an S_N2-type reaction, $R = k(p\text{-}NO_2BzI)(KI)$, and a plot of $R/(p\text{-}NO_2BzI)$ vs. (KI) should yield a straight line passing through the origin. The data are plotted in Fig. 1. It is seen that in both solvents, as discussed elsewhere,[2] there is no evidence for the S_N1-type reaction.

The Activation Energies.—The curves shown in Fig. 2 are semi-logarithmic plots of the average values for the specific reaction rate constant k against the reciprocal of the absolute temperature. The experimental activation energies for the exchange reaction in methanol and ethanol as determined from these plots are 15,570 ± 200 cal. and 16,460 ± 200 cal., respectively.

It is of interest to compare the above activation energies with the values 16,200 and 17,300 cal. obtained for the exchange reaction between benzyl iodide and potassium iodide[2] in methanol and ethanol, respectively. The observed decrease in activation energy accompanying the substitution of a nitro group for hydrogen in the *para* position is consistent with the observation that, in general, the increase in positive character of the carbon atom being attacked, more than compensates for the

concomitant tightening of the C–I bond when the attacking agent is an ion.[11]

The Rate Laws.—From the foregoing discussion it is reasonable to assume that the exchange reaction is first order with respect to both the potassium iodide and *p*-nitrobenzyl iodide concentrations in methanol and ethanol over a temperature range from 0 to 30.9°. The total iodide concentration ranged from 0.000986 to 0.00609 M and 0.000983 to 0.00599 M, respectively. The rate laws for the exchange reaction are

$$R = 3.60 \times 10^{11} e^{-15,570/RT}(p\text{-}NO_2BzI)(KI) \text{ (in methanol)}$$
$$R = 5.42 \times 10^{12} e^{-16,460/RT}(p\text{-}NO_2BzI)(KI) \text{ (in ethanol)}$$

where the units of R are moles liter^{-1} min.$^{-1}$.

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ALBUQUERQUE, NEW MEXICO

The Exchange of Iodine between Organic Iodides and Inorganic Iodine in Aqueous Solution

BY H. V. D. STRAATEN AND A. H. W. ATEN, JR.

With I^{131} as a tracer reaction rates of the iodine exchange between iodoacetic acid, the sodium salt and the methyl ester of this acid and iodide ions have been determined. The exchange of iodine between iodoacetic acid and free iodine or triiodide ions is much slower than it is with the monoiodide.

Introduction

The exchange between primary and secondary aliphatic halides and halogen ions probably occurs by means of a Walden inversion.[1] The free halogen ion approaches the carbon atom which carries the organic halogen atom from the opposite direction following a line through the carbon atom and the organic halogen atom. Some experiments have been made to prove this theory by using aliphatic halides containing an asymmetric carbon atom. The differences between the rate of racemization and the rate of the exchange reactions were lower than 10% in these cases.[1]

Most of the experiments with organic halides have been carried out in organic solvents. The exchange reaction of α-bromopropionic acid and inorganic bromide has been investigated in aqueous acid solution by Koskoski, Dodson and Fowler.[2] They found a bimolecular reaction mechanism. The reaction was independent of the concentration

of the sulfuric acid, which had been used to suppress the ionization of the acid.

In this paper the results of some exchange reactions of aliphatic iodides and inorganic iodide or iodine in aqueous solution are given.

The following reactions have been investigated (the labeled iodine atom is represented by I*)

	Reaction	Table
(A)	$CH_2ICOOH + I^{*-} \rightleftarrows CH_2I^*COOH + I^-$	I
(B)	$CH_2ICOO^- + I^{*-} \rightleftarrows CH_2I^*COO^- + I^-$	I
(C)	$CH_2ICOOH + I_2^* \rightleftarrows CH_2I^*COOH + I_2$	
(D)	$CH_2ICOOH + I_3^{*-} \rightleftarrows CH_2I^*COOH + I_3^-$	II
(E)	$CH_2ICOOCH_3 + I^{*-} \rightleftarrows CH_2I^*COOCH_3 + I^-$	I

