view of the smallness of the lowering of the phenol moment, no interaction of resonance effects should be detectable in these moments. This conclusion is in harmony with the absence of any considerable difference between the acid constants of phenol and hydroquinone, although these constants are much more easily influenced by small differences in charge than are the dipole moments. Furthermore, the calculated moments[9] for p-methyl, p-chloro-, and p-bromophenol and for p-methyl, p-fluoro, p-chloro, p-bromo and p-iodoanisole agree fairly well with the observed values, giving no evidence of an interaction of resonance effects. On the other hand, the moments calculated for p-nitro and p-nitrosophenol are considerably lower than the observed values and the calculated moment for p-nitroanisole is somewhat lower than that observed. There a marked interaction of the resonance effects is shown.

Birtles and Hampson[10] have shown that the moments of nitrodurene and aminodurene are lower than those of the corresponding benzene derivatives and close to those of the corresponding alkyl compounds. Presumably, steric repulsion of the adjacent methyl groups in the durenes tends to keep the atoms attached to the nitrogen from lying in the plane of the ring and, thereby, reduces the contributions from highly polar doubly-bonded structures in which these atoms must lie in that plane. Other nitro compounds have also been discussed[8] from this standpoint. Among the contributing structures of hydroquinone and hydroquinone dimethyl ether, those

with a double bond between the oxygen and the ring should have the hydroxyl hydrogen or the methoxy methyl in the plane of the ring. cis structures with maximum moment and trans structures with zero moment should be equally probable so that any rigidity of the oxygen-to-ring bonds caused by contributions from these structures should not alter the resultant moment. However, in the di-t-butylhydroquinone and its dimethyl ether, the cis form would be impossible because of the repulsion of the t-butyl groups; hence, the contribution of the doubly-bonded structures to the observed moment would be zero. The rather small moment lowering produced by the two t-butyl groups is thus additional evidence for the smallness of the amount of double bond character in the oxygen-to-ring bonds in these molecules.

Summary

Di-t-butylhydroquinone and di-t-butylhydroquinone dimethyl ether have been prepared. The dielectric constants and densities of their solutions in benzene have been measured and used to calculate the dipole moments of the compounds.

The steric repulsion of the t-butyl groups restricts the rotational freedom of the hydroxy and methoxy groups in such a way as to cause a moderate reduction in the moments of the molecules. The moments of these and other hydroxy- and methoxybenzenes suggest that the bond between the oxygen and the ring has only a small amount of double bond character.

(9) Ref., 5, pp. 390, 398.
(10) Birtles and Hampson, J. Chem. Soc., 10 (1937).

The Exchange Reaction between Simple Alkyl Iodides and Iodide Ion[1]

BY HERMAN SEELIG AND D. E. HULL

The work of several investigators who have used radio-iodine as an indicator has shown that an exchange of iodine can be effected between the simple aliphatic iodides and the iodide ion.[1a] In 1937 Hull, Schiflet, and Lind[2] discovered a marked temperature effect in the exchange between sodium iodide and ethyl iodide in alcohol

solution. The reaction was fast at 80°, but did not proceed appreciably in five minutes at room temperature. McKay[3] reported a similar result in this exchange, and also in the case of several other aliphatic iodides. These experiments were only qualitative in nature, and no calculation of the energy of activation could be made from them.

Quantitative experiments have been done in similar exchanges with bromide ion in aqueous

(1) This paper is based on a thesis submitted by Herman Seelig to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
(1a) Juliusberger, Topley and Weiss, J. Chem. Phys., 3, 437 (1935).
(2) Hull, Schiflet and Lind, THIS JOURNAL, 58, 1822 (1936).

(3) McKay. Nature, 139, 283 (1937).

acetone solution by Sugden and his co-workers.[4,5] They were able to calculate the energy of activation in these reactions. Fowler and his collaborators[6,7] have recently reported similar measurements of exchanges with an alkyl bromide and with a chloride. No quantitative experiments involving iodine exchanges have been reported.

Because it was believed that the method of measuring rates of exchange could be considerably improved by a combination of experimental techniques used in this Laboratory, an investigation of the exchange between iodide ion and ethyl, propyl, and isopropyl iodides in alcoholic solution at various temperatures was undertaken in the hope that the reaction rates and energies of activation might be determined with an accuracy of 1%.

The exchange reactions studied in this work can be represented by the equation

$$RI + {}^*I^- = RI^* + I^- \qquad (1)$$
$$a \quad\; y \qquad x \quad\; b$$
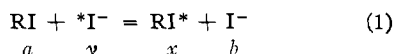
Using the letters under the formulas to represent concentrations (in moles/liter) of the respective reactants, the rate constant can be calculated from measurements of these concentrations as a function of time, t, by the following equation

$$k = -\frac{2.303}{t(a+b)} \log\left[1 - \frac{x}{x+y}\left(1 + \frac{b}{a}\right)\right] \qquad (2)$$

Since x and y are involved in this equation only in a ratio, they may be expressed in any convenient units, such as, in this case, the counting rate recorded by the counter when the material is placed in a certain position. The concentrations a and b must, however, be measured in absolute units.

