

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON, EUGENE, OREGON]

**Mechanism of Exchange between Iodoacetone and Elementary Iodine**BY SHAIOWEN WONG<sup>1</sup> AND RICHARD M. NOYES

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Iodoacetone exchanges with iodine in 1,2-dichloroethane by parallel paths involving one and two molecules of iodine. The very low entropy of activation indicates that at least for the path with one molecule of iodine the transition state resembles an ion pair. Less satisfactory kinetics were obtained in hexane, and reaction in this solvent may be sensitive to impurities such as atmospheric moisture.

**Introduction**

Primary and secondary alkyl iodides undergo isotopic exchange with elementary iodine at temperatures above 130°. The kinetics indicate a free-radical mechanism involving iodine atoms.

For compounds like *t*-butyl<sup>3</sup> and benzoyl<sup>4</sup> iodides in which the organic group can more readily support a positive charge, the rate of exchange is first or higher order in iodine molecules. The low entropies of activation and the strong rate dependence on solvent indicate that the transition states for these reactions resemble ion pairs,  $R^+I_3^-$ .

Another mechanism involving iodine molecules is observed for allyl iodide<sup>5</sup> where unsaturation exists between the carbons  $\beta$ - $\gamma$  to the exchanging iodine. Charge separation is much less than in the ion-pair mechanisms, and the exchanging molecule of iodine obviously interacts with the double bond even though the exchange usually takes place on the  $\alpha$ -carbon that bore the original iodine.<sup>6</sup>

Iodoacetone is of interest because its exchange could conceivably take place by any of these three mechanisms. At sufficiently high temperatures, it would undoubtedly exchange by the atomic mechanism observed for primary alkyl iodides. Since the acetyl carbonium ion,  $CH_3COCH_2^+$ , is probably not so stabilized as the benzoyl carbonium ion,  $C_6H_5CO^+$ , exchange by the ion-pair mechanism is possible but could not necessarily compete with the atomic mechanism. Finally, the unsaturated bond of the carbonyl group offers the possibility of a molecular mechanism similar to that observed with allyl iodide.

Since the dominant mechanism could not be confidently predicted *a priori*, the present study was undertaken.

**Experimental**

**Materials.**—Iodoacetone was prepared from commercial chloroacetone and potassium iodide by the method of Emmerling.<sup>7</sup> The product was washed, dried, and distilled at 35° and 2 mm. Iodine formed by decomposition was removed by treating with copper overnight in a cold room, and the remaining liquid was filtered and dissolved in solvent. When such a solution was hydrolyzed with aqueous sodium hydroxide, the titration of the resulting iodide gave about 98% of the value calculated from the weight of iodoacetone dissolved. Solutions could be stored for several weeks at 6°; they were discarded when they began to develop the color of free iodine.

Solvent hexane was prepared from commercial petroleum ether by treatment with fuming sulfuric acid and was stored over

sodium. It contained impurities capable of reacting with  $5 \times 10^{-6}$  mole/l. of iodine.

Solvent 1,2-dichloroethane (ethylene dichloride) was treated with concentrated sulfuric acid and distilled and stored over magnesium sulfate. It contained impurities capable of reacting with  $5 \times 10^{-6}$  mole/l. of iodine.

Reagent grade resublimed iodine was used without further purification. Solutions were activated with aqueous carrier-free iodine-131 obtained from the Oak Ridge National Laboratory.

**Procedures.**—Solutions were analyzed spectrophotometrically for iodine and iodoacetone. The extinction coefficients at the optical wave lengths are presented in Table I. At the concentrations used in our experiments, absorbancies of solutions containing both iodine and iodoacetone did not differ from those predicted from the separate components.

TABLE I  
EXTINCTION COEFFICIENTS OF REACTANTS

Solvent	Solute	Wave length, $m\mu$	Extinction coefficient, l./mole cm.
$C_2H_5I_2$	$I_2$	275	$40 \pm 6$
		525	$905 \pm 9$
	$C_6H_5OI$	275	$395 \pm 6$
		525	Negligible
$C_2H_4Cl_2$	$I_2$	271	$87 \pm 7$
		496	$894 \pm 5$
	$C_6H_5OI$	271	$378 \pm 5$
		496	Negligible

Solutions of radioactive iodine and of inactive iodoacetone were mixed in Pyrex volumetric flasks and immersed in an oil thermostat. The flasks were wrapped with foil, and laboratory lighting was kept to a minimum until the reactants had been separated. Aliquot samples were withdrawn from each flask at successive intervals, the reactants were separated, and the radioactivity of one or both of these reactants was measured and compared with the total initial activity.

