1154. *Dilatometric Study of a Second-order Reaction.*

By PETER JONES, W. R. PORTEOUS, and W. F. K. WYNNE-JONES.

A number of computational methods have been applied to the calculation, from dilatometric data, of rate constants for the alkaline hydrolysis of 2-chloro-ethanol in aqueous and aqueous-alcoholic solutions at 25°.

THE dilatometric technique is, in principle, applicable to most slow or moderately rapid reactions which take place in solution. Its use has been restricted to first-order reactions because the initial reading is not an accessible quantity, and because infinity readings are commonly of low precision. For first-order reactions these difficulties are overcome by the procedure due to Guggenheim[1] or its modification by Swinbourne.[2] Mathematical techniques for obtaining rate constants from second-order curves, without a knowledge of the initial and final readings, have been described[3,4] but have not been tested with experimental data.

In this work we have used Sturtevant's method,[4] both in its original form and in a modified form, and also an alternative curve-fitting procedure, to calculate rate constants for the

[1] Guggenheim, *Phil Mag.*, 1926, **1**, 538.
[2] Swinbourne, *J.*, 1960, 2371.
[3] Roseveare, *J. Amer. Chem. Soc.*, 1931, **53**, 1651.
[4] Sturtevant, *J. Amer. Chem. Soc.*, 1937, **59**. 699.

alkaline hydrolysis of ethylene chlorohydrin (2-chloroethanol) from dilatometric studies of the reaction. Measurements were made at unequal initial reactant concentrations. The reaction has been the subject of a number of investigations by a variety of techniques, and data are available both for aqueous solutions[5-9] and for non-aqueous solvents.[10]

Methods of Computation.—(1). The integrated second-order rate equation for unequal initial concentrations (a and b, respectively, where $a > b$) is:

$$k = \frac{1}{(a-b)t}\log_e\left[1 + \frac{(a-b)}{a}\cdot\frac{h_t - h_0}{h_\infty - h_0}\right] \tag{1}$$

where h_0, h_t, h_∞ are the dilatometric heights at $t = 0$, $t = t$, and $t = \infty$, respectively. h_0 is not measurable; h_∞ is not measurable with adequate accuracy. The problem is thus to calculate or eliminate h_0 and h_∞ in order to obtain k.

Sturtevant[4] showed that the following method may be applied. If a set of readings, h_1, h_2, h_3, and h_4, are taken at times t, $t+\Delta t$, $t+2\Delta t$, $t+3\Delta t$, respectively (Δt is a constant time integral), then:

$$k(a-b)\Delta t = \cosh^{-1}[(A-1)/2] \tag{2}$$

where

$$A = [(h_3 - h_2)(h_4 - h_1)]/[(h_2 - h_1)(h_4 - h_3)] > 3$$

Sets of readings are used to obtain values of A and hence k. The calculation is most conveniently performed by expanding the inverse hyperbolic cosine to give:

$$k^2(a-b)^2\Delta t^2 = (A-3)[1-(A-3)/12+\ldots] \tag{3}$$

(2). Sturtevant emphasized that, when A is not much greater than 3, there is serious magnification of errors using the above method. Such is the case in our experiments. Sturtevant suggested an alternative procedure. Writing

$$k(a-b)\Delta t = \log_e\alpha \tag{4}$$

and

$$c = b/a \tag{5}$$

For sets of reactant *concentration* decrements x_1, x_2, x_3, at times t, $t+\Delta t$, $t+2\Delta t$, respectively, the following equations apply:

$$a = [\alpha x_1(x_3 - x_2) - x_3(x_2 - x_1)]/[\alpha(x_3 - x_2) - (x_2 - x_1)] \tag{6}$$

$$b = [x_1(x_3 - x_2) - \alpha x_3(x_2 - x_1)]/[(x_3 - x_2) - \alpha(x_2 - x_1)] \tag{7}$$

$$c = \{[\alpha(x_3 - x_2) - (x_2 - x_1)]/[(x_3 - x_2) - \alpha(x_2 - x_1)]\}\alpha^{(t+\Delta t)/\Delta t} \tag{8}$$

The difficulty in transposing from concentration units to dilatometer readings means that (8) is the only suitable equation for our purpose. Equation (8) must be solved by successive approximation, using as a first approximation

$$\alpha = (A-1)/2 \pm \{[(A-1)/2]^2 - 1\}^{1/2} \tag{9}$$

This proved to be, not only cumbersome, but also well-nigh impossible, as the exponent of α in equation (8) cannot be determined with accuracy in the dilatometric technique.

