

An Acree Equation Analysis of Kinetic Data for the Iodide Ion — Iodoacetic Acid Displacement Reaction

EVA NORLING and PER BERONIUS

Division of Physical Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Kinetic data for the displacement reaction in water solution at 25°C between iodide ion and iodoacetic acid are analyzed by means of the Acree equation. By this procedure the specific reaction rates of the two different exchange reactions involving molecular iodoacetic acid and iodoacetate ion, respectively, are determined.

In the literature, a great number of papers have been published, dealing with the kinetics of halogen exchange in aqueous solution between molecular haloacetic acid and the corresponding halide ion



where X = Cl, Br, or I, and between haloacetate ion and the corresponding halide ion



Kinetic data for reactions involving chloroacetic acid or chloroacetate ion are reported in Refs. 1 and 2, for bromoacetic acid or bromoacetate ion in Refs. 3–5, and for iodoacetic acid or iodoacetate ion in Refs. 3, 6, and 7. Reactions of type (1a) were investigated after adding strong acid to the reaction mixture to suppress the ionization of molecular haloacetic acid, whereas alkaline media were used to study reactions of type (1b).

The aim of the present paper, which concerns the iodide ion — iodoacetic acid exchange reaction in water, is to show that specific reaction rates of the two kinds of displacement reactions discussed above may be determined without adding any strong acid or base to the reaction mixture. To that end, the dependence of the overall rate constant on the total concentration of haloacetic acid is established and the rate data have been analyzed by means of an Acree equation,⁸ modified as described in Ref. 9, to take into account the kinetic salt effect.

EXPERIMENTAL

Reagents. Iodoacetic acid (Merck, *p.a.*) was purified by four recrystallizations from diethyl ether and dried *in vacuo* for 2 h at room temperature. Argentometric analysis indicated an iodide content within 0.3 % of the calculated value.

Sodium iodide (Merck, *suprapur*) was dried at 120°C for 2 h.

Carrierfree $^{131}\text{I}^-$ (the Atomic Energy Establishment, Kjeller, Norway) in aqueous sodium thiosulphate solution was used to label the iodoacetic acid according to a procedure reported in Ref. 10.

Distilled water with an electrolytic conductivity of $1 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ was used as solvent.

Solutions were prepared immediately before each kinetic run.

Kinetic procedure. The rate of the exchange reaction at $25.00 \pm 0.02^\circ\text{C}$ was measured electroanalytically (*cf.* Ref. 11).

Approximately 2 μmol of iodoacetic acid, labelled with 15 μCi ^{131}I , was added to the thermostated reaction vessel containing 50 ml of an aqueous solution of inactive iodoacetic acid and sodium iodide. The specific activity, S , of the ionic iodide was determined at different reaction times. Between three and six analyses were made. The equilibrium specific activity, S_∞ , of this constituent was determined after at least 20 half-times of exchange.

RESULTS

The overall second-order ⁶ rate constant, k , of the exchange reaction was evaluated by the method of least squares from the McKay equation in the form

$$\ln (S_\infty - S) = \ln S_\infty - (a + b)kt \quad (2)$$

where a = total concentration of iodoacetic acid, b = concentration of sodium iodide, and t = time of exchange. The results are quoted in Table 1, in which the degree of dissociation, α , of iodoacetic acid also has been included.

Table 1. Kinetic data for exchange of ^{131}I between iodoacetic acid and sodium iodide in aqueous solution at 25°C.

$a \times 10^4$ M	$b \times 10^3$ M	k $\text{M}^{-1} \text{min}^{-1}$	α
104.0	0.978	0.4005	0.2459
78.9	0.968	0.3884	0.2761
49.64	0.977	0.3729	0.3334
26.13	0.968	0.3358	0.4255
13.61	1.011	0.2693	0.5321
8.37	0.968	0.2313	0.6144
7.90	1.006	0.2374	0.6248
6.67	0.968	0.2124	0.6528

The latter quantity was calculated by successive approximations using the dissociation constant, $K = 6.68 \times 10^{-4}$, of iodoacetic acid at 25°C according to Ives and Pryor¹² and the empirical Davies equation for the activity coefficient. The Davies equation was used in the form¹³

$$-\log \gamma_i \simeq -\log f_i = 0.5 z_i^2 \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\mu \right) \quad (3)$$

where γ_i = molar activity coefficient, f_i = rational activity coefficient, z_i = valency of ion i , and μ = ionic strength. In calculating ionic strengths the inorganic iodide was assumed to form no ion-pairs.