Preparation of Materials.—The sodium iodide was the customary analytical grade. The organic iodides were prepared by the Eastman Kodak Company. Their purity was tested by measuring the boiling ranges and by analyzing them for iodine. The results of these tests are shown

Compound	Boiling range, °C.	Iodine, % Found	Calcd.
Ethyl iodide	71.8– 72.6	79.0	81.4
Propyl iodide	102.4–104.0	73.4	74.7
Isopropyl iodide	88.8– 90.1	74.7	74.7

The propyl iodide was yellow, but when it was shaken with mercury and then distilled a water-white sample was obtained. All the samples were dry.

Absolute alcohol was used as a solvent throughout. It contained so little water that no reaction was evident during refluxing with calcium carbide.

(4) LeRoux and Sugden, *J. Chem. Soc.*, 1279 (1939).

(5) Elliot and Sugden, *ibid.*, 1836 (1939).

(6) Koskoski, Dodson and Fowler, THIS JOURNAL, **63**, 2149 (1941).

(7) Koskoski, Thomas and Fowler, *ibid.*, **63**, 2451 (1941).

The radio-iodine used in the experiments with ethyl iodide and propyl iodide was obtained by bombarding for several hours with neutrons from a radon–beryllium source of 100–170 millicuries, 1 liter of iodobenzene in a soft-glass flask all surrounded by water. On account of the longer time required with isopropyl iodide, the radio-iodine used in these expts. (except the first two) was prepared by bombardment for ten to twenty minutes with neutrons from a deuteron–beryllium source in the Physics Department.[8] These samples were about 100 times as strong as those from the radon-beryllium source. After removal from the neutron source, the iodobenzene was transferred to a separatory funnel containing 20 ml. of an aqueous solution of 0.01 M sodium iodide. The mixture was thoroughly shaken. As soon as possible the water and the iodobenzene layers were separated and the iodobenzene was returned to the flask ready for bombardment in the next experiment. No care was taken to wash the inorganic salt completely out of the organic iodide. The aqueous layer, however, was washed with ether to remove any dissolved or suspended iodobenzene, and was then separated and evaporated to dryness. The residue contained approximately 200 micromoles of sodium iodide in which was concentrated a considerable fraction of the radio-iodine from the iodobenzene.

Experimental

The reaction vessel in which the exchanges were carried out is shown in Fig. 1. "Nolub" ground-glass joints, which give a good seal without any grease, were used in its construction. The stopcock was the usual lubricated type. The upper part of the vessel was calibrated to contain 5.00 ml.
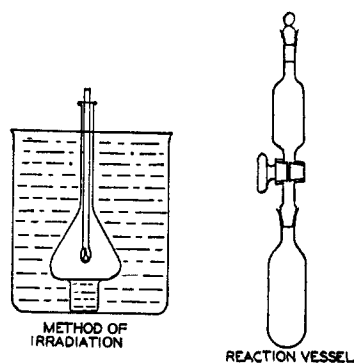

METHOD OF IRRADIATION   REACTION VESSEL

Fig. 1.

The steps in a typical experiment were as follows:

(1) 5 ml. of a 0.04 M solution of alkyl iodide in absolute alcohol, of accurately known concentration, was pipetted into the lower part of the vessel. The upper part, with stopcock closed, was connected, and the lower part was immersed in a dry-ice–acetone slush. The upper part was connected to a vacuum pump and the stopcock was opened for ten to twenty seconds and then closed. Thus a good vacuum was produced in the lower part of the vessel without any appreciable loss of solvent. The vessel was removed from the freezing mixture and placed in an oil-filled thermostat so that the lower part was submerged.

(2) The freshly prepared sample of sodium radio-iodide was dissolved in about 3 ml. of absolute alcohol and transferred to the upper part of the reaction vessel. More alcohol was used for rinsing and to bring the total volume up to the 5-ml. mark. The upper part was now stoppered and the whole vessel was lowered until it was almost completely submerged in the oil-bath. It was allowed to stand for at least twelve minutes, which time was found adequate to bring the solutions to the temperature of the thermostat, at least within 0.1°.

(3) When both the solutions had attained the temperature of the thermostat, they were mixed by momentarily raising the vessel halfway out of the oil-bath and opening the stopcock. Since the highest temperature used was less than the boiling point of alcohol, the lower vessel was still under a reduced pressure, and the sodium iodide was drawn down very quickly and with considerable turbulence, indicating good mixing. The time required for this operation was less than one second. The upper vessel was allowed to drain for about ten seconds, the stopcock was closed, and the vessel was lowered back into the oil-bath. The mixture was allowed to stand in the thermostat for the allotted time, counting from the moment of opening the stopcock.

(4) At the end of the reaction time, the vessel was quickly removed from the thermostat and plunged into a Dewar flask full of a petroleum ether–dry-ice mixture.[9] The vessel was vigorously shaken in the flask and the freezing mixture was stirred in order to provide as rapid cooling as possible.
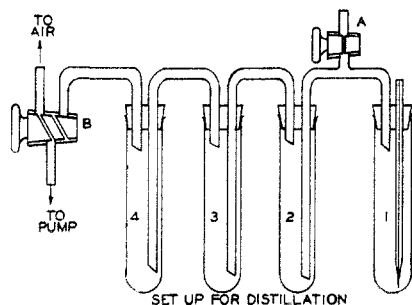

Fig. 2.