(3). To avoid difficulties of transposition and successive approximation, a more convenient modification is as follows. Two sets of three dilatometer readings (h_1, h_2, h_3;

[5] Porret, *Helv. Chim. Acta*, 1941, **24**, 80E.; 1944, **27**, 1321.
[6] Winstrom and Warner, *J. Amer. Chem. Soc.*, 1939, **61**, 1205.
[7] Twigg, Wise, Lichtenstein, and Philpotts, *Trans. Faraday Soc.*, 1952, **48**, 699.
[8] Ballinger and Long, *J. Amer. Chem. Soc.*, 1959, **81**, 2347.
[9] Swain, Ketley, and Bader, *J. Amer. Chem. Soc.*, 1959, **81**, 2353.
[10] Stevens, McCabe, and Warner, *J. Amer. Chem. Soc.*, 1948, **70**, 2449.

h_4, h_5, h_6) are taken at equal time intervals (t, $t+\Delta t$, $t+2\Delta t$; t', $t'+\Delta t$, $t'+2\Delta t$), yielding two equations for b (say) which may be equated. This gives for α the quadratic:

$$(h_6-h_5)(h_3-h_2)(h_4-h_1)\alpha^2 - [(h_5-h_4)(h_3-h_2)(h_6-h_1)$$
$$- (h_6-h_5)(h_2-h_1)(h_3-h_4)]\alpha + (h_2-h_1)(h_5-h_4)(h_6-h_3) = 0, \qquad (10)$$

which may be solved for α and hence k.

(4). A different approach from those outlined above is a curve-fitting method in which all the experimental data are utilized simultaneously. Taking the second-order rate equation in the form

$$\log_e [(b-x)/(a-x)] = (a-b)kt+c \qquad (11)$$

we may transpose from concentration decrements to dilatometer readings by putting $h = (x-\mu)/\lambda$, where μ and λ are transposition constants. Equation (11) may now be rearranged to yield

$$h_t = (Ae^{-\beta t}+C)/(De^{-\beta t}+1) \qquad (12)$$

where $\qquad A = [(\mu-a)/\lambda]e^c, \qquad \beta = (b-a)k, \qquad C = (b-a)/\lambda, \qquad D = -e^c$

We now require a method for obtaining first estimates of the parameters A, C, D, and β, and a suitable iterative procedure to introduce variations of these parameters so that we may obtain the best fit of the data to equation (12) by minimizing the sum of the squares of the residuals. First estimates were obtained by use of two approximation functions. First, considering sets of readings, h_0, h_1, $h_2 \ldots h_n$, etc., at times 0, Δt, $2\Delta t \ldots n\Delta t$, etc., respectively, we may use the parabolic approximation

$$h_0 = h_3 - 3(h_4-h_3) + 6(h_5-2h_4+h_3) \qquad (13)$$

to estimate h_0. Alternatively, we may put

$$h_n = h_\infty + pZ^n \qquad (14)$$

where p is negative, and Z is large corresponding to $e^{-\beta\Delta t}$. Considering three points, h_n, h_{n+1}, h_{n+2},

$$h_\infty = (h_n h_{n+2} - h_{n+1}^2)/(h_n - 2h_{n+1} + h_{n+2}) \qquad (15)$$

and $\qquad Z = (h_{n+2}-h_{n+1})/(h_{n+1}-h_n)$, hence $\beta \qquad (16)$

From equation (12) when $t = 0$,

$$h_0 = (A+C)/(D+1) \qquad (17)$$

and, when $t = \infty$, $h_\infty = C$, whence, by substitution, the required estimates are obtained.

The iterative process for obtaining the best fit to the data was carried out in the following way. Considering equation (12) to be of the form $h_t = F(t, A, \beta, C, D)$, and writing:

$$\frac{\partial F}{\partial A}(t) = F_1; \qquad \frac{\partial F}{\partial \beta}(t) = F_2; \qquad \frac{\partial F}{\partial C}(t) = F_3; \qquad \frac{\partial F}{\partial D}(t) = F_4$$

The sum of the squares of the residuals:

$$S = \sum_t (F+F_1\delta A+F_2\delta\beta+F_3\delta C+F_4\delta D-h)^2 \qquad (18)$$

will be a minimum when

$$\frac{1}{2}\frac{\partial S}{\partial \delta A} = \frac{1}{2}\frac{\partial S}{\partial \delta\beta} = \frac{1}{2}\frac{\partial S}{\partial \delta C} = \frac{1}{2}\frac{\partial S}{\partial \delta D} = 0 \qquad (19)$$

Solution of the four equations (19) yields the alteration to the first values of A, β, C, D necessary to give the best least-squares fit.

EXPERIMENTAL

2-Chloroethanol (B.D.H., purity 99%) was twice fractionally distilled in an all-glass apparatus. The fraction of b. p. 128—128·5° was collected. Distilled water was redistilled first from alkaline permanganate and then from a trace of phosphoric acid, and stored in a nitrogen atmosphere.

Carbonate-free sodium hydroxide solutions (B.D.H.) were used, and were standardized against constant-boiling hydrochloric acid. Ethanol was purified by the method of Lund and Bjerrum[11] and stored in a nitrogen atmosphere.

The dilatometer was a slightly modified version of the apparatus described by Brönsted, Kilpatrick, and Kilpatrick.[12] It was mounted in a thermostat controlled to $25 \pm 0.001°$. Small quantities of 2-chloroethanol were measured out accurately, using as a micropipette a hypodermic syringe which had been fitted with stops.

