235. *Iodine Complexes in Inert Solvents. Part IX.* The Reaction between Solid Sodium Hydroxide and Iodine dissolved in Inert Solvents.*

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Quantitative data are given for the slow decoloration of iodine solutions in contact with solid sodium hydroxide. Carbon tetrachloride, cyclohexane, and n-heptane, which do not react with iodine or sodium hydroxide, were the solvents used. Empirical relations which describe the data are given.

THE violet colour of iodine in contact with pellets of sodium hydroxide in inert solvents gradually disappears during several days. The pellets become pale brown within 2 hours of their addition to the iodine solutions, and they slowly swell to at least twice their initial volume. Absorption-spectra measurements showed that molecular iodine and solid sodium hydroxide do not themselves react with the inert solvents used. We now report a quantitative study of the reactions involved.

EXPERIMENTAL

Fisher Scientific Spectroanalysed Grade carbon tetrachloride, n-heptane, and cyclohexane, Fisher Scientific Certified Resublimed iodine, and Fisher Scientific Anhydrous diethyl ether were all used without further purification. They were shown not to contain detectable amounts of water. Certified Reagent Grade Electrolytic sodium hydroxide pellets, supplied by Fisher Scientific Company, and taken from four freshly opened bottles, were placed in a vacuum-desiccator (10^{-3} mm. Hg) for several hours, then stored in the pure solvent (previously saturated with dry nitrogen) of the system in which they were to be used. Sets of sample solutions were made by diluting measured portions of standard iodine-inert solvent solutions with the appropriate pure solvent to 50 or 100 ml. in volumetric flasks fitted with ground-glass stoppers.

Absorption spectra in the ultraviolet and visible region for each sample were measured against the appropriate pure inert solvent with a calibrated [1] Beckman DU Spectrophotometer. The samples were stored at set temperatures in the range −5 to 45°. The sodium hydroxide pellets were added to the temperature-equilibrated samples and the spectra were measured again before the fifth hour after addition of the pellets, and at stated times during the next week or two. In addition, the absorption spectra of a sample containing no sodium hydroxide, and that of solvent in contact with sodium hydroxide, were measured at the same times. Care was taken to minimize the loss of solution in filling and emptying the quartz spectrophotometer cells. Such losses could easily be kept under 1% of the original volume.

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* Part VIII, de Maine and Peone, *J. Mol. Spectroscopy*, 1960, **4**, 262.

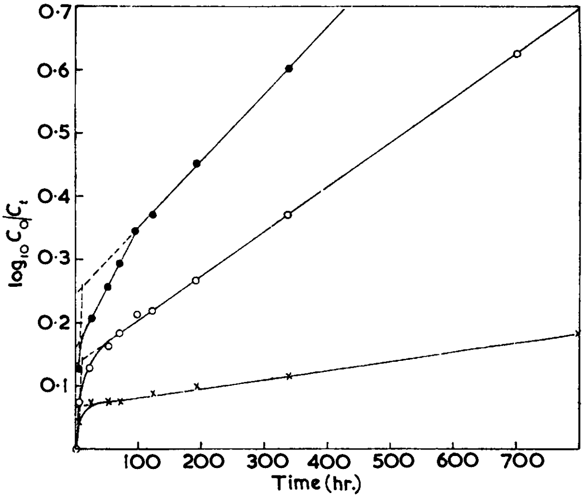
[1] de Maine, *J. Chem. Phys.*, 1957, **26**, 1192.

RESULTS AND DISCUSSION

In separate experiments it was shown that the decoloration of iodine solutions in contact with solid sodium hydroxide is not due to any separate reaction between the iodine or sodium hydroxide and the solvent.

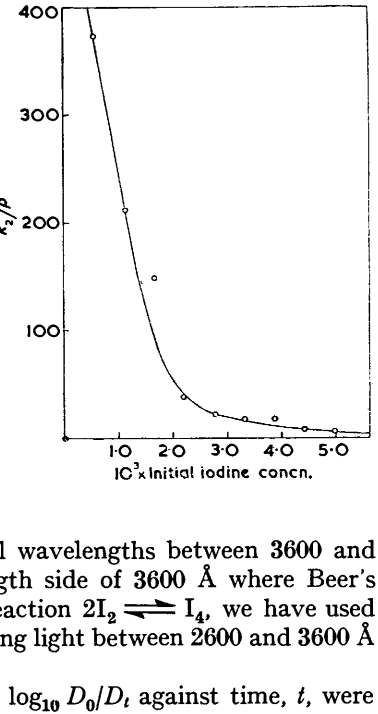
For the long-wavelength side of 3600 Å (the region where Beer's law is normally obeyed by iodine-inert solvent solutions) the ratio D_0/D_t (D_0 and D_t are optical densities measured at the same wavelength for a solution before addition of pellets and at t hours after the addition, respectively) will be independent of wavelength only if no new absorbing species pass into the solution during time t. In the present work D_0/D_t values at different times are constant (maximum deviation less than 2%) for all wavelengths between 3600 and 7500 Å. For the spectral region to the short-wavelength side of 3600 Å where Beer's law is not normally obeyed because of the reversible reaction $2I_2 \rightleftharpoons I_4$, we have used published data [2-4] to confirm that no new species absorbing light between 2600 and 3600 Å passes into the solution.

FIG. 1. *Plots of* $\log_{10}(C_0/C_t) \equiv (D_0/D_t)$ *against time (hr.) for carbon tetrachloride–iodine solutions in contact with solid sodium hydroxide at 21°.*



The initial iodine concentration (mole/l.) and number of sodium hydroxide pellets in a 100 *ml. flask of solution are as follows:* ●, 3·319 × 10^{-3}, 3; ○, 2·766 × 10^{-3}, 2; ×, 4·425 × 10^{-3}, 2.