(5) The chilled solution was transferred quantitatively, by rinsing with denatured alcohol, into a dry, cold test-tube, and the tube was inserted in position 1 in the distilling system shown in Fig. 2. Tubes 3 and 4 were already surrounded by freezing mixtures of dry-ice and acetone. When the vacuum pump was turned on, distillation of ethyl alcohol and alkyl iodide from tube 1 to tube 3 took place, leaving sodium iodide behind. The capillary in tube 1 served to prevent bumping. If, in spite of this precaution, some of the sodium iodide solution boiled over, it was caught in and recovered from tube 2. A beaker of water at room temperature was placed around tube 1, as otherwise the collection of frost on the tube cut down the rate of heat transfer so much that twice the time was required to complete the distillation. A thin film of ice sometimes formed on the outside of tube 1 near the end of the distillation, and would always form if the beaker of

water was removed momentarily, thus showing that the temperature of the boiling solution was considerably below zero. After tube 1 appeared to be dry, pumping was continued for about one more minute. Then the two Dewar flasks were removed and the stopcock, B, was closed. Then stopcock, A, was slowly opened to allow the system to come to atmospheric pressure. Then the test-tubes could be removed, no. 1 containing the dry sodium iodide, and no. 3 the alkyl iodide in alcohol solution. No liquid was ever observed in tube 4, which indicates that the alkyl iodide was completely recovered.

(6) The alkyl iodide was prepared for measurement first. Two methods were used in this step. (a) The ethyl iodide samples were hydrolyzed by adding 10 ml. of 4 N sodium hydroxide to the contents of tube 3 and placing the tube in a beaker of water at 80° for seven to ten minutes. Then the base was neutralized with 4 N nitric acid, and silver nitrate solution was added. This gave almost quantitative yields of silver iodide from ethyl iodide, but gave very small yields from propyl iodide. An alternative method was therefore used, as follows. (b) An alcoholic solution of silver nitrate was added directly to the contents of tube 3, and it was placed in a beaker of water at about 75°. Precipitation took place rapidly and was almost complete in five minutes.

The silver iodide thus formed from the alkyl iodide was filtered by suction through a fine-grained 50 mm. filter paper in a Büchner funnel.[10] The filter paper had been previously washed with water, alcohol, and ether, dried and weighed. Filtration of the silver iodide was carried out while it was still finely divided, so that the first filtrate was usually murky. This was collected and poured through the filter a second time, after which the filtrate was always clear. With this technique, the precipitated silver iodide was uniformly distributed in a thin layer over the surface of the filter paper, and had no tendency to coagulate in lumps. The filter and precipitate were then washed with water, alcohol, and ether, dried and weighed as before. Then the filter paper was covered with a 2% solution of cellulose nitrate in acetone, 1 to 1.5 ml. being required; the evaporation of the acetone left the precipitate covered with a thin film which held it firmly in place while it was being mounted on the counter and during measurements.

(7) The sodium iodide was then prepared for measurement in a similar manner, omitting the hydrolysis. The sodium iodide left in tube 1 was dissolved in alcohol, taking care to recover any salt in tube 2 and all that adhering to the capillary or the connecting tube. The solution was warmed and an alcoholic silver nitrate solution was added to precipitate the iodide. Under these conditions also, the silver iodide came down in fine crystals which were very uniformly distributed across the filter paper.

Measurement of Activities.—The radioactivities of the samples were measured with a thin-walled, all-glass β-ray counter similar to that previously described by one of us, except that it is filled with argon instead of air.[11] This is connected in a Neher–Harper quenching circuit and amplifier essentially that described by Lifschutz.[12] The high

(9) Petroleum ether was used at this point in order to dissolve the oil from the thermostat off the reaction vessel.

(10) Our obligation to the Coors Porcelain Company, who kindly made for us two funnels of a special size for this work, is gladly acknowledged.

(11) Hull, *Rev. Sci. Instruments*, **11**, 404 (1940).

(12) Lifschutz, *ibid.*, **10**, 21 (1939).

voltage which is supplied to the counter wire is monitored by a potentiometric circuit which is sensitive to changes of 0.1 volt. The argon-filled counter has a plateau in the counting rate vs. voltage curve with a slope of 0.3% per volt. The reproducibility and relative accuracy of this counter, and its calibration, are described elsewhere.[13]

The filter paper with the precipitate mounted as described above was wrapped around the sensitive portion of the counter and held in place with a rubber band. The diameter of the filter papers used was just equal to the circumference of the counter cylinder, so that the two edges of the filter paper met without overlapping. The length of the counter cylinder was 2 cm. greater than the diameter of the filter paper. The paper was always mounted on the counter in approximately the same position (within 1 or 2 mm.).

Each sample was measured long enough to reduce the probable error due to statistical fluctuations to 1%, except when the initial activity was not sufficient to permit this. The time of beginning each measurement was noted on an electric clock; the duration of the measurement was timed by a stop watch. The background was measured before and after each measurement of a sample. The background remained constant at 1.17 ± 0.03 counts per sec. during several weeks of work through the summer.

Reliability of Method for Weighing Samples.—Since one of the two most important errors inherent in this method of determining specific activities lies in the weight of the samples, particular attention was given to this point. First, a study was made of the reproducibility in weight of a filter paper after being washed with water, alcohol, and ether, and dried. It was found that, while the weight changed from the weight of the unwashed filter paper as much as 2 or 3 mg. on the first washing, subsequent washings produced no changes greater than 0.6 mg., and the probable error in subsequent weighings was found to be 0.3 milligram. The error in the weight of a sample obtained by difference, therefore, would be 0.4 mg.