RESULTS AND DISCUSSION

Rate constants, calculated by methods 1, 3, and 4, from experimental data at 25° in aqueous solution are shown in the Table. Values obtained by methods 1 and 4 agree to

Comparison of rate constants in aqueous solution at 25°C.

Initial [NaOH]	Initial [ClCH$_2$·CH$_2$·OH]	k (1. mole^{-1} min.$^{-1}$)		
		Method 1	Method 3	Method 4
0·08	0·044	0·641	0·655	0·645
0·08	0·044	0·735	0·715	0·705
0·08	0·044	0·652	0·850	0·668
0·08	0·044	0·615	0·601	0·641
0·08	0·044	0·763	0·776	0·740
0·156	0·040	0·543	0·621	0·611
0·156	0·040	0·631	0·749	0·653
0·166	0·050	0·651	0·635	0·626
0·118	0·040	0·690	0·635	0·619
0·118	0·040	0·625	0·614	0·612
0·118	0·040	0·553	0·538	0·571

better than 10%, and the average rate constant was 0.65 ± 0.04 for method 4. Rate constants calculated by method 3 agree less well with those calculated by the other methods and show much greater spread. The main effect appears to be that values calculated by method 3 are sometimes very high. This effect seems to arise in some cases because it was necessary to use data in the range where the dilatometer readings were changing slowly with time. Method 3 is clearly much less reliable than either Sturtevant's original procedure (method 1) or the curve-fitting method (method 4).

In Fig. 1 the rate constants obtained by method 4 are compared with values obtained by other workers using direct titrimetric methods. The rate constant is not truly independent
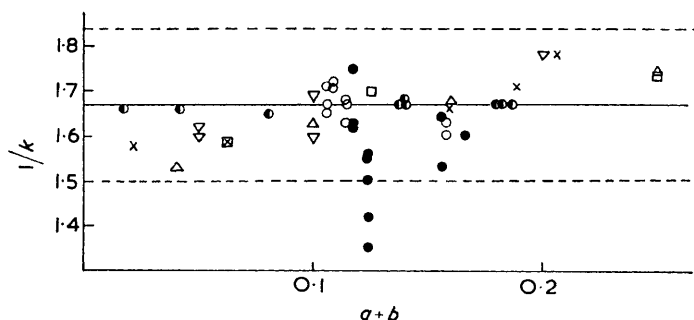

FIG. 1. Rate constants for dilatometric experiments compared with results of other workers; aqueous solutions at 25°.

●, This work;
◑, ref. 6;
×, ref. 6 (without adequate protection from CO$_2$);
○, ref. 9;
△, ref. 7;
▽, ref. 8;
□, ref. 5.

[11] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.
[12] Brönsted, Kilpatrick, and Kilpatrick, *J. Amer. Chem. Soc.*, 1929, **51**, 428.

of reactant concentration although the change in the concentration range relevant to the present work is small. Nevertheless, the plot suggested by Twigg *et al.*[7] is convenient for purposes of comparison. As might be expected, the indirect dilatometric method is considerably less precise than the direct titrimetric methods. The average dilatometric rate constant is about 10% larger than the overall mean titrimetric rate constant. Ballinger and Long[8] report a similar disagreement between titrimetric and conductometric rate constants for this reaction, but do not quote numerical values. The origin of the effect is obscure.

In Fig. 2 our results for aqueous–alcoholic solution are compared with values interpolated at 25° from Arrhenius plots of data[10] at 15° and 30°. The latter were obtained by titrimetric
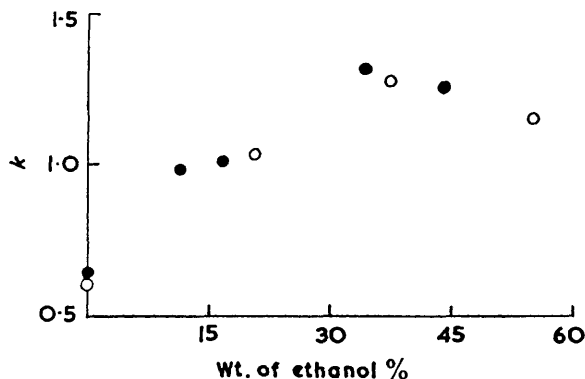

FIG. 2. Rate constants from dilatometric experiments (●) in ethanol–water mixtures at 25° compared with other workers' results (○).[10]

methods. The agreement is within our experimental error but again the mean dilatometric rate constants are higher than those obtained by titrimetry.

The labour of calculation and the relatively low precision make the indirect dilatometric method for second-order reactions undesirable if alternative direct methods are available, but the methods of calculation are not restricted to dilatometry and can be applied generally where initial and final readings are inaccessible. The interval method, first suggested by Sturtevant, and the curve-fitting procedure, which is formally more satisfactory, yield similar results, the former method requiring less computational labour.

(P. J. and W. F. K. W.-J.) DEPARTMENT OF PHYSICAL CHEMISTRY,
    UNIVERSITY OF NEWCASTLE UPON TYNE.
(W. R. P.) THE GRAMMAR SCHOOL, JARROW, CO. DURHAM.   [*Received, November 20th, 1964.*]