficient factor at $I = 0{\cdot}2$ (ref. 2).

The acid dissociation constant of the ester was determined at 25° by measuring the pH of partly neutralized solutions of ester, with a Cambridge pH meter and an " Alki " glass electrode, calibrated with 0·05M-borax solution. The solutions were made up to an ionic strength of 0·2 with potassium chloride. The observed pH changed slowly with time, probably because of hydrolysis of the ester, but could be extrapolated back to zero time. In calculating the thermodynamic value of pK it was again assumed that $f_{\pm}^2 = 0{\cdot}6$. Successive experiments with degrees of neutralization between 0·25 and 0·60 gave pK (thermodynamic) = 10·94, 11·01, 10·94, 10·85; mean 10·94.

In determining the equilibrium proportion of enol in aqueous solution, ester solutions were kept at 25° for 19 hr. in acetate buffer solutions with $[OAc^-] = 0{\cdot}08$ and [HOAc] between 0·005 and 0·24. The concentration of ester was throughout about 0·001M. According to Bell and Goldsmith's kinetic measurements[3] the half-time for reaching enolization equilibrium in these solutions should be less than 1 hr. The acetate ions were then neutralized by a slight excess of hydrochloric acid, and the enol estimated by rapid titration with 0·001M-bromine in 1M-potassium bromide, the depolarization method being used for detecting the first appearance of free bromine. According to Bell and Goldsmith the half-time for enolization in these slightly acid solutions is 20 hr., and in fact reproducible results were obtained, successive experiments giving for the enol content 2·05, 1·97, 1·99, 2·00, and 2·17%: mean 2·04% of enol.

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[2] Larsson and Adell, *Z. phys. Chem.*, 1931, **156**, 352.
[3] Bell and Goldsmith, *Proc. Roy. Soc.*, 1952, *A*, **210**, 322.

Apparent first-order velocity constants (10^4k; *k in sec.*$^{-1}$) *for reaction of iodo-ester with iodide ions at* 250°. (*The corresponding calculated values are given in parentheses.*)

$10^4[I^-]$: $10^7[H^+]$	206	307	406	506
146	67 (70)	115 (121)	173 (180)	243 (250)
296	107 (103)	178 (173)	260 (255)	351 (351)
413	131 (130)	219 (217)	322 (317)	442 (434)
583	172 (168)	281 (278)	410 (402)	563 (551)
876	231 (233)	382 (383)	536 (554)	724 (750)

DISCUSSION

The calculated velocity constants in the Table are obtained from the expression

$$k = 0{\cdot}106[I^-] + 3{\cdot}77[I^-]^2 + 8{\cdot}91 \times 10^3[H^+][I^-] + 9{\cdot}17 \times 10^4[H^+][I^-]^2 \quad . \quad (2)$$

where the numerical coefficients were obtained graphically from the experimental results by using either plots of $k/[I^-]$ against $[H^+]$ at constant values of $[I^-]$, or of $k/[I^-]$ against $[I^-]$ at constant values of $[H^+]$. The observed and calculated values of k agree within experimental error, and since all the terms in eqn. (2) contribute appreciably to the velocity the four numerical coefficients are all known to better than about ±10%. As in the work of Bell and Engel[1] the rate law corresponds to eqn. (1), and the results can be used to derive the velocity constants of the fast halogenation steps. Our own measurements give $K_E = 0{\cdot}0204$, and $K_{EH} = 1{\cdot}15 \times 10^{-11}/f_{\pm}^2 = 1{\cdot}9 \times 10^{-11}$ at $I = 0{\cdot}2$. Similarly, from Bell and Gelles's measurements[4] we have $K = 0{\cdot}505/f_{\pm}^2 = 0{\cdot}842$, and $K_I = 714$ from Jones and Kaplan.[5] Inserting these values in eqn. (1) and (2) we find the following velocity constants:

Reaction	Velocity constant	Reaction	Velocity constant
Enol + I_2	$3{\cdot}8 \times 10^5$ l. mole^{-1} sec.$^{-1}$	Enol ion + I_2	$4{\cdot}7 \times 10^9$ l. mole^{-1} sec.$^{-1}$
Enol + I_3^-	$5{\cdot}4 \times 10^3$,,	Enol ion + I_3^-	$2{\cdot}3 \times 10^8$,,

These values are of the same order of magnitude as those derived by Bell and Engel[1] for the iodination of ethyl malonate, and also those observed directly by Bell and Spiro;[6] from the bromination of ethyl malonate at low bromine concentrations: they are, however, more reliable than any previous estimates of the halogenation velocities of enols and their ions.

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[4] Bell and Gelles, *Proc. Roy. Soc.*, 1952, *A*, **210**, 310.
[5] Jones and Kaplan, *J. Amer. Chem. Soc.*, 1928, **50**, 1845.
[6] Bell and Spiro, *J.*, 1953, 429.