Radioactive Iodine.—In all cases the inorganic fraction has been labeled with iodine-131. This isotope has a soft β-radiation and a γ-radiation with a half-life of 8.0 days. The amount of I^{131} has been determined by counting the β-rays with a Geiger–Müller counter. Throughout the investigation the activity of the iodine was measured on samples of silver iodide, sedimented on copper discs. The corrections for self absorption of these samples were determined with the graphic method.[3] As this

(1) E. D. Hughes, F. Juliusberger, S. Masterman, B. Topley and J. Weiss, *J. Chem. Soc.*, 1525 (1935); E. D. Hughes, F. Juliusberger, A. D. Scott, B. Topley and J. Weiss, *ibid.*, 1173 (1936); W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *ibid.*, 1252 (1937); W. A. Cowdrey, E. D. Hughes, T. P. Nevell and C. L. Wilson, *ibid.*, 209 (1938).

(2) W. K. Koskoski, R. W. Dodson and R. D. Fowler, THIS JOURNAL, **63**, 2149 (1941).

(3) A. H. W. Aten, Jr., *Nucleonics*, **6**, No. 2, 68 (1950); *Chem. Weekblad.* **47**, 554 (1951).

TABLE I

REACTION CONSTANTS AND ACTIVATION ENERGIES FOR EXCHANGE AGAINST RADIOACTIVE MONOIODIDE

Reaction	Temp., °C.	k, l. mole^{-1} sec.$^{-1}$	E, kcal.	Limits of concn. used of organic reactant (moles l.$^{-1}$)	Limits of concn. used of KI (moles l.$^{-1}$)
$CH_2ICOOH \rightleftarrows I^-$	24.8	0.0087		0.003–0.009	0.003–0.02
	59.9	.149	16	.003	.008
$CH_2ICOO^- \rightleftarrows I^-$	24.8	.00080		.003–0.007	.008–0.017
	59.9	.0149	16	.003	.008
$CH_2ICOOCH_3 \rightleftarrows I^-$	24.8	.0075		.004–0.007	.007–0.015
	0	.00058	17	.004	.015

correction method is reliable only in cases of simple β-spectra, whereas the β-spectrum of iodine-131 is complex, the applicability of the method for this isotope has been verified by special measurements.

Separation Method.—It takes a long time to precipitate the iodine from the organic iodine compounds used with silver nitrate at 0°. This fact has been used to separate the inorganic iodine ions from the iodine bound in the organic molecules.

After the exchange reaction the reaction mixture was cooled with ice and the free iodide ions were precipitated with silver nitrate and nitric acid. In the cases where free iodine had been used this was first reduced to iodide ions with a solution of sulfite. This silver iodide was filtered off quickly on a glass filter, washed, dried at about 120°, weighed and counted. To the filtrate containing the organic fraction an inactive solution of potassium iodide was added which prevented contamination of the organic fraction with the inorganic fraction by diluting the amount of iodine which had passed through the filter as a colloid. The inactive silver iodide precipitate formed in this way was again filtered off quickly and discarded. To remove all traces of silver iodide, this filtration was repeated. During all these manipulations the solutions were cooled with ice to prevent the decomposition of the organic iodide before the separation was finished. The solution of the organic fraction prepared in this way was boiled for some hours to precipitate as silver iodide the iodine bound in the organic molecules. This precipitate was filtered off on a glass filter, dried, weighed and counted. Only the methyl ester of iodoacetic acid was decomposed in a different way. In this case the organic fraction was made strongly alkaline and kept overnight in a stoppered bottle. The following day the solution was made acid again and boiled for some hours with a reflux condenser till the iodide was precipitated completely by the silver ions present. This was desirable because of the volatility of the ester.

Experiments.—Experiments have been made with different concentrations of organic halide and inorganic iodide at 24.8 and 59.9°. Only with the methyl ester of iodoacetic acid experiments have been made at 24.8 and 0° because of its volatility. The experiments with free iodine were made at 24.8° only.

Sulfuric acid (0.005 molar) has been used to suppress the ionization of the iodoacetic acid in the cases where free iodoacetic acid has been used. To investigate whether the concentration of the sulfuric acid had any influence on the reaction rate, some experiments have been made with a double concentration of sulfuric acid.