For some runs in hexane, separation involved shaking the solution with mercury to remove iodine and filtering the solution. At low concentrations of iodine, separation was not complete because of solubility of mercuric iodide as observed by Warrick, Wewerka, and Kreevoy.<sup>8</sup>

The mercury separation procedure was unsatisfactory with dichloroethane as solvent. If this solvent was extracted rapidly with an acidified solution of aqueous sodium sulfite, iodine could be removed with only about 4% hydrolysis of iodoacetone also present. In hexane solutions, iodoacetone was more extensively hydrolyzed during extraction with aqueous sulfite, but a procedure was developed in which the solution from a run in hexane was diluted with dichloroethane before it was extracted. The kinetic data indicate that sulfite extraction induced about 20% of exchange, but radioactivities measured at different times were consistent with the postulate that we were studying a conventional homogeneous exchange reaction.

Spectrophotometric measurements indicated that decomposition of iodoacetone seldom increased iodine concentration by more than 3% during a run.

**Results**

**Dichloroethane.**—Exchange data in dichloroethane are presented in Table II. Most of the rates reported

(1) Based on the M.S. Thesis of S.-W. S. Wong.

(2) J. E. Bujake, Jr., W. W. T. Pratt, and R. M. Noyes, *J. Am. Chem. Soc.*, **83**, 1547 (1961).

(3) J. E. Bujake, Jr., and R. M. Noyes, *ibid.*, **83**, 1555 (1961).

(4) A. Goldman and R. M. Noyes, *ibid.*, **79**, 5370 (1957).

(5) D. J. Sibbett and R. M. Noyes, *ibid.*, **75**, 761 (1953).

(6) W. P. Cain and R. M. Noyes, *ibid.*, **81**, 2031 (1959).

(7) O. Emmerling, *Chem. Ber.*, **29**, 1558 (1896).

(8) P. Warrick, Jr., E. M. Wewerka, and M. M. Kreevoy, *J. Am. Chem. Soc.*, **85**, 1909 (1963).

in this table are based on six or more radioactivity measurements made at different times.

TABLE II

## EXCHANGE IN DICHLOROETHANE (SULFITE EXTRACTION)

Temp., °C.	10 <sup>2</sup> [IA], moles/l.	10 <sup>4</sup> [I <sub>2</sub> ], moles/l.	10 <sup>3</sup> v, moles/l. sec.	10 <sup>3</sup> k <sub>α</sub> , 1./mole sec.
50.0	0.87	9.82	4.10	4.80
	4.23	0.59	1.28	5.15
	4.23	1.63	3.14	4.52
	4.29	3.13	4.62	3.44
	4.36	4.72	6.42	3.12
	4.03	5.19	8.58	4.10
	4.27	5.19	8.09	3.65
	4.21	7.62	8.92	2.78
	4.61	7.71	14.32	4.03
	4.21	10.08	20.50	4.83
	5.14	9.84	25.83	5.11
	8.69	2.19	7.95	4.17
	8.74	4.46	11.63	2.98
	8.81	10.23	45.28	5.02
		Av.	4.12 ± 0.15	
40.0	0.91	6.16	1.33	2.37
	4.51	6.36	5.94	2.07
	5.41	2.65	3.30	2.30
	5.89	8.94	20.18	3.84
	6.77	10.03	33.58	4.94
	8.29	6.42	19.37	3.64
	8.76	13.14	48.97	4.26
		Av.	3.35 ± 0.28	
25.0	4.2	2.62	1.89	1.68
	5.4	6.48	8.76	2.47
	8.5	12.98	32.11	2.90
		Av.	2.35 ± 0.24	

The results could be fitted to a fair approximation by the equation

$$v = k_{\alpha} [IA][I_2] \quad (1)$$

where  $v$  is the rate of exchange and IA is iodoacetone. Values of the second-order rate constant  $k_{\alpha}$  are presented in the last column. Uncertainties indicated are probable errors of the means.

Although the data show considerable scatter, the deviations from eq. 1 suggest an equation of this form.

$$v = k_0[IA] + k_1[IA][I_2] + k_2[IA][I_2]^2 \quad (2)$$

These exchange kinetics have been exhibited more clearly by unsubstituted<sup>4</sup> and substituted<sup>9</sup> benzoyl iodides. Therefore, the data were also treated by rejecting the runs at very low iodine concentrations and using the other runs to evaluate the constants  $k_1$  and  $k_2$ . These values are presented in Table III.

