859. *Kinetics of the Isotopic Exchange between 1-Iodo-2,4-dinitronaphthalene and Iodides in Methanol*

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The isotopic exchange reaction between 1-iodo-2,4-dinitronaphthalene and potassium iodide has been followed in methanol solution using iodine-131 as tracer, at various temperatures and over a wide range of concentration of iodide ion.

To follow the increasing activity of the organic compound, a liquid scintillator technique has been adopted.

Specific rates and the Arrhenius parameters have been calculated.

The isotopic exchange reactions between various aromatic iodo-nitro-compounds and iodides labelled with iodine-131, have been studied.[1-9] However, a definite mechanism for these reactions has not yet been deduced.

Besides, the order of the reaction seems to change either with the solvent or with the concentration of iodide. Thus, the isotopic exchange between 1-iodo-2,4-dinitrobenzene and iodide, has been found to follow second-order kinetics in acetone solution,[10] whilst the rate of the same reaction in absolute methanol [11] is independent of the concentration of iodide, except in the region of very low iodide concentrations where the rate does not seem to follow a clear first-order law.

In order to obtain more kinetic data another similar system was studied, *i.e.*, the isotopic exchange between 1-iodo-2,4-dinitronaphthalene and potassium iodide in methanol solution. Kinetic data of this reaction are reported below.

Experimental.—Solutions. Stock solutions of potassium iodide and of iododinitronaphthalene were prepared in methanol, free from ethanol and carbonyl compounds. The water content was 0·3% w/v. Iodine-131 was obtained, as a solution of iodide ions in dilute thiosulphate, from the nuclear research centre " Democritus," Greece. The solution was evaporated to dryness, the cooled residue dissolved in methanol, and the solution evaporated. This was repeated twice and the stock solution of [^{131}I] iodide was prepared by dissolving the dry residue in methanol.

Run solutions were prepared by mixing 100 ml. of the iododinitronaphthalene solution with 9·0 ml. of potassium iodide solution, of the appropriate concentrations, in a dry flask at room temperature. The flasks were placed in a thermostat-controlled bath at the required temperature. After $\sim\frac{1}{2}$ hr. the [^{131}I] iodide solution (1·0 ml.) was injected and the time noted as zero time. Since the same stock solutions were used throughout the water content of all runs was the same. The concentration of [^{131}I] iodide was very low (10^{-11}M) in comparison to that of potassium iodide (10^{-4}—10^{-2}M) so the effect of the [^{131}I] iodide on the overall iodide concentration was negligible.

Experimental techniques. At suitable time intervals samples (2·0 ml.) of the reaction mixture were taken, added to 5·0 ml. of toluene, and extracted with 15·0 ml. of water in a separatory funnel. From the clear toluene layer 2·50 ml. were pipetted, they were mixed with 1·0 ml. of abs. MeOH in a small polyethylene tube and were measured on a scintillator counter with a Well-type crystal. The count-rates X_t were corrected for background and decay.

The rates (R) of the reaction were followed by the increasing activity of the organic compound

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[1] A. M. Kristjianson and C. A. Winkler, *Canad. J. Chem.*, 1951, **29**, 154.
[2] S. May, M. Saraf, A. Vobauré, and P. Daudel, *Compt. rend.*, 1951, **233**, 744.
[3] S. May and B. Giraudel, *Compt. rend.*, 1952, **234**, 2280.
[4] S. May, A. Fava, and B. Giraudel, *Compt. rend.*, 1955, **236**, 286.
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[6] P. Manno, *Diss. Abs.*, 1956 **16**, 1219.
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[8] D. Lin, *Diss. Abs.*, 1958, **18**, 1998.
[9] S. Levine, *Diss. Abs.*, 1957, **17**, 1675.
[10] S. Kanchanalai, Thesis, Leicester College of Technology, 1960.
[11] C. A. Marcopoulos, *Chimika Chronica*, 1962, **27***A*, 151.

and they were calculated from the well-known equation of McKay:[12] $-\ln(1 - F) = tR(a + b)/ab$ where a and b are the concentrations of the organic and inorganic compound, respectively, and F is the fraction of exchange at time t, equal to X_t/X_∞ where X_∞ is the count rate of the organic compound at infinite time, *i.e.*, after equilibrium has been reached.

X_∞ was calculated by the expression $X_\infty = Ca/a + b$ where C is the total count (for both the organic and inorganic compounds) remaining constant throughout the experiment. C was calculated as follows: 1·0 ml. of the reaction mixture was mixed with 2·50 ml. of toluene in a polyethylene tube and the sample was measured. Corrections were made for background and decay.

The counting-error in all measurements was no more than 1%.

Results.—Rates and specific rates. The reaction was followed at 25, 35, 45, and 55°, and with a range of concentrations of potassium iodide between 0·0001 and 0·01M. The concentration of iododinitronaphthalene was kept constant at 0·0025M. At each temperature and potassium iodide concentration the reaction was run in duplicate. The slopes of the straight lines obtained when $\log(1 - F)$ was plotted against time were calculated by the method of least squares. The relative standard deviations of the slopes obtained were found to be between ± 1 and $\pm 8\%$.

To determine the order of the reaction, values of $\log R$ have been plotted against $\log b$. These plots are curves rather than straight lines. However, they approach the linearity (especially for 25, 35, and 45°) and they show only a rather limited dependence of R on b. Taking it broadly they could be taken to show zero-order reaction with respect to iodide.

