

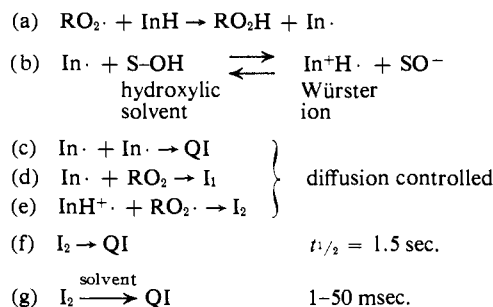
This work, using only three aromatic amines of similar structure, has encountered virtually all possible combinations of behavior for inhibition. There is no doubt that complexes form, and on the basis of the limited data in this study, it would appear that polar solvents enhance their stability. However, even in cyclohexane, N-methylaniline was shown to yield a short-lived complex which precluded determination of the absolute rate constant for the peroxy radical reaction.

Diphenylamine reacted in a rate-controlling step with peroxy radicals but did not exhibit an isotope effect. This is in agreement with Hammond's early work; and while it does not prove the equilibrium nature of the peroxy radical-amine reaction, it does prove that a complex is formed.

In all cases examined, complexes were formed in ethanol. The lifetimes of these complexes are strongly influenced by the solvent. A tentative mechanism which explains the result in alcohols is shown in Scheme I. In the presence of strong base, I₂ formation is favored. In neutral solution, both I₁ and I₂ are formed, and in acidic media the Würster ion is formed directly. Reaction a is written as a hydrogen abstraction because the yield of Würster ion is not enough to explain the total amount of QI formed and because this ion can be suppressed completely by added water. The difference between I₁ and I₂ may be in the position of

- (12) J. R. Thomas, *J. Am. Chem. Soc.*, **85**, 591, 593, 2166 (1963).
 (13) J. R. Thomas and C. A. Tulman, *ibid.*, **84**, 2930 (1962).

Scheme I



attachment of RO₂. Reaction c is needed to explain the 20 to 30% QI formation that occurs as a rapid reaction following the beam pulse.

From the effect of acid and base on the product formation rates in alcohols, it should be possible to obtain the absolute rate of ethanol peroxy reaction with N,N'-DPPD by working in acidic media where the Würster salt is stable, and only one peroxy radical is required per inhibition. Preliminary experiments indicate this approach will work, and a rate constant of approximately 10⁷ l./mole sec. was obtained for rate of Würster ion formation in ethanol containing dissolved oxygen.

Acknowledgments. It is a pleasure to acknowledge J. M. White for assistance in carrying out these experiments and Dr. C. W. Stephens of E. I. du Pont de Nemours and Co., Textile Fibers Department, for the N,N'-DPPD.

The Exchange Reaction of Ethyl Iodide and Iodine^{1,2}

Edward D. Cohen² and C. N. Trumbore

Contribution from the Department of Chemistry, The University of Delaware, Newark, Delaware. Received August 19, 1964

The thermal-exchange reaction of ethyl iodide and iodine was investigated in the liquid phase. The exchange rate was independent of iodine concentration from 10⁻⁸ to 10⁻³ M and had an average value of 0.50 × 10⁻⁶ M/hr. in CCl₄ solvent at 23°. The over-all exchange rate was dependent on ethyl iodide concentration and may be expressed by R_{ex} = k(EtI)². This rate law was applicable from 0 to 40° with an activation energy of 22 kcal./mole. Isopropyl iodide was found to exchange at a significantly lower rate. The rate-controlling step is postulated to be the slow formation of diethyl iodonium iodide followed by a fast attack of iodine on the iodonium iodide whose decomposition leads to exchange. The implications of this study on the radiolysis reaction of ethyl iodide are discussed.

The thermal-exchange reaction between ethyl iodide and iodine has been studied by several authors³⁻⁸

- (1) This research was supported by the U. S. Atomic Energy Commission.
 (2) Taken in part from the Ph.D. Dissertation of E. D. C., University of Delaware, 1964.

since the initial study by Lind, *et al.*,⁹ in 1936. The main feature of these studies has been the irreproducibility of the data which was obtained and has resulted in very few kinetic treatments of this system.

At iodine concentrations of 10⁻³ to 10⁻⁴ M and 6 M in ethyl iodide and from 40 to 70°, Darbee and Harris⁷ were unable to obtain consistent exchange results. At concentrations greater than 10⁻² M I₂, an exchange rate law of R_{ex} = k(I₂) was obtained, but no mechanistic interpretation was presented. It was stated that the exchange probably involved the addition complex of ethyl iodide and iodine. At concentrations of 10⁻⁴ to 10⁻⁵ M, Herbst⁸ obtained two different rate laws for the same system depending on his method of solution preparation. If the iodine was produced by decom-

- (3) R. E. Bujake, W. T. Pratt, and R. M. Noyes, *J. Am. Chem. Soc.*, **83**, 1547 (1961).
 (4) R. M. Noyes, *ibid.*, **70**, 2614 (1948).
 (5) R. M. Noyes, *ibid.*, **75**, 767 (1953).
 (6) M. B. Neiman, V. B. Miller, and Y. M. Shapovalov, *Zh. Fiz. Khim.*, **30**, 492 (1956).
 (7) L. R. Darbee and G. M. Harris, *J. Phys. Chem.*, **61**, 111 (1957).
 (8) R. Herbst, *Anales Fac. Quim. Farm. Univ. Chile*, **12**, 207 (1960).
 (9) D. E. Hull, C. H. Schuffert, and S. C. Lind, *J. Am. Chem. Soc.*, **58**, 535 (1936).

position of PdI_2 directly into ethyl iodide, $R_{\text{ex}} = k(\text{I}_2)$ was obtained, but upon distillation of the I_2 into a trap and then sublimation into the iodide, $R_{\text{ex}} = k(\text{I}_2)^{-1}$ was obtained. At 140° Noyes and co-workers³ were unable to obtain consistent results. The explanation given for this was the sensitivity of the reaction to organic impurities both in the starting material and those produced during the course of the reaction.

The thermal exchange has been studied in relation to the photolysis and radiolysis of this system.¹⁰⁻¹² It has been stated¹⁰⁻¹² that the thermal exchange at room temperature is not measurable or important, and that, therefore, the exchange observed is due only to the radiation absorbed.

In studies on the Szilard-Chalmers effect,¹³ several theories for the retention of I^{128} activity in the organic phase have been proposed.^{14,15} The exchange between ethyl iodide and iodine has been assumed to be slow under the conditions of this reaction, and therefore it has not been considered as a contributing factor in the retention.¹⁵ Shaw and Collie¹⁶ have suggested that the retention is due to a thermal exchange reaction between ethyl iodide and an iodine-containing species. In studies on this effect, Schuler¹⁷ has noted that there is a post-irradiation exchange. However, the exchange has not been generally accepted as a contributing factor to this retention.