DISCUSSION

The data in Table 1 reveal that the overall second-order rate constant depends upon the degree of dissociation of iodoacetic acid. This behaviour reflects the different reactivities of molecular iodoacetic acid and iodoacetate ion.

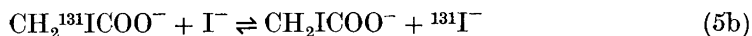
To analyze the kinetic data with respect to specific reaction rates of molecular iodoacetic acid and iodoacetate ion we shall adopt the Acree hypothesis⁸ according to which we may write

$$k = k_i\alpha + k_m(1 - \alpha) \quad (4)$$

where k_m is the second-order rate constant for the exchange reaction involving molecular iodoacetic acid



and k_i the corresponding rate constant for the reaction involving iodoacetate ion



Let us now assume that reaction (5a), which involves one reactant without net charge, is not subject to any kinetic salt effect, *i.e.* that k_m is independent of the ionic strength.

The kinetic salt effect of reaction (5b) involving charged reactants should, however, be considered. In terms of the transition-state theory the rate constant of this reaction is given by the equation

$$k_i = \kappa \frac{kT}{h} K_0^\ddagger \frac{f_1 f_2}{f_3} \quad (6)$$

where f_1 is the activity coefficient of the iodide ion, f_2 the activity coefficient of the iodoacetate ion, and f_3 the activity coefficient of the transition-state complex. The other symbols in eqn. (6) have their usual meanings.

Let us denote by k_i^∞ the rate constant at infinite dilution when the activity coefficient fraction, $f_1 f_2 / f_3$, is equal to unity. According to eqn. (6) we then have

$$k_i^\infty = \kappa \frac{kT}{h} K_0^\ddagger \quad (7)$$

and hence

$$k_i = k_i^\infty \frac{f_1 f_2}{f_3} \quad (8)$$

Combining eqns. (8) and (4) yields

$$k = k_i^\infty \alpha f + k_m(1 - \alpha) \quad (9)$$

where

$$f = \frac{f_1 f_2}{f_3} \quad (10)$$

The individual activity coefficients in the activity coefficient fraction, $f_1 f_2 / f_3$, were calculated from eqn. (3).

With $z_1 = z_2 = -1$ (reactants) and $z_3 = -2$ (transition-state complex) we may then, by use of eqns. (3) and (10), deduce the following expression:

$$\log \frac{f_1 f_2}{f_3} = \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3 \mu \quad (11)$$

To evaluate k_i^∞ and k_m it is convenient to rewrite eqn. (9) in the form

$$\frac{k}{f\alpha} = k_i^\infty + k_m \frac{1 - \alpha}{f\alpha} \quad (12)$$

A graph of $k/f\alpha$ vs. $(1 - \alpha)/f\alpha$ according to this equation is shown in Fig. 1. The relative error in $k/f\alpha$ is fairly independent of $(1 - \alpha)/f\alpha$ for the range of concentrations investigated. The straight line in Fig. 1 has therefore been

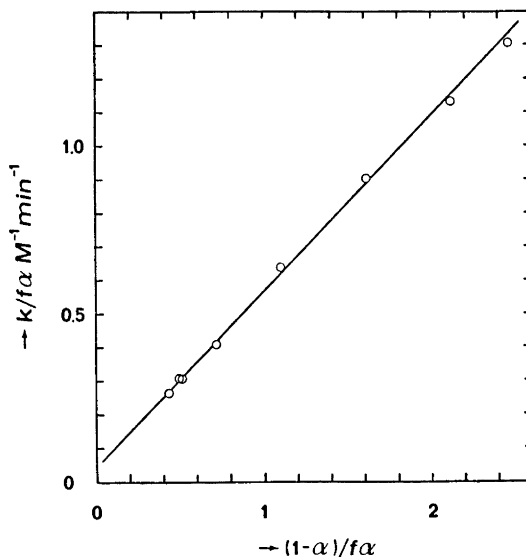


Fig. 1. Graph of $k/f\alpha$ as a function of $(1 - \alpha)/f\alpha$ according to eqn. (12).