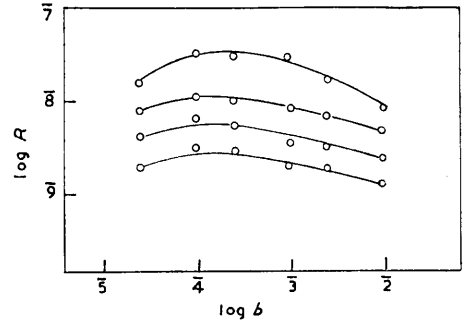

FIGURE 1. Logarithms of rate as a function of logarithms of concentration of potassium iodide. Curves give the approximate order of the reaction.

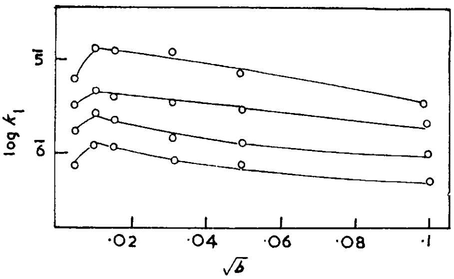

FIGURE 2. Logarithms of specific rate as a function of the square root of the concentration of potassium iodide

To establish the order of the reaction with respect to iododinitronaphthalene, some runs were followed at 45° with a standard concentration of iodide ($b = 0{\cdot}0025$M) and with a range of concentrations of iododinitronaphthalene between 0·0001 and 0·0025M. The plot of $\log R$ against $\log a$ is also a curve with a good approach to linearity showing a first-order dependence of R on a. Taking it broadly it could be taken to show first-order reaction with respect to iododinitronaphthalene. Consequently, the reaction could be considered to be of first total order. By dividing all R values by the corresponding concentration of iododinitronaphthalene, specific rates were obtained.

In Table 1 the specific rates, k_1 (sec.$^{-1}$), for the corresponding temperature and concentration of iododinitronaphthalene (a) and potassium iodide (b) are given. The relative standard deviations of k_1 vary between ± 1 and $\pm 10\%$.

The plots of $\log k_1$ *vs.* square root of the concentration of potassium iodide are rather straight lines for the region of b between 0·0001 and 0·01M showing a slight negative salt effect, as expected from the theory for reaction between an ion and an uncharged molecule.

Arrhenius parameters. From the graph of the plot $\log k_1 : \sqrt{b}$, values of k_1 at different temperatures for the concentrations 0·0001, 0·00025, 0·001, 0·0025, and 0·01M of b have been taken and plotted against $1/T$. From the slopes of the straight lines obtained, the Arrhenius parameters E_a and A have been calculated.

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[12] H. A. C. McKay, *Nature*, 1938, **142**, 997.

TABLE 1

Specific rates of iodide exchange between iododinitronaphthalene and labelled potassium iodide

Run No.	Temp.	a (M)	b (M)	$k_1 \times 10^6$ (sec.$^{-1}$)
1	55°	0·0024005	0·00009602	13·44 ± 0·672
2	,,	,,	0·00024005	12·79 ± 0·256
3	,,	,,	0·0009602	12·80 ± 0·140
4	,,	,,	0·0024005	7·34 ± 0·450
5	,,	,,	0·009602	3·58 ± 0·276
6	45	0·002429	0·00009716	4·67 ± 0·374
7	,,	,,	0·0002429	4·07 ± 0·326
8	,,	,,	0·0009716	3·47 ± 0·243
9	,,	,,	0·002429	2·86 ± 0·162
10	,,	,,	0·009716	2·04 ± 0·041
11	35	0·002446	0·00009828	2·72 ± 0·109
12	,,	,,	0·0002446	2·32 ± 0·176
13	,,	,,	0·009828	1·46 ± 0·073
14	,,	,,	0·002446	1·28 ± 0·026
15	,,	,,	0·0009828	0·98 ± 0·068
16	25	0·002485	0·00009943	1·23 ± 0·086
17	,,	,,	0·0002485	1·16 ± 0·093
18	,,	,,	0·0009943	0·83 ± 0·029
19	,,	,,	0·002485	0·80 ± 0·021
20	,,	,,	0·009943	0·51 ± 0·036
21	45	0·00009716	0·002429	2·27 ± 0·193
22	,,	0·0002429	,,	2·44 ± 0·241
23	,,	0·0004858	,,	3·27 ± 0·325
24	,,	0·0007287	,,	3·51 ± 0·316
25	,,	0·0009716	,,	3·47 ± 0·319

TABLE 2

Arrhenius parameters

b (M)	0·0001	0·00025	0·001	0·0025	0·01
E_a (kcal./mole)	16·46 ± 1·19	16·72 ± 1·75	17·22 ± 2·74	15·37 ± 1·55	12·93 ± 0·36
A (sec.$^{-1}$)	$1·25 \times 10^6$	$1·76 \times 10^6$	$3·87 \times 10^6$	$1·28 \times 10^5$	$0·15 \times 10^4$

The values of activation energy (kcal./mole) and frequency factor (sec.$^{-1}$) are given in Table 2. The data obtained indicate a unimolecular mechanism. However, to establish a mechanism for the reactions under consideration, more kinetic data from similar systems are needed.

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