In the exchange of methyl iodide and iodine, Behrens and Maddock^{18,19} and Behrens²⁰ have reported that the exchange might be occurring through a heterogeneous process. They also indicated a great deal of irreproducibility in their data and did not attempt a mechanistic interpretation of this system.

The present work was undertaken in an effort to clarify the kinetics of this exchange reaction. It was felt that the results of this study might help in the understanding of other research areas involving this system.

Experimental

Commercially obtained ethyl iodide (Baker and Adamson White Label or Fisher Certified) was used after washing with a basic solution of sodium bisulfite, drying with commercially obtained activated alumina, and distilling under a stream of argon gas in a Whitmore-Lux column. A reflux ratio of 5:1 was used and the constant-boiling middle fraction at 72.4° (760 mm.) was retained for use. The purified material was kept in the dark and used as soon as possible after distillation. Gas chromatography, using a flame ionization detector, revealed trace impurities of acetone and isopropyl iodide. These impurities were no greater than 0.01% of the ethyl iodide. The index of refraction was

(10) W. H. Hamill and R. H. Schuler, *J. Am. Chem. Soc.*, **73**, 3466 (1951).

(11) R. J. Hanrahan and J. E. Willard, *ibid.*, **79**, 2434 (1957).

(12) E. O. Hornig and J. E. Willard, *ibid.*, **79**, 2429 (1957).

(13) L. Szilard and T. A. Chalmers, *Nature*, **134**, 462 (1934).

(14) For a review see (a) M. Haissinsky, "Nuclear Chemistry and Its Applications," Addison-Wesley Publishing Co., Reading, Mass., 1964, Chapter 17; (b) J. E. Willard, *Ann. Rev. Nucl. Sci.*, **3**, 183 (1953).

(15) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 244.

(16) P. E. D. Shaw and C. H. Collie, *J. Chem. Soc.*, 1217 (1949).

(17) R. H. Schuler, *J. Chem. Phys.*, **22**, 2026 (1954).

(18) H. Behrens and A. G. Maddock, *ibid.*, **22**, 139 (1954).

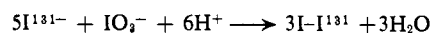
(19) H. Behrens and A. G. Maddock, "Radioisotope Conference," Vol. II, Butterworth and Co., Ltd., London, 1954, pp. 30-40.

(20) H. Behrens, "Proceedings of the Inter-American Symposium on the Peaceful Application of Nuclear Energy," Book 1, U. S. Atomic Energy Commission, May 1957, p. 330.

1.5107 (25°). Other alkyl iodides were treated in a similar manner. Carbon tetrachloride was purified by drying over alumina and distilling in a Whitmore-Lux type column. The center cut was collected. All additional chemicals used were reagent grade without further purification.

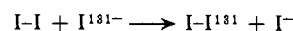
Two radioactive iodine isotopes were used. Iodine-131 was obtained in carrier-free form from E. R. Squibb and Sons, Volk Radiochemical Co., and Atomic Energy of Canada, Ltd. The isotope was obtained in millicurie amounts and contained no bisulfite or preservatives. Iodine-125 was obtained in millicurie amounts containing no bisulfite or preservatives from Union Carbide Nuclear Corp., Oak Ridge, Tenn., in carrier-free form.

Three methods were used to prepare the reaction solutions of ethyl iodide and labeled iodine. In the first method labeled iodine was prepared according to the equation



The labeled iodine was then transferred into ethyl iodide by extracting the aqueous solution with ethyl iodide. The reaction solution was then separated and dried by passing over activated alumina.

In the second method, a solution was prepared by dissolving solid iodine in ethyl iodide. The iodine was then labeled by contacting the ethyl iodide solution with aqueous iodide and allowing the following rapid exchange²¹ to take place. The organic phase was then



separated, dried as in the previous method, and used.

In the third method, sodium iodide and the carrier-free NaI^{131} solution were evaporated to dryness under vacuum. Powdered ceric bisulfate or potassium dichromate was then introduced on top of the residue and the container evacuated and sealed. This mixture was then warmed and the iodide was oxidized to iodine.²² The iodine was then collected by vacuum distillation into solid ethyl iodide. In some runs the iodine was distilled into a trap and stored under vacuum and then redistilled into ethyl iodide at the start of a run.

At the start of a run, aliquots of the labeled stock solutions were diluted to the required concentrations with appropriate solvents such as $\text{C}_2\text{H}_5\text{I}$ or CCl_4 , placed in glass vessels, sampled, and stored in complete darkness. A thermostat was used to maintain the desired temperature to $\pm 0.1^\circ$. All solution preparation was carried out in a darkened hood.

Pyrex reaction vessels were used after washing with detergent, rinsing with distilled water, and drying at 100° . Vessels of other materials were also used and treated in a similar manner. The vessels were wrapped in aluminum foil to keep out light during transfer and sampling operations. Degassed solutions were prepared in containers which allowed the oxygen to be removed by argon bubbling. Sampling was accomplished under positive argon pressure to prevent oxygen from diffusing back into the vessel.

Reaction solutions were sampled at various intervals by withdrawing an aliquot, diluting it with carbon tetrachloride, and extracting it with a basic solution of

(21) A. C. Wahl and N. A. Bonner, ref. 15, p. 337.

(22) J. E. Willard and S. U. Choi, *J. Phys. Chem.*, **66**, 1041 (1962).

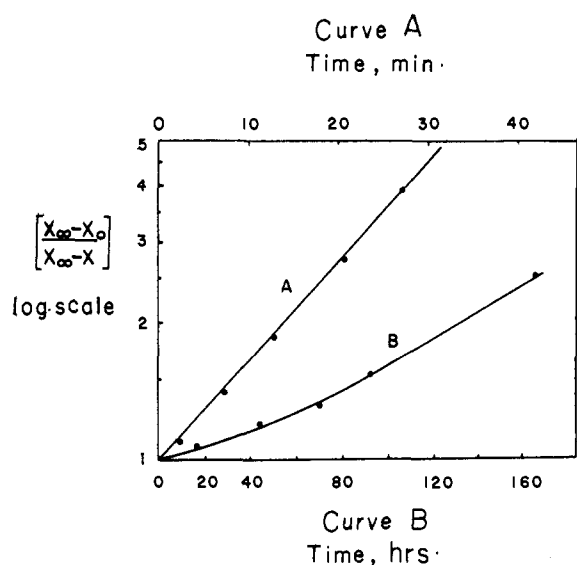


Figure 1. Typical plots of ethyl iodide-iodine exchange data. Curve A represents a typical linear case I plot indicating that the apparent exchange rate is constant. Curve B represents a typical case II plot which shows an induction period and is interpreted as coming from an isotopic impurity which causes an acceleration in the apparent exchange rate: A, $2.04 \times 10^{-6} M I_2$ (35°); B, $1.32 \times 10^{-4} M I_2$ (25°).

sodium bisulfite. The activity, measured in counts per minute (c.p.m.), in the resulting aqueous layer is then a measure of the unexchanged iodine, and the activity in the organic phase is a measure of the exchanged ethyl iodide. The ratio of organic activity to total activity is thus a measure of the per cent iodine exchanged with ethyl iodide.

$$\frac{\text{c.p.m. organic phase} \times 100}{\text{c.p.m. aqueous phase} + \text{c.p.m. organic phase}} = \% \text{ exchange}$$

Five-milliliter aliquots were counted in a γ -ray scintillation counting system.