In the cases of the iodoacetic acid ions 0.01 molar sodium hydroxide has been used to form the sodium salt of the acid. In this case too the influence of the hydroxide concentration on the reaction rate has been investigated.

The data of the experiments are given in Tables I and II. In these tables the concentrations are given in mole liter^{-1}, the temperature in degrees centigrade and the reaction time in minutes.

Standard samples have been made in all cases to compare the total activity of the active iodide solution used and the total activity of the fractions of the exchange experiments. No large differences have been found.

The reaction rate can be calculated from the following formula[4]

$$R = \frac{ab}{a + b} \frac{0.69}{T_{1/2}}$$

in which

a and b = concn. of the reactants in mole l.$^{-1}$

$T_{1/2}$ = exchange time in sec. after which the specific activity of the originally inactive fraction, x, is one-half of the specific activity in case of total exchange, x_∞

R = reaction rate in moles l.$^{-1}$ sec.$^{-1}$

According to the quantitative exchange law[4] the plot of $\ln (1 - x/x_\infty)$ versus the time t is a straight line. From this plot $T_{1/2}$ can be read off.

For a second-order reaction $R = abk$ in which k is the reaction constant in liter moles^{-1} sec.$^{-1}$.

Conclusion

Experiments with Monoiodide.—The reactions A, B and E appeared to be second order. The experiments with a double concentration of hydrogen and hydroxyl ions gave the same results within experimental error. The reaction constant k in liter moles^{-1} sec.$^{-1}$ and the energy of activation of these reactions are given in Table I. The energy of activation has been calculated with the use of the equation

$$\ln k = A - E/RT$$

in which E is the activation energy in cal. and A is a constant.

The k-values for the reactions with the undissociated acid in Tables I and II include a small correction to take into account the incomplete dissociation of the acid. (The concentration of iodoacetic acid in Table II is the analytical concentration.)

It is seen from Table I that the reaction constant of the free acid is about ten times larger than the reaction constant of the sodium salt, whereas the former is very nearly equal to the reaction constant of the ester. It is not possible to conclude from the experimental results whether the difference in velocity between the reaction in acid and in basic environments is a result of a difference in activation energy or in activation entropy.

With the free acid and the ester a good agreement is found between the classical collision theory and the experiments, and also the entropy of activation according to Glasstone, Laidler and Eyring[5] is small. The reaction with the sodium salt is about one-tenth as fast; this will be due to the electrostatic repulsion of the two negatively charged ions.

Experiments with Free Iodine.—The reaction between the free iodine and the iodoacetic acid is even slower; in this case we find a reaction constant $k = 5 \times 10^{-4}$ liter mole^{-1} sec.$^{-1}$ at 24.8° (experiment C).

Experiment with Triiodide.—To investigate the influence of free iodine on the reaction rate of

(4) G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 287.

(5) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., Inc., New York, N. Y., 1941, p. 21.

iodide ions, reaction D has been investigated with different concentrations of free iodine and constant concentrations of potassium iodide and iodoacetic acid. In D1 the quantity of free iodine was equivalent to $1/3$ of the quantity of iodide present, in D2 this ratio was $1/2$ and in D3 it was $2/3$. The concentration of sulfuric acid has been 0.005 molar in all experiments.

TABLE II

OBSERVED AND CALCULATED REACTION CONSTANTS FOR EX-
CHANGE AGAINST RADIOACTIVE MONOIODIDE AND TRIIODIDE

	Reaction A	Reaction D1	Reaction D2	Reaction D3
Concn. KI (moles l.$^{-1}$)		0.0046	0.0046	0.0046
Concn. I$_2$ (moles l.$^{-1}$)	0	.00147	.0023	.0030
Concn. CH$_2$ICOOH (moles l.$^{-1}$)		.0093	.0093	.0093
Exp. react. const. (moles l.$^{-1}$ sec.$^{-1}$)	0.0087	.0049	.0041	.0031
Calc. concn. I$^-$ / total concn. I$^-$ × 0.0087 (moles l.$^{-1}$ sec.$^{-1}$) (calcd. with equil. const. = 0.0014)	.0087	.0067	.0057	.0049
Calc. concn. I$^-$ / total concn. I$^-$ × 0.0087 (moles l.$^{-1}$ sec.$^{-1}$) (calcd. assuming no free I$_2$ in sol.)	.0087	.0059	.0043	.0030