Since about 200 micromoles of sodium iodide was used to extract the iodine, and a similar quantity of alkyl iodide was added for the exchange, about 47 mg. of silver iodide would be obtained in each sample if the recovery were 100%. Allowing for some loss of sodium iodide during the extraction, and of alkyl iodide in the hydrolysis or precipitation, about 40 mg. was actually obtained in most of the experiments. Thus one would expect an error in the weight of the samples as obtained by this method of about 1%. Table I shows the weights of silver iodide obtained in a series of analyses of weighed samples of the sodium iodide

Table I

Weight of Silver Iodide

Found, mg.	Calcd., mg.	% Dev.
32.9	33.2	−0.9
33.0	33.1	−0.3
35.9	35.0	+2.6
40.0	39.9	+0.3
52.5	53.5	−1.9
49.2	49.1	+0.2
38.2	37.8	+1.1
36.2	35.7	+1.4

used in the expts., compared with the expected weights, together with the percentage deviation. The deviation of the mean observed weight from that expected is +0.3%, and the probable error in the weight of a single sample is ±1.0%, in good agreement with the expected error.

Reliability of Radioactive Measurements.—It has already been shown[11] that the counter used in these experiments is reliable to 0.2% for relative measurements of samples whose geometrical relation to the counter is held constant or can be accurately reproduced. With the experimental arrangement here used, the question of the reproducibility of the measurements of β-rays from the radio-iodine in the samples must be considered from two standpoints: (1) the error introduced by variations in absorption in samples of varying thickness, and (2) the error introduced in placing the sample in a fixed position with respect to the counter.

The first point may be settled by calculating the absorption to be expected in the silver iodide itself and in the covering layer of cellulose nitrate. Since the area of the filter paper is about 20 sq. cm., 40 mg. of silver iodide corresponds to a surface density of 2 mg./sq. cm., and 20 mg. of cellulose nitrate to a surface density of 1 mg./sq. cm. The absorption coefficient of the 2.4 m. e. v. β-rays from radio-iodine is about 17 cm.$^{-1}$ in aluminum, or 0.0063 sq. cm./mg. The absorption expressed in this latter unit is, to a first approximation, independent of the atomic number of the absorber. Variations in distribution of the precipitate of the order of the average thickness of the precipitate, 2 mg./sq. cm., would therefore lead to variations in absorption of the β-rays of at most 1.3%. However, the uniform appearance of the precipitate on the filter paper gives reason to believe that the average variations in thickness from one sample to the next are much smaller than this. By similar calculations, it can be shown that variations up to 50% in the thickness of the film over the precipitate would introduce errors in absorption of only 0.3%.

The error in attaching the sample to the counter was studied experimentally by using a 50-mm. filter paper on which was spread a small quantity of a uranium compound, covered with the usual film.[14] This was mounted in the usual position on the counter and measured. Then it was taken off and measured in another position, then brought back to the original position and measured again. When the filter paper is rotated about the axis of the counter, or shifted toward either end, the counting rate changes by a few per cent., but on being replaced in its original position on the counter, the original counting rate is found. The values obtained in this experiment are listed in Table II. The last three measurements were obtained by rotating the filter paper about its own center by successive 90° angles, keeping it in the same position on the counter. The possible small deviations indicated in these measurements could be caused only by a non-uniform distribution of the precipitate on the filter paper. The uranium was not distributed on the paper as uniformly as the usual silver iodide precipitate. Nevertheless, the results shown in Table II indicate that the reproducibility of the measurements is quite good even though no special precautions are taken to replace the filter paper in pre-

(13) Hull and Seelig, Phys. Rev., **60**, 553 (1941).

(14) The β-rays from the UX$_1$ in this sample have a maximum energy of 2.3 m. e. v., almost the same as the iodine β-rays.

cisely the same position. It is concluded from these results that the error in placing the sample on the counter can be held at least as low as 0.4%.

TABLE II

ACCURACY OF ATTACHING SAMPLES TO COUNTER

Measured activity	Dev.
49.00 ± 0.18	−0.35
49.48 0.18	+0.13
49.33 0.21	−0.02
49.20 0.21	−0.15
49.48 0.18	+0.13
49.55 0.21	+0.20
49.40 0.21	+0.05

Mean 49.35.
P. E. of a single measurement ±0.13.

Calculation of Rate Constant.—The experimental data and related quantities calculated

from them are shown in Table III for ethyl iodide, propyl iodide, and isopropyl iodide, respectively. The temperature of each group of experiments is shown in the first column. The duration of each experiment is given in column 2. The following two columns contain the weights of silver iodide obtained from the alkyl iodide and sodium iodide, respectively.