The aqueous and organic solutions measured had a difference in density and self-absorption characteristics. Therefore, a given amount of activity gave less counts in the organic phase than in the aqueous phase. This was compensated for by experimentally determining correlation factors of 1.123 for I^{131} and 5.0 for I^{125} which were applied to measured counts. The higher value for I^{125} is due to its emission of weak γ -rays (27.2–32 kev.) which are more easily absorbed than the strong γ -rays of I^{131} .

Iodine concentrations were determined at 478 $m\mu$. An extinction coefficient of 1287 l./mole cm. was obtained and compared favorably with a reported value¹² of 1286. This value has been reported to be the same for all alkyl iodides.¹²

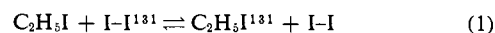
In order to determine the experimental error involved in the extraction procedure, multiple extractions on duplicate samples were taken and analyzed. This procedure indicated that the standard deviation of the measured exchange values was $\pm 7\%$ of the mean value. This indicates the degree of precision in repeating the measurements on a sample.

Reaction solutions were analyzed for reaction products by vapor phase chromatography and infrared spectroscopy. In addition, solutions were analyzed to determine if the organic product was in fact ethyl

iodide-131. This was done by removing the iodine from a reaction solution of ethyl iodide-131 and iodine, and diluting the ethyl iodide with methyl, ethyl, and *n*-propyl iodide. This mixture was distilled in a Whitmore-Lux column at a high reflux ratio and the various iodides were separated. Various distillation cuts were then assayed for radioactivity.

Treatment of Data

The data obtained were analyzed in the following manner. If the reaction for isotopic exchange is given by eq. 1, then eq. 2 can be derived,^{10, 23–26} where



$$R = \frac{(I_2)}{t} \ln \left(\frac{X_\infty - X_0}{X_\infty - X} \right) \quad (2)$$

X_∞ is the fraction exchanged at infinite time, X is the fraction exchanged at time t , and X_0 is the fraction exchanged at initial time; (I_2) is the concentration of iodine (moles/l.); t is the time (hr.); and R is the gross rate of exchange of all iodine molecules (moles $l^{-1} \text{ hr}^{-1}$).

The over-all rate R determined from this equation should be time independent.

Equation 2 can be solved graphically by plotting $\ln(X_\infty - X_0)/(X_\infty - X)$ vs. t . This gives a linear plot with a slope of $R/(I_2)$ and an intercept at the origin. The rate determined in this manner is an average rate, and error limits can be determined by graphically determining the standard deviation of the data.

It was found that the data obtained fell into two different categories. In the first case (I), the data could be fitted to normal exchange kinetics and a time-independent rate R_{av} could be calculated. A sample exchange plot is given in Figure 1.

In the second case (II), the log plots were not linear over the entire time range studied. The rates in these cases increased to a maximum value and were linear throughout the rest of the run. This plot had extrapolated intercepts which did not pass through the origin. Rate calculations were difficult for these runs since the derivation of R in eq. 2 requires R to be constant with time. In addition, in a true exchange reaction there is no compositional change in the system and the rate has to be constant. This difficulty was solved by calculating the rate in two different ways.

In the first method (used for case I) the slope of the linear portion was determined and this was used to calculate the rate according to the equations

$$S = \frac{\ln \left(\frac{X_\infty - X_0}{X_\infty - X_4} \right) - \ln \left(\frac{X_\infty - X_0}{X_\infty - X_3} \right)}{(t_4 - t_3)} \quad (2a)$$

$$S(I_2) = R$$

The differential equation for this system which is used to derive eq. 2 is

$$\frac{dX}{dt} = R \left(\frac{X}{X + X^1} \right)$$

(23) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, p. 192.

(24) H. McKay, *J. Am. Chem. Soc.*, **65**, 702 (1943).

(25) A. C. Wahl and N. A. Bonner, ref. 15, p. 172

(26) H. McKay, *Nature*, **142**, 997 (1938).

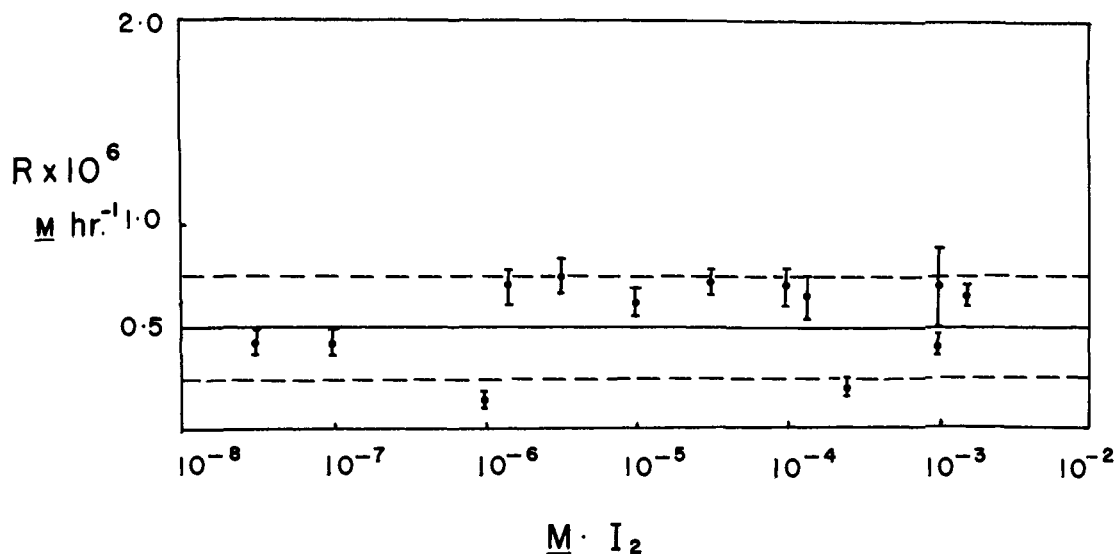


Figure 2. The dependence of the rate of ethyl iodide-iodine exchange at 23° on iodine concentration (no solvent): dotted line indicates standard deviation from mean value (solid line).

where X is the number of $I-I^{131}$ molecules, X^1 is the number of $I-I$ molecules, and R is the gross rate of exchange of all iodine species. This equation is adapted to the specific case of this study where $(C_2H_5I) \gg (I_2)$.²⁷

The differential term was calculated from the per cent exchange vs. time plot by determining the slope of the curve at time t . The ratio $X/(X + X^1)$ is also known at this point, thereby allowing an instantaneous rate to be calculated. The two methods for calculating rates gave identical results on case I runs.