fitted to the experimental points by means of a relative deviation least squares method¹⁴ to give the same weights to all points. From the equation of this line we obtain the rate constant

$$k_m = 0.524 \pm 0.0102 \text{ M}^{-1} \text{ min}^{-1} \quad (13a)$$

for reaction (5a), and

$$k_i^\infty = 0.043 \pm 0.0074 \text{ M}^{-1} \text{ min}^{-1} \quad (13b)$$

for reaction (5b). The errors quoted in (13a) and (13b) are standard deviations.

Our value of $k_m = 0.524 \text{ M}^{-1} \text{ min}^{-1}$ in (13a) for the displacement reaction involving undissociated iodoacetic acid deviates insignificantly from the values of $k_m = 0.531$ and $0.524 \text{ M}^{-1} \text{ min}^{-1}$ in Table 2, according to Refs. 6 and 7,

Table 2. Comparison of rate constants for the exchange reaction between molecular iodoacetic acid and iodide ion in aqueous solution at 25°C.

Ref.	Medium	k_m $\text{M}^{-1} \text{ min}^{-1}$
Van der Straaten and Aten ⁶	H ₂ O containing 0.005 M H ₂ SO ₄	0.531
Hinton and Johnston ³	H ₂ O containing 0.6 M HNO ₃	0.467
Beronius ⁷	H ₂ O containing 0.1 M HNO ₃	0.524
Present work	H ₂ O	0.524

respectively. The two latter rate constants were determined at considerably higher ionic strengths ($\mu = 0.02$ to 0.1) than in the present work ($\mu = 0.01$). Apparently the reaction between molecular iodoacetic acid and iodide ion is not subject to any significant kinetic salt effect.

Table 3. Comparison of rate constants for the exchange reaction between iodoacetate ion and iodide ion in aqueous solution at 25°C.

Ref.	Constituents of reaction mixture	k_i^∞ $\text{M}^{-1} \text{ min}^{-1}$
Van der Straaten and Aten ⁶	H ₂ O 0.01 M NaOH 0.003–0.007 M CH ₂ ICOOH 0.008–0.017 M KI	0.038 ^a 0.036 ^b
Present work	H ₂ O 0.0007–0.01 M CH ₂ ICOOH 0.01 M NaI	0.043 ± 0.007^c

^a Value obtained upon recalculation of $k_i = 0.049 \text{ M}^{-1} \text{ min}^{-1}$ (Ref. 6) from ionic strength, $\mu = 0.018$, to infinite dilution.

^b Value obtained upon recalculation of $k_i = 0.049 \text{ M}^{-1} \text{ min}^{-1}$ (Ref. 6) from ionic strength, $\mu = 0.027$, to infinite dilution.

^c Standard deviation.

Van der Straaten and Aten⁶ studied the kinetics of the iodoacetate ion-iodide ion displacement reaction after addition of 0.01 M sodium hydroxide to the reaction mixture, the composition of which is given in the middle column of Table 3. Their rate constant determinations were made at different ionic strengths in the interval $0.018 \leq \mu \leq 0.027$. For comparison with our value of k_i^∞ according to (13b) their value of $k_i = 0.049 \text{ M}^{-1} \text{ min}^{-1}$ at 25°C must be recalculated to zero ionic strength. A recalculation of this value of k_i from the minimum ionic strength ($\mu = 0.018$) to infinite dilution by means of eqn. (11) yields $k_i^\infty = 0.038 \text{ M}^{-1} \text{ min}^{-1}$, whereas the corresponding recalculation from the maximum ionic strength employed ($\mu = 0.027$) yields a slightly different value, viz. $k_i^\infty = 0.036 \text{ M}^{-1} \text{ min}^{-1}$. These values of k_i^∞ which have been quoted in the last column of Table 3, and the value $k_i^\infty = 0.043 \text{ M}^{-1} \text{ min}^{-1}$ according to the present investigation are equal within experimental errors.

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