The results are given in Table II. Apart from the concentrations used and the experimental values of the reaction constant k, the values of the reaction constant found in the monoiodide experiments multiplied with the ratio of the real monoiodide concentration and the concentration of added potassium iodide are given too. This real monoiodide concentration has been calculated with the aid of the equilibrium: $I^- + I_2 \rightleftarrows I_3^-$, using an equilibrium constant of about 0.0014^6 and also assuming that no free iodine remains in the solution. The formation of higher polyiodides has been neglected. If the exchange of radioactive iodine between the organic molecules and the I_3^-

(6) J. S. Carter, J. Chem. Soc., 2227 (1928).

ions is very slow compared with the exchange with normal iodide ions, we can calculate the experimental velocity constant in the following manner[7]

a = concn. CH$_2$ICOOH + CH$_2$I*COOH
b = total concn. I$^-$ + I*$^-$ + I$_3^-$ + I$_3^{*-}$
c = real concn. I$^-$ + I*$^-$
x = concn. CH$_2$I*COOH at time t
y = total concn. I + I$_3^{*-}$ at time t
z = real concn. I*$^-$ at time t
k_e = exptl. bimolecular reaction constant calcd. with the assumption that I$^-$ and I$_3^-$ react with equal ease
k_t = theoretical bimolecular reaction constant calcd. with the assumption that I$_3^-$ reacts much slower than I$^-$

The formation velocity of active iodoacetic acid is

$$\mathrm{d}x/\mathrm{d}t = k_e[y(a - x) - x(b - y)] = k_e(ya - xb) \quad (1)$$

or

$$\mathrm{d}x/\mathrm{d}t = k_t[z(a - x) - x(c - z)] = k_t(za - xc) \quad (2)$$

The exchange between the free iodine and the iodine ions is very fast,[8] so

$$z/c = y/b \quad (3)$$

$$\mathrm{d}x/\mathrm{d}t = k \frac{c}{tb}(ya - xb) \quad (4)$$

$$k_e = c/bk_t \quad (5)$$

From Table II it is seen that the exchange reaction between I_3^- and CH$_2$ICOOH is much slower than the reaction between I$^-$ and CH$_2$ICOOH; no conclusions can be drawn regarding the velocity of the former process.

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AMSTERDAM, HOLLAND

The Kinetics of the Reduction of Perchlorate Ion by Ti(III) in Dilute Solution

BY FREDERICK R. DUKE AND PAUL R. QUINNEY

The reduction of perchlorate ion by Ti(III) in dilute solutions appears to proceed by several paths. The reaction has [H$^+$] dependent as well as [H$^+$] independent paths. The addition of chloride retards the reaction, apparently due to the formation of TiCl^{+2} ion. The reaction is linear in ClO$_4^-$ at concentrations below about 1.0 M. Above this concentration the reaction rate increases, this probably being due to the increased activity coefficient of the perchlorate ion at higher concentrations. There was insufficient complex ion formation between Ti(III) and ClO$_4^-$ to be kinetically detectable. The activation energies for the various reactions were calculated and a mechanism proposed.

Introduction

The reduction of perchlorate ion by Ti(III) at room temperatures and slightly above proceeds to completion at a convenient rate with the production of Cl$^-$ and Ti(IV)

$$8Ti(III) + ClO_4^- + 8H^+ \longrightarrow 8Ti(IV) + Cl^- + 4H_2O$$

Preliminary work on the reduction of perchlorate

ion by Ti(III) in dilute solutions was done by Bredig and Michel.[2] They studied the kinetics of the oxidation of trivalent titanium compounds with perchloric acid in aqueous sulfuric acid and hydrochloric acid solutions, as well as the rate of reaction of HClO$_4$ with Cr(II) and Mo(II) compounds.

This present work examines more in detail the Ti(III)–ClO$_4^-$ reaction in solutions containing chlo·

(2) G. Bredig and J. Michel, Z. physik. Chem., 100, 124 (1922).