In case II, the instantaneous rates R_i (slopes of the curves obtained from Figure 1B) were determined for a series of different times in a given run and were found to approach a limiting rate R_L asymptotically. R_L was found to be the same for both methods of calculation.

The rates used in this study are the average rates from case I or the average limiting rates ($R_{L,av}$) from case II. The cause of the behavior noted in case II is discussed in a later section.

Results

Rate Law. It was found that exchange could be detected at 23° and the rate of this exchange was independent of iodine concentration. As indicated in Figure 2, the iodine concentration in pure liquid ethyl iodide was varied from 5×10^{-8} to 2×10^{-3} M, and the rate was constant over this range with an average value of $R_{ex} = 0.50 \pm 0.25 \times 10^{-6}$ M hr.⁻¹. Similar results were obtained at 25 and 35° with rates of $0.88 \pm 0.15 \times 10^{-6}$ and 2.52×10^{-6} M hr.⁻¹, respectively.

As shown in Figure 3 the rate was dependent on the ethyl iodide concentration and appeared to be bimolecular. The bimolecular rate constants in CCl_4 solvent were calculated assuming the rate to be $R = k_b(EtI)^2$ and were found to be (M hr.⁻¹) 3.5×10^{-9} at 23°, 5.8×10^{-9} at 25°, 1.8×10^{-8} at 35°, and 3.1×10^{-8} at 40°.

Sample Preparation. The methods of sample prepara-

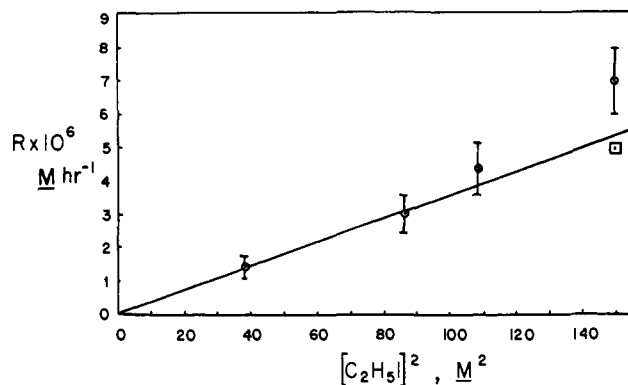


Figure 3. The dependence of the ethyl iodide-iodine exchange rate at 23° on ethyl iodide concentration, using CCl_4 as solvent (points on extreme right represent pure ethyl iodide): $\frac{1}{2}$, values for one set of runs (CCl_4 as solvent, 2×10^{-6} M I_2); \square , average value of many different runs with pure ethyl iodide at 23° and over wide ranges of iodine concentration (10^{-7} – 10^{-3} M). Plots of corresponding data at higher temperatures are similar to this one.

tion already described were compared within the experimental errors obtained in this work. There was no statistical difference in the three methods.²⁷

Radiation Intensity and Nature of Isotope. There was no effect owing to the different isotopes used in this study. In addition, the activity level was varied from 10^{-4} to 10^{-7} c./ml. for several samples which were identical in all other respects. The average rates were $0.63 \pm 0.05 \times 10^{-6}$ M/hr. for I^{125} and $0.50 \pm 0.07 \times 10^{-6}$ M/hr. for I^{131} . This variation was within statistical limits.

Oxygen. The results of oxygenated (1.2×10^{-3} M O_2) and degassed runs are presented in Table I. There was no detectable effect which could be attributed to oxygen.

Reaction Products. No organic products other than the trace impurities of less than 0.01% originally present in the ethyl iodide could be detected. The distillation procedure indicated that all of the organic activity was present as ethyl iodide-131. Schuler,

(27) E. Cohen, Ph.D. Thesis, University of Delaware, 1964.

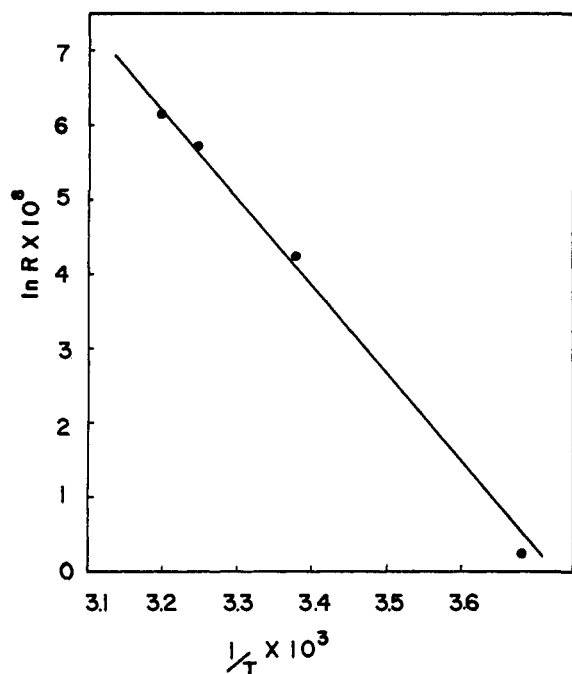


Figure 4. Arrhenius plot of ethyl iodide-iodine exchange rates: pure ethyl iodide, $2 \times 10^{-6} M I_2$.

et al.,²⁸ obtained the same result. The concentrations of the two impurities were followed with a flame ionization gas chromatograph detector during the course of an exchange. Neither product showed any detectable change in concentration. In addition, in a run with $5.4 \times 10^{-2} M$ acetone the rate was unaffected. Unpurified ethyl iodide was also used in one sample and compared with purified material. No change in rate was observed.