TABLE III

## RATE CONSTANTS IN DICHLOROETHANE

Temp., °C.	10 <sup>3</sup> k <sub>1</sub> , 1./mole sec.	k <sub>2</sub> , 1. <sup>2</sup> /mole <sup>2</sup> sec.
50.0	2.24 ± 0.21	2.65 ± 0.28
40.0	2.08 ± .45	2.09 ± .50
25.0	1.52 ± .10	1.12 ± .10

Temperature dependence of the rate constants could be described by these equations.

$$k_{\alpha} = 10^{0.5 \pm 0.5} e^{-(4.3 \pm 0.8)/1000RT} \text{ 1./mole sec.} \quad (3)$$

$$k_1 = 10^{-0.6 \pm 0.6} e^{-(3.0 \pm 0.8)/1000RT} \text{ 1./mole sec.} \quad (4)$$

$$k_2 = 10^{4.9 \pm 0.7} e^{-(6.6 \pm 1.0)/1000RT} \text{ 1.<sup>2</sup>/mole<sup>2</sup> sec.} \quad (5)$$

(9) D. W. Hamilton, private communication.

The indicated uncertainties are based on those estimated for individual rate constants, and the fit to these equations was always closer than those estimates.

**Hexane.**—Exchange data in hexane are presented in Table IV. The results are less satisfactory than in dichloroethane.

TABLE IV

## EXCHANGE IN HEXANE

Temp., °C.	10 <sup>2</sup> [IA], moles/l.	10 <sup>4</sup> [I <sub>2</sub> ], moles/l.	10 <sup>3</sup> v, moles/l. sec.	10 <sup>3</sup> k <sub>α</sub> , 1./mole sec.
Sulfite Extraction				
50.0	1.13	4.54	1.41	2.76
	1.13	9.25	2.70	2.58
	4.62	8.55	9.37	2.37
	5.02	0.91	1.11	2.43
	5.09	4.37	4.75	2.14
	7.71	8.40	16.98	2.62
	9.62	9.00	19.13	2.21
	9.67	4.43	9.57	2.23
	9.71	0.86	1.42	1.70
			Av.	2.34 ± 0.07
40.0	3.97	4.63	4.13	2.25
	7.98	8.97	15.89	2.22
	9.51	8.21	17.28	2.21
		Av.	2.23 ± 0.01	
Mercury Extraction				
40.0	1.01	7.23	0.32	0.42
	1.58	7.50	.68	.58
	1.72	4.70	.64	.79
	2.67	16.75	5.49	1.24
	2.68	8.40	2.16	0.96
	2.68	23.78	8.94	1.40
	2.67	7.33	1.92	0.98
	2.90	5.63	1.61	0.98
	5.29	7.30	5.09	1.33
	5.30	7.37	4.05	1.08
7.77	7.31	9.87	1.73	
7.92	7.38	9.68	1.69	

When mercury was used to separate reactants, the apparent rate of exchange increased during each run even though no evidence could be found for chemical change in the system. The rates reported are based on the times for 50% exchange. These rates are distinctly less than under comparable conditions in dichloroethane, and initial rates in these solutions are smaller still. Values of  $k_{\alpha}$  tend to increase with concentrations of both reactants.

When sulfite was used for extraction, runs showed the time behavior expected for isotopic exchange. Rates at 40 and 50° were not much slower than in dichloroethane under comparable conditions, and the data did not justify application of any rate expression except eq. 1. Runs at 25° exhibited a very rapid initial exchange that virtually stopped before the calculated position of isotopic equilibrium was reached. This peculiar behavior was repeated with another preparation of iodoacetone.

## Discussion

Under these conditions, the chief mechanism for exchange clearly does not involve free iodine atoms. The rates are faster than has been observed for any thermal exchange involving such atoms, the kinetics are clearly more than half order in molecular iodine, and the activation energies are much less than the 17.5

kcal./mole corresponding to half the bond dissociation enthalpy of iodine.

The ion-pair<sup>3,4</sup> and molecular<sup>5,6</sup> mechanisms exhibit similar concentration dependence for the rates; they differ chiefly in the extent of charge separation in the transition state. For runs in dichloroethane, the pre-exponential factors in eq. 3 and 4 are about ten orders of magnitude smaller than would be expected for a reaction of neutral molecules; this very large effect seems inexplicable unless the transition state is so polar as to be virtually an ion pair.