Since x and y are very small as compared (in the same units) with a and b, the latter two quantities can be regarded as constant in any given experiment. They were determined as follows: (a) A standard solution of the alkyl iodide was prepared by weighing. This concentration was halved in the reaction mixture by the addition to the standard solution of an equal volume of

TABLE III

RATE OF EXCHANGE OF IODINE BETWEEN ALKYL IODIDES AND SODIUM IODIDE

1 Temp., °C.	2 Time, min.	3 Mg AgI RI	4 NaI	5 a millimoles/l.	6 b	7 Activity AgI RI	8 NaI	9 ΔT_m min.	10 x counts/sec.	11 y	12 $k \times 10^4$ sec.$^{-1}$
						Ethyl Iodide					
50.05	90	42.2	40.8	19.91	17.38	3.52	6.43	25.20	3.90	12.93	29.0 ± 7
	30	44.3	40.7	19.91	17.33	4.03	20.61	25.60	4.25	41.9	29.0 5
	15	45.5	41.7	19.91	17.76	3.63	31.5	30.88	3.73	74.1	28.8 5
	60	44.8	41.6	19.91	17.72	4.78	12.59	24.60	4.99	24.9	28.7 5
										Av.	28.9 ± 3
59.74	30	43.5	40.2	19.91	17.12	8.07	16.22	26.29	8.67	33.6	74.8 ± 1.2
	15	45.3	40.5	19.91	17.25	7.47	26.66	27.29	7.71	56.8	78.5 1.2
	60	45.6	36.6	19.91	15.59	4.65	4.10	27.76	4.77	8.85	79.7 1.8
	30	46.2	41.3	19.91	17.59	16.36	43.6	13.09	16.56	62.7	77.0 1.2
	7	43.9	41.4	19.91	17.63	7.15	66.1	21.27	7.61	119.2	79.2 1.2
	60	42.7	43.1	19.91	18.36	6.65	6.61	28.00	7.28	14.37	78.5 2.0
	7	45.4	43.4	19.91	18.48	4.08	29.63	28.84	4.20	65.9	79.2 1.2
	^{a}30	45.3	42.6	19.91	18.14	10.21	18.98	25.00	10.54	38.0	(81.5) 1.3
										Av.	78.1 ± 5
70.10	30	44.6	41.7	19.91	17.76	42.90	43.5	18.00	44.97	71.5	203 ± 5
	3.5	43.8	39.7	19.91	16.91	12.33	94.9	19.66	13.16	163.7	202 3
	7	42.7	40.9	19.91	17.42	24.06	101.6	16.56	26.34	160.8	207 3
	15	45.5	41.2	19.76	17.55	24.51	45.1	16.51	25.00	71.2	212 3
	15	44.7	38.1	19.76	16.23	27.88	51.5	16.03	28.94	80.3	215 3
										Av.	207 ± 1
						Propyl Iodide					
49.76	30	34.4	37.8	19.30	16.10	3.35	31.9	27.77	4.41	69.0	18.8 ± 3
	60	35.9	40.5	19.30	17.25	3.42	18.21	21.59	4.32	33.1	19.2 3
	90	37.6	41.4	19.30	17.63	1.77	4.03	35.73	2.13	10.85	19.3 5
	45	33.9	37.9	19.30	16.14	2.94	22.15	19.98	3.93	38.5	20.0 3
	90	25.0	40.4	19.30	17.21	1.42	4.54	38.59	2.57	13.24	19.2 5
	45	42.6	40.1	19.30	17.08	8.17	48.8	19.43	8.69	83.6	20.5 3
	45	42.3	40.2	19.30	17.12	7.47	50.8	15.43	8.00	77.9	20.2 3
	60	44.3	41.8	19.76	17.80	5.99	23.99	24.40	6.27	47.2	19.2 3
	45	45.6	38.4	19.76	16.35	3.72	19.41	23.10	3.79	36.8	19.7 3
	90	46.2	41.0	19.76	17.46	4.24	10.07	26.88	4.26	21.22	19.3 3
	30	44.8	41.8	19.76	17.80	6.64	59.9	18.43	6.88	99.9	19.8 3
	60	45.0	41.4	19.76	17.63	5.07	22.17	20.83	5.23	39.5	19.0 3
	45	44.5	41.0	19.76	17.46	6.93	43.0	17.43	7.23	69.8	19.8 3
										Av.	19.5 ± 1

TABLE III (*Concluded*)

1 Temp., °C.	2 Time, min.	3 RI	4 NaI	5 a	6 b	7 RI	8 NaI	9 ΔTm min.	10 x	11 y	12 k × 10⁴ sec.⁻¹
		Mg AgI		millimoles/l.		Activity AgI			counts/sec.		
59.97	30	44.5	38.9	19.76	16.57	14.91	55.1	15.60	15.55	84.9	53.3 =± 8
	60	45.1	41.0	19.76	17.46	9.39	17.17	17.39	9.66	27.8	51.7 8
	15	43.0	41.8	19.76	17.80	13.48	94.5	17.66	14.55	154.2	55.0 8
	45	44.4	39.5	19.59	16.82	27.06	61.8	18.55	28.04	103.4	53.3 8
										Av.	53.3 ± 4
70.10	15	44.5	38.8	19.59	16.52	32.8	90.2	18.04	33.9	148.7	136 =± 2
	30	43.7	40.7	19.59	17.33	33.6	56.2	13.04	35.3	80.7	136 2
	45	44.5	34.0	19.59	14.48	32.0	35.0	13.00	33.1	50.2	135 3
	7	44.3	37.9	19.59	16.14	20.8	138.0	13.04	21.6	198.1	139 2
										Av.	136 ± 1
					Isopropyl Iodide						
70.10	15	45.1	39.0	19.88	16.61	2.15	87.3	16.1	2.23	136.6	9.6 =± 2
	90	42.7	40.1	19.88	17.08	1.43	8.35	24.0	1.56	16.25	9.4 2
	60	43.3	34.0	19.88	14.48	76.8	67.6	103.0	82.8	1176	10.3 2
	180	42.0	43.3	19.88	18.44	52.6	90.7	44.5	58.5	312	9.3 1
										Av.	9.6 ± 1
60.02	30	44.4	39.7	19.88	16.91	43.8	93.5	133.5	46.1	3787	3.53 =± 4
	180	43.8	40.9	19.88	17.42	7.12	58.1	23.4	7.58	111.2	3.30 5
										Av.	3.42 ± 3
44.72	150	43.7	38.7	19.88	16.48	10.18	129.4	77.3	10.87	1103	0.56 ± 1