Table I. Oxygen Effect^a

$[I_2] \times 10^4, M$	O_2 removed	$R \times 10^4, M \text{ hr.}^{-1}$	
		Aerated soln. ^b	O_2 satd. ^c
0.78	0.37 ± 0.04	0.22 ± 0.04	0.30 ± 0.03
1.94	0.66 ± 0.08	0.49 ± 0.05	
1.81	0.31 ± 0.03	0.38 ± 0.03	
2.64	0.24 ± 0.03	0.20 ± 0.02	
0.97	0.38 ± 0.05	0.75 ± 0.02	

^a Pure EtI, 23°. ^b $[O_2] = 1.2 \times 10^{-3} M$ (est. from ref. 12). ^c $[O_2] = 6 \times 10^{-3} M$ (est. from ref. 12).

Temperature. The activation energy of the exchange was measured by running identical solutions at temperatures from 0 to 40°. An Arrhenius plot showing some of the data obtained is shown in Figure 4 and the activation energy determined from this plot and all other data was found to be 21.5 kcal./mole. The entropy of activation²⁹ was calculated to be -42 ± 3 cal./mole deg.

Heterogeneous Contribution. The exchange was examined for heterogeneous contribution by increasing the surface to volume ratio with glass helices and by

(28) R. G. Badger, C. T. Chmiel, and R. H. Schuler, *J. Am. Chem. Soc.*, **75**, 2498 (1953).

(29) A. A. Frost and R. G. Pearson, ref. 23, p. 99.

using vessels of materials other than glass. It was found that a 200% increase in glass surface area increased the exchange rate by 30%, and a 600% increase in surface area increased the exchange rate 50%. There was no marked change in the rate with such varied materials as Teflon, quartz, stainless steel, and polypropylene. A large increase in surface was achieved with Chromosorb-P, 14 m.² vs. 50 cm.² for the standard vessel, and no rate increase was noted. Various surface treatments were applied to the glass vessels and the results indicated that acid increased the rate in certain instances. However, this was not reproducible, and since it was close to the variation normally obtained it was probably not significant. The results of these effects are summarized in Table II.

Light. When several exchange solutions were exposed to ambient room light, no additional induced exchange was noted.

2-Iodopropane Exchange. The exchange rate of 2-iodopropane was found to be zero order in iodine with an average of $0.33 \pm 0.17 \times 10^{-7} M/\text{hr.}$ over the concentration range studied (1.5×10^{-5} to $2.02 \times 10^{-4} M$).

Solvent Effects. In one set of runs the ethyl iodide volume fraction was held constant at 0.8 and carbon tetrachloride, nitrobenzene, and 2-iodopropane were added in separate runs as diluents. The carbon tetrachloride and 2-iodopropane runs (after correction for the slow 2-iodopropane-iodine exchange) gave identical exchange rates. The rate calculated from the nitrobenzene run was about 5-6 times higher than that in the carbon tetrachloride and 2-iodopropane runs.

Discussion

Induction Period. In normal isotopic exchange the per cent exchange vs. time curve should asymptotically approach isotopic equilibrium greater than 99.9% iodine activity in ethyl iodide (at iodine concentrations used in these studies) at a constantly decreasing rate. The appearance of an induction period in this curve indicated that there was an unusual process occurring. This could suggest that isotopic exchange was not occurring and another reaction was being observed. The S-shaped curve is similar to that obtained for the autocatalytic reaction of $A \rightarrow B$, where B catalyzes the conversion of A. There were several factors which indicated that the predominant reaction was thermal exchange. The first was the observation of normal exchange kinetics in a majority of runs. The runs with induction periods gave normal exchange kinetics after the completion of this period. The product analysis also indicated that the product of the exchange reaction was ethyl iodide-131. It was, therefore, concluded that the S-shaped curves were due to an induction period in the exchange reaction.

This induction period could have been due to an impurity which retarded the exchange. Once the impurity was "consumed" the normal exchange process would then be observed. In addition, identical runs with and without this behavior appeared to give essentially the same rates if the maximum rate and normal rate, respectively, were compared.

There could be several possible sources of this impurity. The first source could be the organic impurities which were present in small amounts in the ethyl

Table II. Heterogeneous Contributions^a

[I ₂] × 10 ⁴ , M	R × 10 ⁶ , M/hr.				
1.51	Glass 0.42 ± 0.04	Quartz 0.33 ± 0.03	Polypropylene 0.60 ± 0.07		
0.04	Glass 0.68 ± 0.10	Acid wash 0.72 ± 0.11	Helices 0.68 ± 0.15	St. steel 0.72 ± 0.11	Teflon 0.72 ± 0.11
0.66 ± 0.10	Glass (50 cm. ²) 0.72 ± 0.04	Glass (180 cm. ²) 0.92 ± 0.04	Glass (399 cm. ²) 1.14 ± 0.05		
0.0386	Glass 0.56 ± 0.07	Teflon 0.37 ± 0.05	Polypropylene 0.50 ± 0.06	Chromosorb P (14 m. ²) 0.51 ± 0.16	
0.23	Glass 0.42 ± 0.05	HCl wash 0.94 ± 0.14	Det. film 0.26 ± 0.07	Clean sol. 0.88 ± 0.10	

^a Pure C₂H₅I, 23°.

iodide. One of the impurities, acetone, was deliberately added to the reaction solution; yet it failed to affect the rate. The use of unpurified ethyl iodide had no effect on the rate. Chromatographic studies did not show any change of concentration of the impurities while the rate was increasing to its limiting value. If acetone were the cause of this behavior, one of these tests should have revealed it. The small amount of isopropyl iodide present should have little effect on the rate.

It is possible that an impurity was formed from the thermal decomposition of ethyl iodide and catalyzed the exchange.

In several runs samples containing low iodine concentration were prepared by diluting an aliquot from a more concentrated sample, which had been sitting for a longer period of time. It was found in these cases that the dilution from a high concentration eliminated this induction period behavior and gave normal exchange kinetics. If an organic impurity caused this behavior, it should have been present at the same concentration in these runs and they should also possess an induction period.

Since there was some indication that the exchange might be influenced by surface, there was a possibility that some property of the surface was involved. This process could be either an impurity on the glass or a slowly occurring absorption process. There were some runs in which acid treatment of the surface gave an induction period and the standard treatment did not. However, this could not be reproduced in several successive runs. Additional glass surface did not alter the shape of the curve or the time to maximum rate (R_L). Variation of surface materials did not change the curve shape or rate outside the statistical fluctuations established in studies of other effects. Therefore, it is probable that the induction period was not a surface phenomenon.

It seemed possible that the rate increase was due to oxygen present in the system. The induction period could have been due to the oxygen being consumed and retarding the exchange. The data did not reveal any oxygen influence on the induction period.