An ion-pair transition state should lead to very different rates in dichloroethane (dielectric constant 10.1) and in hexane (dielectric constant 1.9). Thus the ratio of  $k_1$  values in these two solvents is 60 for exchange of benzoyl iodide<sup>4</sup> and 2000 for *t*-butyl iodide.<sup>3</sup> The apparent factor for iodoacetone seems to be much smaller and is more like the ratio of about 6 observed for allyl iodide.<sup>6</sup>

Although the mechanistic conclusion must be somewhat equivocal, we believe that the very low entropy of activation in dichloroethane requires that the transition state in that solvent has charge separation approaching that of an ion pair. The observed rates in

hexane are too rapid to accommodate to the same model. The difference may reflect a change in mechanism on going to this solvent. The unsatisfactory kinetics may also reflect side effects. Thus, when mercury was used to remove iodine, the peculiar accelerations suggest formation of a catalyst during each run. Such a catalyst might be HI formed from hydrolysis of iodoacetone by atmospheric moisture. The runs in which iodine was removed by sulfite were faster than those in which mercury was used, although the true rate of exchange could not possibly be influenced by a choice between separation procedures that did not induce exchange in the initial solution and that were not applied until *after* the period of exchange. The discrepancies strongly suggest that the experiments in hexane were influenced by trace impurities probably associated with the action of atmospheric moisture. Other work in these laboratories<sup>9</sup> has indicated the great difficulty of getting reproducible rates for exchange by apparently ion-pair mechanisms in this solvent.

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## Mechanisms of Elimination Reactions. V. Sulfur Isotope Effects in Some Reactions of *t*-Butyldimethylsulfonium Iodide<sup>1</sup>

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The E2 reaction of *t*-butyldimethylsulfonium ion with ethoxide ion in 97% ethanol at 24° shows a <sup>32</sup>S/<sup>34</sup>S isotope effect of 0.72%. The SN1-E1 solvolysis of the same compound in 97% ethanol at 40° shows a <sup>32</sup>S/<sup>34</sup>S isotope effect of 1.03%. These results are compared with earlier work, and their mechanistic significance is discussed.

Some time ago, we showed that the E2 reaction of 2-phenylethyldimethylsulfonium ion with hydroxide ion at 59° occurs with a very small sulfur isotope effect (0.15%).<sup>3</sup> We took this result as evidence for a high degree of carbanion character in the transition state, a conclusion supported by data on substituent effects<sup>4</sup> and deuterium isotope effects.<sup>5</sup> At that time there was no evidence on whether low sulfur isotope effects were general for E2 reactions of sulfonium salts, or only to be expected when the β-hydrogens were activated by some group such as phenyl. The present research was an effort to settle this problem.

The reactant chosen was the *t*-butyldimethylsulfonium ion. We had used the isotope effect in its SN1-E1 reaction in water as an experimental "upper limit" in our previous work,<sup>3</sup> and hoped to study its E2 reaction with hydroxide ion in water. Unfortunately, we could not attain conditions under which the first-order reaction was not an important fraction of the total reaction. Both the first- and second-order reactions of *t*-butyldimethylsulfonium ion have been

studied in 97% ethanol,<sup>6</sup> and the rate constants shown to be sufficiently different to permit isolation of the second-order reaction

We determined the kinetics of both reactions in 97% ethanol under conditions feasible for the isotope-effect studies. No special effort to attain high precision was made for the rate constants given in Table I, though on the one comparison possible with the literature,<sup>6</sup> the E2 reaction at 24°, agreement is excellent (8.0 vs.  $7.97 \times 10^{-4}$ ) in spite of slight differences in the ionic strength and the method of making up solvent. From these constants, times for 5% completion of the E2 reaction at 24° and of the SN1-E1 reaction at 40° were calculated to be 5.5 min. and 3.8 hr., respectively. Similar calculations for 99% reaction gave 2.8 hr. at 75° for the E1-SN1 and 1.0 hr. at 35° for the E2 reactions.<sup>7</sup> The isotope-effect runs were carried out and the isotopic ratios of the resulting dimethyl sulfide

(6) E. D. Hughes, C. K. Ingold, and L. I. Woolf, *J. Chem. Soc.*, 2084 (1948).

(7) Calculations based on an equation given by Melander<sup>8</sup> show that the isotope ratio of <sup>32</sup>S to <sup>34</sup>S in the dimethyl sulfide collected should be the same within experimental error for samples taken at 2 and 5% completion assuming an isotope effect of 1.8%; so 5% completion was chosen so as to permit smaller reaction mixtures. Similarly, the isotopic composition of samples taken after 99% reaction can be shown to be within experimental error of the isotopic composition of the original reactant.

(8) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960, eq. 3-3, p. 49.

(1) This work was supported by the National Science Foundation.

(2) Alfred P. Sloan Foundation Fellow.

(3) W. H. Saunders, Jr., and S. Asperger, *J. Am. Chem. Soc.*, **79**, 1612 (1957).

(4) W. H. Saunders, Jr., and R. A. Williams, *ibid.*, **79**, 3712 (1957).

(5) W. H. Saunders, Jr., and D. H. Edison, *ibid.*, **82**, 138 (1960).