ᵃ This experiment was done in 95% alcohol–5% water solution.

sodium radio-iodide solution, and a further correction was made for the expansion of the alcohol from room temperature to that of the thermostat according to Young's equation.[15] The corrected concentration of alkyl iodide in the reaction mixture is given in the fifth column of the table. (b) The concentration of sodium iodide varied from one experiment to another, because no attempt was made to recover it completely in the iodobenzene separation. However, all the sodium iodide in the reaction mixture was recovered and weighed as silver iodide, so that its concentration in the reaction mixture may be calculated from this. The values given in column 6 include a correction as before for expansion of the solvent.

The counting rates of the two silver iodide samples, averaged over the interval measured in each case, have been corrected (positively) for counting losses and (negatively) for background. The corrected values are given in columns 7 and 8.

Since the half-life of iodine is so short that considerable decay occurs during measurement, the activity of the silver iodide from the sodium iodide (which was always measured last) must be corrected back to the time of measurement of the silver iodide from the alkyl iodide. Furthermore, since the intervals over which the two samples were measured were not, in general, of equal

(15) "International Critical Tables," Vol. III, p. 27.

length, a mean time must be calculated for each interval, and the correction for decay must be applied over the difference in these mean times. For this purpose the mean time is defined as the time during the interval at which the instantaneous counting rate is equal to the average counting rate observed over the whole interval. Mathematically, this may be stated

$$e^{-\lambda T_m} \equiv \frac{1}{T}\int_0^T e^{-\lambda t}\,dt = \frac{1}{\lambda T}(1 - e^{-\lambda T}) \quad (3)$$

where T is the length of the interval of measurement, λ is the decay constant, and T_m is the desired mean time. Solving for T_m

$$T_m = \frac{1}{\lambda}\ln\frac{\lambda T}{1 - e^{-\lambda T}} \quad (4)$$

By means of this equation, the mean time of each measurement has been calculated, and the difference in mean times of measurement of corresponding samples is given in the ninth column. Using this, the corrected activity of sodium iodide has been calculated by multiplying the measured activity by the factor $e^{\lambda \Delta T_m}$. The values of y thus obtained are listed in column 11.

Since not all the alkyl iodide was recovered and measured as silver iodide, it is necessary to correct the activity listed in the seventh column by multiplying by the ratio of weight of silver iodide expected from the alkyl iodide to the weight

of silver iodide found. This corrected activity, x, is given in the tenth column.

Using the values thus determined for t, a, b, x, and y, the values of the specific rate constant, k, have been calculated according to Eq. (2) and are given in the last column.

Accuracy of Experimental Data.—The temperature of the thermostat was measured with a $0.1°$ thermometer which had been previously calibrated against a set of thermometers certified by the Bureau of Standards. Readings were estimated to the nearest $0.01°$. The range of temperature observed during an on-off cycle of the thermostat was about $0.1°$. It is believed that the mean temperatures given are reliable to $0.05°$.

The largest error in the measurement of the time of reaction lies in the time of quenching the reaction. It was found experimentally that about eight seconds were required to bring the temperature of the reaction mixture down to $0°$.[16] Therefore, the error in any experiment lasting fifteen minutes or longer must amount to considerably less than 1%.

The accuracy in a, the concentration of alkyl iodide, is limited by the accuracy of chemical analysis of the compounds. The uncertainty on this point might introduce an error as large as 0.5% into the absolute values of k; the relative values, however, and hence the determination of the heat of activation, would not be affected by this. It should also be noted that the value of a does not depend upon the efficiency of recovery of alkali iodide from the reaction mixture.

Since b, the concentration of sodium iodide, is calculated from the equivalent weight of silver iodide, it is subject to a probable error of 1%. The activity of alkyl iodide involves both a weight and an activity measurement, each with a probable error of 1%, making a 1.4% error in x. The time intervals as measured by the stop watch and the electric clock agreed closer than 0.1%.

In some of the experiments with isopropyl iodide the sodium iodide sample was so strong that it was necessary to wait as much as five half-lives for its activity to come within a counting range suitable for accurate measurement. The use of the exponential correction factor to an accuracy of 1% over such an interval requires a

(16) At $0°$, the reaction may be assumed to be stopped, as the rate constant is about 100 times smaller than at $50°$. The temperature was actually maintained considerably below $0°$ during the twelve to fifteen minutes required for distillation.

knowledge of the decay constant to 0.3%. Since no determination of this constant reported in the literature had the requisite accuracy, it was necessary to measure it for this research. This work has been published elsewhere.[18] The value found for the half-life of iodine was 24.99 ± 0.02 min., corresponding to a decay constant of 0.02773 min.$^{-1}$. This value was used in calculating the values of y (and also the mean times of measurement). The probable error in y is thus held to 1%.