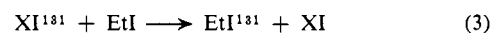
The original isotope solution before dilution was at activity levels high enough to cause some radiolysis of the aqueous iodide solution. There was a possibility that inorganic species other than I⁻ were present in the isotope solution and they might have been transferred into the organic reaction solution. To eliminate this possibility the iodine was prepared by vacuum oxidation and distillation, but the induction behavior was

still observed. The impurity could have similar physical properties to the iodine and may not have been removed by this procedure.

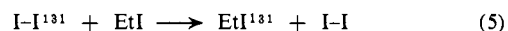
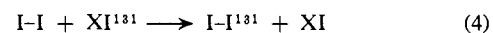
There are several studies³⁰⁻³² on the properties and purification procedures of carrier-free iodine-131 solutions. They indicate the presence of several unusual species which are not observed in normal iodine-127 solutions. These species are believed to be in oxidation states which do not correspond to known stable iodine oxidation states. These unusual states are from +2 to +5 and could be characterized by species such as HIO₂ or IO₂. These species are characterized by their resistance to chemical change by the oxidation or reduction techniques used and their slow exchange with iodine, iodide, and iodate.³³ If one of these species was present in the original isotope shipment, it would then be very difficult to remove.

Since one iodide-131 shipment was used for several successive runs, each reaction solution was self-irradiating and could be building up one or more of these impurities. The isotope solutions could also contain the impurity when they were sent from the manufacturer. A correlation of isotope shipment vs. rates indicated that a high activity (~8 mc./ml.) in the original shipment gave the induction period and that lower original activity (~1 mc./ml.) did not. In addition, if the same lot was used for an identical run after standing for several weeks, it exhibited an induction period. An iodine impurity in the isotope shipment would be consistent with the dilution effect noted previously.

There are several possible methods by which the iodine impurity XI¹³¹ could affect the exchange rate. It could react directly with ethyl iodide as in eq. 3 or



it could react through an intermediate as in reactions 4 and 5. If the induction period were due to reaction 3,



this would require the rate to decrease with time and fall off after the impurity was consumed. This reaction would be in addition to the normal exchange reaction and the resultant rates would be additive.

(30) R. H. Herber "Inorganic Isotope Synthesis," W. A. Benjamin, Inc., New York, N. Y., 1962, Chapter 9.

(31) M. Kahn and A. C. Wahl, *J. Chem. Phys.*, **21**, 1185 (1953).

(32) H. M. Eiland and M. Kahn, *J. Phys. Chem.*, **65**, 1317 (1961).

(33) The half-time of the exchange reaction between one of these species and iodine was reported³² to be 41 hr. at 29.2°.

It appears that reactions 4 and 5 are responsible for the induction period. The original activity present is probably not all in the form of I-I¹³¹ and, until all activity is in the I₂, a true rate is not observed.

The exchange reaction between iodide and iodate has been studied using I¹³¹ tracer and a similar induction period has been noted.³⁴ Induction periods in the data reported were from 1.5 to 8 hr.

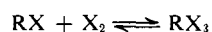
An analysis of the kinetics of this induction process was made as follows. It was assumed that ($R_L - R$) was a measure of the amount of XI¹³¹ present in the system and that the conversion was a pseudo-first-order process in XI¹³¹. (I-I is present in excess of 10⁻⁴ M to approximately 10⁻¹¹ M XI¹³¹.) The concentration of A is given by $A = A_0 e^{-k_A t}$, where A is the concentration of impurity in eq. 4 and therefore

$$A = z(R_L - R) = z(R_L - R)_0 e^{-k_A t}$$

where z is a proportionality constant. Thus a plot of $\ln(R_L - R)$ vs. time should be linear. These plots were found to be linear and the half-time of the reaction calculated from the initial slope of these curves was found to be about 60 hr. This is in agreement with a reported value³⁶ of 41 hr. for the reaction of an unidentified iodine species and iodine. This reported value was at 29.2° and the half-life would be longer at 23° where these runs were conducted.

Iodine Independence. The rate law for the exchange reaction was independent of the iodine concentration over the range studied. The iodine concentration was varied by a factor of 100,000, and the rate varied randomly over a range of only 0.25 to 0.75 × 10⁻⁶ M/hr.

A general type of halide-halogen exchange mechanism involves the 1:1 addition complex of alkyl halides and halogens. These complexes arise from the equilibrium



where RX = alkyl or phenyl halide, X = halide, and X_2 = halogen or interhalogen. Keefer and Andrews³⁵ have calculated the equilibrium constants of several of these systems by analysis of their absorption spectra. The equilibrium constant for the ethyl iodide-iodine complex was measured in carbon tetrachloride and found to be 0.29. The exchange mechanisms of alkyl and benzyl halides with iodine monochloride are believed to involve this addition complex.^{36,37} Iodine monochloride complexes the halide and then an attack on the complex by another iodine monochloride leads to reaction. This yields a rate law of $-d(\text{ICl})/dt = k(\text{ICl})^2$. Darbee and Harris⁷ have obtained a rate law of $R = k(\text{I}_2)$ for the exchange mechanism of ethyl iodide and iodine at a higher temperature (60°) and at higher iodine concentration (0.03–0.3 M I₂) and indicated that the complex is involved. Their rates extrapolated to lower temperatures were higher by several orders of magnitude than those reported here. Bujake and Noyes,³⁸ in a study of the *t*-butyl iodide exchange, found that the exchange proceeded through two mechanisms. One of them was a bimolecular process with a rate

(34) H. J. Arnikaar and R. Tripathi, *J. Chromatog.*, **7**, 362 (1962).

(35) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **74**, 1891 (1952).

(36) R. M. Keefer and L. J. Andrews, *ibid.*, **75**, 543 (1953).

(37) R. M. Keefer and L. J. Andrews, *ibid.*, **76**, 253 (1954).

(38) R. E. Bujake and R. M. Noyes, *ibid.*, **83**, 1955 (1961).

law of $R = k(t\text{-BuI})(\text{I}_2)$ and the other a termolecular process with a rate law of $R = k(t\text{-BuI})(\text{I}_2)^2$. The latter process was attributed to attack by iodine on the addition complex.

If the ethyl iodide exchange mechanism proceeds through iodine attack on the addition complex, then an iodine dependence would have to be seen in the rate law.

Heterogeneous Reactions. Heterogeneous reactions of alkyl halide-halogen exchanges have been shown in several gas phase systems and the rate laws presented have contained iodine independent terms.^{39–41} In addition Behrens and Maddock^{18–20} have suggested that the methyl iodide-iodine exchange might be a heterogeneous reaction.

In conjunction with the known affinity of iodine for glass,^{42,43} there was reason to believe that this exchange might be surface controlled. Iodine independence would arise if surface sites were saturated with iodine and the adsorbed iodine then led to exchange.

The surfaces tested did not significantly vary the rate of exchange. A highly reactive surface such as polypropylene did not give a higher rate than an unreactive surface such as Teflon. The large increase in surface area from the Chromosorb P did not drastically increase the rate. Additional glass surface did increase the rate, but a plot of surface area vs. the rate did not extrapolate to zero. If the exchange were primarily heterogeneous at zero surface area there should be little or no exchange. There may well be a minor contribution from heterogeneous reaction when a highly reactive surface such as glass is used. However, it does not appear to be the main mechanism of exchange.

A radical process involving the dissociation of ethyl iodide or iodine was not favored because of the lack of influence of oxygen on the exchange rate. Since oxygen concentrations in O₂-saturated solutions exceeded the iodine concentrations used in many experiments, it is probable that an oxygen effect would have been noted. This is especially true because of the wide range of iodine concentrations investigated.

The mechanism proposed for this exchange must account for the following experimental facts: (A) The rate-controlling step involves two or more molecules of ethyl iodide. (B) There are no iodine molecules involved as such in the rate-controlling step(s). (C) This process probably does not proceed through a radical process. (D) There is no significant contribution from the heterogeneous reaction. (E) There is a high negative entropy of activation (–42 e.u.) and an activation energy of 21.5 kcal./mole. The entropy would indicate a highly ordered transition state or possibly a polar complex. (F) The rate of exchange is significantly lower with isopropyl iodide.

In view of these conditions, the rate-determining step is proposed as



The fast reactions which may follow this rate-deter-

(39) J. E. Boggs and L. O. Brockway, *ibid.*, **77**, 3444 (1955).

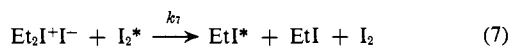
(40) P. Clark, H. O. Pritchard, and A. F. Trotman-Dickinson, *J. Chem. Soc.*, 2633 (1954).

(41) J. B. Peri and F. Daniels, *J. Am. Chem. Soc.*, **72**, 424 (1950).

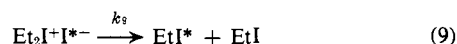
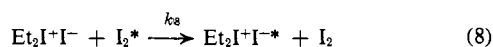
(42) H. Schmied and R. Fink, *J. Chem. Phys.*, **27**, 1034 (1957).

(43) A. J. Urbanic and V. R. Damerell, *J. Phys. Chem.*, **45**, 1245 (1941).

mining step are of several types. First the exchange could accompany a fast collisional decomposition of the complex by iodine as shown in eq. 7. A second

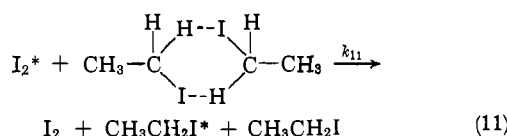
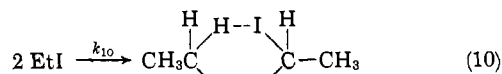


pathway leading to the same kinetics would be that shown by reactions 8 and 9.



For the last two reactions to obey the observed kinetics it would be necessary that $k_9 \ll k_8 \ll k_6$.

There is also another transition state which would be consistent with the observed kinetics and it can be expressed as



The intermediate in the first mechanism is diethyl iodonium iodide. The exchange of a related compound, the diphenyl iodonium iodide, has been studied and it has been shown that one iodine atom in the complex iodide will exchange, but the other one will not.⁴⁴ The second iodine does not exchange since it is bound to the phenyl groups. In addition, the exchange mechanism of aromatic iodides (PI) and iodine at 167 to 200° has been shown to proceed with a rate law which contains a $k(\text{PI})^2$ term.⁴⁵ The mechanism for this has been attributed to an iodonium iodide intermediate.

The data on methyl iodide exchange with I_2 indicate the over-all exchange rate is faster than for ethyl iodide¹⁶⁻¹⁸ and the isopropyl iodide- I_2 exchange rate is the slowest of the three iodides. This trend would indicate steric effects are important. The additional methyl groups in isopropyl iodide would crowd this ion-pair transition state and would hinder the formation of the ion pair.

The proposed iodonium iodide intermediate also results in the formation of a nucleophilic iodine which would be quite susceptible to attack by molecular iodine.

The cyclic intermediate presented in the second mechanism (*i.e.*, eq. 10 and 11) would be held together by the weak hydrogen-bonding forces of the hydrogen and iodine. In addition, the resultant six-membered ring would also add extra stability to this. The steric considerations of the exchange would appear to favor this intermediate since the additional methyl groups would block iodine attack. However, these additional groups are not in the plane of the ring and would not prevent its formation. Thus the only steric retardation would be in blocking iodine attack in its fast step. The forces required to maintain this complex would be weak and it might not have a sufficiently long life to undergo exchange.

(44) H. Juliusberger, B. Topley, and J. Weiss, *J. Chem. Soc.*, 1295 (1935).

(45) S. Levine and R. M. Noyes, *J. Am. Chem. Soc.*, 80, 2401 (1958).

The high negative entropy of activation would appear to be too large for this type of ring, but since this is a highly ordered structure it might be consistent. The weak nature of the forces in this ring would also require a low energy input to break them and give the exchange.⁴⁶ A lower activation energy would appear to be more consistent with this type of ring than the 22 kcal./mole measured.

Of the two intermediates discussed, the diethyl iodonium iodide is favored. It would appear to be more consistent with the thermodynamic parameters and would be more stable than the cyclic species. There is a strong point against this in view of the nature of ethyl iodide which is not a highly ionizing solvent. However, there is probably enough ionic character in iodine to allow this ion pair to be sustained. The increased rate with nitrobenzene solvent would also favor this intermediate since nitrobenzene has a higher dielectric constant. The cyclic intermediate would not be as stable as the ion-pair intermediate and it might decompose before exchange with a resulting kinetic term involving (I_2) .

Reproducibility. In this study much of the irreproducibility mentioned by several authors was overcome, and a kinetic scheme is presented for this system. Several factors which may have lead to previous experimental difficulties with this system are the surface effect with glass and the induction period noted.

The treatment of the data including a variable induction period can lead to erroneous rates and a wide scatter from one run to another. When the induction period is present, the data must be calculated graphically and sufficient experimental points must be taken to ensure that the true limiting rate is seen. Five points in the initial part of a run will give an entirely different rate than one calculated from ten points toward the end of the run. If the rate is calculated by a point-by-point calculation method, the resulting average rate will not be valid.