Several experiments were done to determine a possible influence of small amounts of water upon the reaction. No difference in results was found between early experiments in which the alcohol was dried by distillation from calcium carbide and later ones in which this step was omitted. Also, one experiment (shown in Table III, for ethyl iodide at $60°$) was carried out in alcohol which contained 5% water. It is evident from the results of this experiment that the effect of water is small, and since the ethyl alcohol used in the experimental work has been shown to contain an undetectable amount of water, it may be safely concluded that no error was introduced from this source.

Summing up the foregoing sources of error, one concludes that the chief error in the value of k comes from the error in x. Smaller, but significant, contributions are made by the errors in y, a, and b, and these are taken into account in calculating the error in k which is given in the table.

Energies of Activation and Collision Diameters.—For a bimolecular reaction, the dependence of the specific reaction velocity upon temperature can be expressed in the form

$$\ln \frac{k}{\sqrt{T}} = A - \frac{B}{T} \tag{5}$$

where

$$A = \ln \frac{N_0}{1000} \sigma^2 [8\pi R/(1/M_1 + 1/M_2)]^{1/2}$$
$$= 58.577 + 2 \ln \sigma + \frac{1}{2} \ln \frac{M_1 M_2}{M_1 + M_2} \tag{6}$$

and

$$B = E/R \tag{7}$$

Evaluation of the constants A and B from the data here obtained thus enables one to calculate the energy of activation E and the collision diameter σ from the reaction.

These constants have been determined by the method of least squares, weighting each point in proportion to its accuracy. The results obtained are shown in Table IV.

TABLE IV

ENERGIES OF ACTIVATION AND COLLISION DIAMETERS

Compound	A	B	σ Ångströms	E, cal./mole
Ethyl iodide	24.400	10,706	11.0 ± 1.0	21,270 ± 150
Propyl iodide	23.254	10,455	6.2 0.7	20,770 150
Isopropyl iodide	25.113	12,001	15.8 2.8	23,850 190

The error in the slope, B, was calculated from the probable errors in the values of k by the method outlined by Bond.[17] The error in A was calculated from the error in B, since in the large extrapolation of the curve from the region studied to the intercept, the importance of the vertical displacement of the curve is minimized and variation of the slope becomes the controlling factor.

The average reaction constants at each temperature are shown in Fig. 3, the values of $k/\sqrt{T}$ being plotted on a logarithmic scale against $1/T$ on a linear scale.

This graph shows that propyl iodide exchanges somewhat more slowly with iodide ion than does ethyl iodide, a result which is to be expected in consequence of its greater molecular weight, according to Eq. (6). The curves for ethyl and propyl iodides are almost parallel, indicating a close correspondence of the carbon–iodine bond energy in these two compounds. Isopropyl iodide shows a striking decrease in activity as compared with the straight-chain compound, the exchange occurring about one-fifteenth as rapidly at 60°.

Discussion

Work of previous investigators on the energies of activation of these compounds in other types of reactions has yielded results which are in essential agreement with the present values. Grant and Hinshelwood[18] studied the alkaline hydrolysis of ethyl iodide in alcohol and found an energy of activation of 21,000 cal./mole. The absolute rates of hydrolysis at various temperatures found by them are about 12% lower than the rates of exchange found here. These facts suggest that the mechanism of substitution by iodide ion is the same as the mechanism of hydrolysis.

It has been shown[19] in similar reactions with optically active aliphatic halides, that the rate of substitution is the same as the rate of inversion, and, therefore, it is very probable that inversion accompanies every such substitution. The mech-

(17) Bond, "Probability and Random Errors," E. Arnold & Co., London, 1935.

(18) Grant and Hinshelwood, J. Chem. Soc., 258 (1933).

(19) Hughes, Juliusberger, Mastermann, Topley, and Weiss, ibid., 1525 (1935); Hughes, Juliusberger, Scott, Topley, and Weiss, ibid., 1173 (1936).
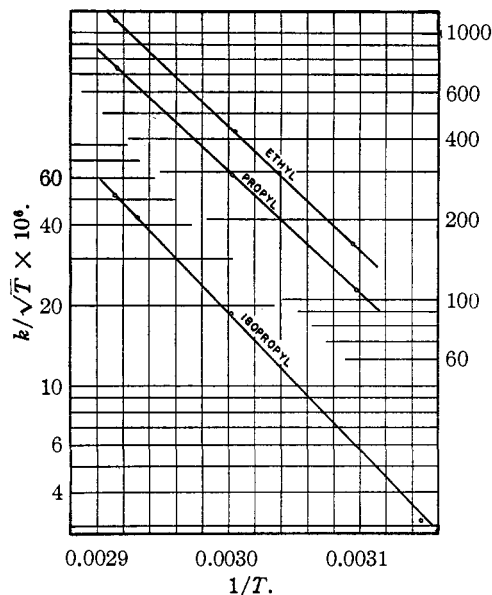
Fig. 3.

anism thus suggested for the exchange in ethyl iodide is the approach of the entering iodide ion to the side of the carbon atom opposite that to which the iodine originally present is attached, and an inversion of the tetrahedral bonds of the carbon atom at the moment of reaction. On this basis the substitution of hydroxyl ion in place of iodide ion might not be expected to greatly alter the energy of activation in the reaction, although its smaller size would mean fewer collisions and a smaller absolute rate of reaction, in qualitative agreement with the experimental data.