In determining a rate law for the ethyl iodide-iodine exchange, a term containing iodine to some power was expected by earlier workers. When this was not observed, it was concluded that irreproducibility of the data was involved and that there was heterogeneous contribution or an unusual sensitivity to impurities. The unusual rate law of $R = k(\text{EtI})^2$ when observed in a limited concentration range is not obvious. The low velocity of the exchange and the iodine independence also make the experimental techniques difficult and further complicate the analysis.

Since the exchange is iodine independent, the McKay equation and the rate law can be combined to yield

$$\ln \left(\frac{X_\infty - X_0}{X_\infty - \bar{X}} \right) = \frac{K(\text{EtI})^2 t}{(\text{I}_2)}$$

The logarithmic term is the experimentally measured value and varies according to the nature of the terms on the right side of the equation. In a given series of runs the ethyl iodide concentration is constant and the iodine concentration varied. As the iodine concentration increases, the measured values decrease and at sufficiently high iodine concentration no apparent

(46) The bond energy of hydrogen bonds is from 2 to 8 kcal./mole depending on the electronegativity of the atoms involved. These bonds would be probably from 4 to 5 kcal./mole.

exchange is measured. A decrease in ethyl iodine concentration also decreases the apparent rate and at low ethyl iodide concentrations no exchange will be observed. The low velocity constant also requires a relatively long time to accurately study this process. A run at $10^{-3} M I_2$ and with no solvent will show a fraction of a per cent exchange per day and at approximately $3 \times 10^{-3} M$ will not be statistically observable.

Comparison with Other Work. This study has shown that there is a significant thermal exchange of ethyl iodide and iodine at room temperature. This fact can help explain some of the anomalies in other studies on the ethyl iodide–iodine system. In the study of the radiation chemistry of alkyl iodide and iodine, Hanrahan and Willard¹¹ were able to predict theoretically the yields of iodine, hydrogen iodide, and the rate of induced exchange. They found that all of their predictions were in agreement with their experimental data except for the rate of induced exchange. The experimental values were higher by a constant increment of $0.020 \mu\text{equiv./min.}$ The reason for this discrepancy was not clear and was attributed to “hot” processes involving ethyl iodide molecules with too little energy to produce radicals. The thermal exchange measured in this study had a value of $0.017 \mu\text{equiv./min.}$, which is in excellent agreement.

Darbee and Harris⁷ have studied this system at conditions close to those of this study and could not obtain reproducible data. At $10^{-2} M$ iodine they obtained a rate law of $R = k(I_2)$ and attributed the exchange to a complex formation. Their irreproducibility at 10^{-3} – 10^{-4} was probably due to the factors

discussed previously. At $10^{-2} M$ the iodine independent mechanism would not be seen.

Behrens and Maddock^{18–20} have reported work on the methyl iodide–iodine system at 35° . They indicated the exchange follows a rate law of $R = k(I_2)^{-1}$. In later work Behrens²⁰ indicated that the exchange was subjected to a heterogeneous contribution, but in the earlier work Behrens and Maddock¹⁸ indicated that under identical conditions their data had not been satisfactorily reproduced. In addition, samples in the same set of vessels with and without glass packing gave similar results. In relation to this work the methyl iodide exchange is faster than that of ethyl iodide at 35° , 7.55×10^{-6} vs. $2.55 \times 10^{-6} M/\text{hr.}$ However, considering the observed irreproducibility in these systems, the agreement is good. There was no indication of a radiation intensity effect in this system and no heterogeneous contribution. This might indicate that methyl iodide has a different exchange mechanism. This was further confirmed by the 8.4-kcal. activation energy for methyl iodide which is considerably lower than the value reported here for ethyl iodide.

Szillard–Chalmers Effect. The data indicate that there is a rapid apparent exchange between ethyl iodide and iodine at low concentrations. This would help to explain some of the inconsistencies in the hot-atom work on ethyl iodide systems.⁴⁷

Acknowledgment. The authors wish to thank Dr. Harold Kwart for many stimulating discussions regarding the mechanism of this reaction.

(47) The possible implications of this work on the Szillard–Chalmers effect are to be discussed elsewhere.

Effects of Resonance and Structure on the Thermochemistry of Organic Peroxy Radicals and the Kinetics of Combustion Reactions¹

Sidney W. Benson

Contribution from the Department of Thermochemistry and Chemical Kinetics, Stanford Research Institute, Menlo Park, California 94025.

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Recent data on the H-bond dissociation energy in H–O₂ and the reasonable assumption that $D^\circ(\text{RO}_2\text{–H}) = D^\circ(\text{HO}_2\text{–H})$, together with ΔH_f° for the peroxides, permit the evaluation of the bond dissociation energies $D^\circ(\text{R–O}_2\cdot)$ and $D^\circ(\text{RO}_2\text{–R})$ for a number of different groups R. Using estimated entropies for radicals and molecules, it is possible to estimate equilibrium constants and ceiling temperatures for the reaction $\text{R}\cdot + \text{O}_2 \rightleftharpoons \text{RO}_2\cdot$. These temperatures are quite high for $\text{R} = \text{H}$ or alkyl radicals, but rather low for $\text{R} = \text{allyl}$ or benzyl. They do indicate that $\text{RO}_2\cdot$ will be important in cool flame reactions. Using similar data, other reactions of $\text{RO}_2\cdot$ radicals are discussed. Additions to olefins are shown to have low ceiling temperatures but not the

additions to dienes or styrene. Internal abstraction of $\text{RO}_2\cdot$ and four-center reactions of $\text{R}\cdot + \text{O}_2$ are shown to be probably unimportant. Termination reactions involving $\text{RO}_2\cdot$ are shown to be likely only for $\text{RO}\cdot$ (disproportionation) and $\text{R}\cdot$ (addition and disproportionation). In solution the reaction $2\text{RO}_2\cdot \rightarrow 2\text{RO}\cdot + \text{O}_2$, which is a propagation reaction, can also lead to a small but important amount of cage recombination of $2\text{RO}\cdot$. It is shown that above 150° the distribution of primary products in hydrocarbon oxidation is given by the expression

$$d(\text{RO}_2\text{H})/d(\text{olefin}) = K_{eq}k_a(\text{RH})/k_1'$$

where K_{eq} is the equilibrium constant for the reaction $\text{R}\cdot + \text{O}_2 \rightleftharpoons \text{RO}_2\cdot$, k_a is the rate constant for $\text{RO}_2\cdot + \text{RH} \rightarrow \text{RO}_2\text{H} + \text{R}\cdot$, and k_1' is for $\text{R}\cdot + \text{O}_2 \rightarrow \text{HO}_2\cdot + \text{olefin}$.

(1) This work has been supported in part by a multisponsor research program on oxidation of hydrocarbons at Stanford Research Institute.