Woolf[20] has studied the reaction of several alkyl halides, including those studied here, with sodium eugenoxide. His results agree closely with those found in the present work for propyl iodide, but for ethyl iodide and isopropyl iodide his energies of activation are 2000 to 3000 cal./mole smaller. Hughes and Shapiro[21] report an energy of activation for the alkaline hydrolysis of isopropyl iodide in 60% alcohol of 20,700 cal./mole. but because of the difference in solvent these results are not directly comparable.

It is of interest to note that Sugden and his co-workers[4,5] found a higher energy of activation for isopropyl bromide in its exchange with bromide ion than for normal propyl bromide. This effect is confirmed in the present experiments with the iodides.

It would appear from a simple interpretation

(20) Woolf, ibid., 1172 (1937).

(21) Hughes and Shapiro, ibid., 1177 (1937).

of the results shown in Table IV that the difference in behavior between isopropyl iodide and normal propyl iodide is due to a stronger bond between carbon and iodine in the former compound. However, this conclusion is wholly at variance with the commonly accepted view of the effect of substituent alkyl groups on the strength of binding between a carbon atom and a negative group. Experiments in which the ease of ionization of the negative group is measured indicate a weakening of this bond when one goes from primary through secondary to tertiary halides. Apparently the present experiments represent a case in which the simple theory expressed in Eq. 5-7 is inadequate to account for the observations. If the steric hindrance of the extra methyl group on the carbon atom in isopropyl iodide is effective in reducing the number of collisions favorable to exchange, then a temperature dependence of considerable magnitude may be placed upon the reaction velocity by this factor, since with increasing temperature steric effects become less important. If this factor were taken into account, the heat of activation would be found to be smaller than that calculated from Eq. (5); also, a smaller collision diameter would be found.[22]

(22) The authors express their indebtedness to Dr. R. T. Arnold for stimulating discussions with him which contributed to the interpretation of these results

Summary

The rate of exchange of iodine between ethyl, propyl, and isopropyl iodides and sodium iodide in alcohol solution has been studied over a temperature range from 50 to 70°, using ^{128}I as a radioactive indicator for the reaction.

The radioactive samples were measured in the form of silver iodide, the precipitate being collected quantitatively in a thin layer on a filter paper which was exposed to a β-ray counter. The reliability of this method of measurement has been studied, and it is shown that measurements are accurate to 1%. Certain improvements in technique over the conventional methods of mixing and separating the reactants are described.

From the specific rate constants measured at three temperatures, an energy of activation has been calculated for each compound. The values are believed to be accurate within 1%. Ethyl and propyl iodides have closely similar energies of activation. However, that of isopropyl iodide appears to be significantly higher, as indicated by a more than 15-fold diminution in rate of exchange at the temperatures studied. A possible explanation of this anomaly is given.

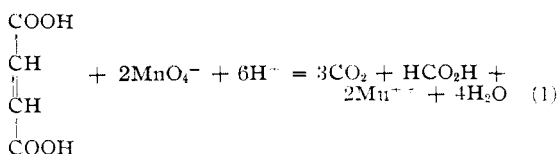Collision diameters are also calculated.

Tracer Studies with Radioactive Carbon and Hydrogen. The Synthesis and Oxidation of Fumaric Acid

BY M. B. ALLEN AND S. RUBEN

When fumaric acid is oxidized in 1.5 N sulfuric acid by potassium permanganate at 35–50°, carbon dioxide and formic acid are formed.[1] The reaction can be represented quantitatively by the equation

$$\begin{array}{l} \text{COOH} \\ | \\ \text{CH} \\ \| \\ \text{CH} \\ | \\ \text{COOH} \end{array} + 2MnO_4^- + 6H^- = 3CO_2 + HCO_2H + 2Mn^{++} + 4H_2O \quad (1)$$

The rate of oxidation of formic acid under these conditions is much slower. The mechanism of reaction (1) is complicated and unknown. Using radioactive carbon as a tracer we have attempted

(1) Perdrix, *Bull. soc. chim.*, [3] **17**, 100 (1897).

to determine whether the formic acid originates from the methine or the carboxyl carbons or both. This study is of interest not only for its own sake but also in connection with certain recent bioorganic discoveries made possible by the use of labelled carbon (C^{11}, C^{13}, C^{14}); namely, the synthesis of fumaric and other four carbon dicarboxylic acids from C^*O_2 by living systems.[2,3,4] Indeed, it was the latter that led to the present investigation since it was necessary to have a rapid and convenient method for determining the distribution of C^* within succinic and fumaric acids.

(2) Wood, Werkman, Hemingway and Nier, *J. Biol. Chem.*, **135**, 789 (1940); **139**, 377 (1941).

(3) Carson and Ruben, *Proc. Nat. Acad. Sci.*, **26**, 418 (1940).

(4) For a review see Van Niel, Ruben, Carson, Kamen and Foster, *ibid.*, **26**, 8 (1941).