FIG. 2. *Plot of* k_2/P *against initial iodine concentration for iodine–carbon tetrachloride solutions in contact with solid sodium hydroxide at 21°. [k_2 is defined by equation (1) and P is the number of moles of iodine required to saturate unit absorbing surface of sodium hydroxide pellet.]*



For 53 of the 71 separate solutions studied, plots of $\log_{10} D_0/D_t$ against time, t, were linear after an interval of 8 hours. For the remaining solutions such plots yielded two intersecting straight lines. The time of these changes in slope corresponded to spontaneous fragmentation of one of the sodium hydroxide pellets in contact with the solution. Fig. 1 shows plots of both types.

If the decoloration mechanism is: I_2 in solution $\xrightarrow{k_1}$ I_2 adsorbed on to NaOH surface $\xrightarrow{k_2}$ I_2 transported into the solid sodium hydroxide, with $k_1 \ggg k_2$, two separate cases

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[2] de Maine, *J. Chem. Phys.*, 1956, **24**, 1091; *Canad. J. Chem.*, 1957, **35**, 573.

[3] de Maine, de Maine, and McAlonie, *J. Mol. Spectroscopy*, 1960, **4**, 271.

[4] Keefer and Allen, *J. Chem. Phys.*, 1956, **25**, 1059.

can be identified. During an initial period when adsorption predominates, decoloration can be described by the equation:

$$-10^{-3}V(\mathrm{d}C_t/\mathrm{d}t) = k_1(S - \Delta S_t)C_t \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

where C_t is the iodine concentration (in moles/l.) in a solution of volume V c.c. standing over solid sodium hydroxide at time t. S and $(S - \Delta S_t)$ are the effective molecular surfaces at times zero and t respectively. If $M(=PS)$ is the number of moles of iodine required to saturate the surface, equation (1) can be written thus:

$$-10^{-3}V(\mathrm{d}C_t/\mathrm{d}t) = k_1C_t[M - 10^{-3}V(C_0 - C_t)]/P \quad . \; . \; . \; . \quad (2)$$

where C_0 is the iodine concentration (moles/l.) before addition of the pellets. No assumptions are made as to the molecular depth of the adsorbed layers. Integration of equation (2) yields

$$k_1/P = \frac{V}{t(VC_0 - 1000M)} \ln \frac{1000MD_t}{1000MD_0 - VD_0(C_0 - C_t)} \quad . \; . \; . \quad (3)$$

where $D_t/D_0 = C_t/C_0$. Equation (3) can be solved for k_1/P with values for M obtained by graphical solution of equation (4).

When the adsorption reaction is complete, the rate of decoloration is described exactly by equation (5), of which the integrated form is (4):

$$\ln C_0/C_t = \ln D_0/D_t = \frac{1000}{V} k_2St + \ln \frac{C_0}{C_0 - 1000M/V} \quad . \; . \; . \quad (4)$$

Equation (4) may also be derived from the rate equation

$$-(V/1000)\,\mathrm{d}C_t/\mathrm{d}t = k_2SC_t \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

A plot of $\log_{10} D_0/D_t$ against time (greater than 40 hr.) would be linear with slope equal to $1000Sk_2/2{\cdot}304V$ and one intercept $\log_{10}[C_0/(C_0 - 1000M/V)]$. Since V and C_0 are known, M may be calculated exactly; k_2/P can be obtained by dividing M into the slope multiplied by $2{\cdot}304V/1000$. The specific rate constants for the adsorption process (k_1/P) have been obtained by solving equation (3) with the values for M obtained by the method already given.

TABLE 1. *Values for* k_2/P *in carbon tetrachloride at* 8° *in systems containing iodine and sodium hydroxide pellets.*

$1000C_0$ (mole/l.)	No. of NaOH pellets	k_2/P	
1·241	1	16·6	Average 14·5
1·241	2	12·9	
1·241	2	14·1	
3·102	2	1·03	Average 1·11
3·102	2	1·12	
3·102	1	1·17	
8·686	2	0·30	Average 0·40
8·686	2	0·50	
12·41	1	0·33	Average 0·29
12·41	2	0·22	
12·41	3	0·36	
12·41	4	0·23	
12·41	3	0·30	
12·41	1	0·27	

Data for the 53 samples which yielded straight-line plots for $\ln D_0/D_t$ against time after 8 hr. fit equation (5). The quantity k_2/P, which describes the second reaction, is independent of the molecular surface, S, of the solid hydroxide (Table 1) but is a function of the initial molecular iodine concentration (Fig. 1). The quantity, k_1/P, which describes the irreversible adsorption of molecular iodine on to the surface of the solid material, is independent of the molecular surface, S, the initial iodine concentration, and the temperature (to a first approximation) (Table 2). Our calculations with data for carbon tetrachloride, n-heptane, and cyclohexane suggest that k_2/P and k_1/P are both independent of the nature of the solvent.

Analyses of the swollen pellets at the end of each experiment indicated that most of the absorbed material is actually present as molecular iodine. Thus the second reaction, which predominates after the eighth hour (see equation 5) may well describe the transportation of molecular iodine from the solution or the interface to inside the solid material. However, no mathematical relation between k_2/P and the initial iodine concentration could be found. Thus a complete examination in terms of known diffusion equations cannot be reported.

TABLE 2. *Values for* k_1/P, *from data for a time of* 5 *hr. and at the temperatures indicated.*

$1000C_0$ (mole/l.)	No. of pellets	Temp.	$10{,}000M$ (mole)	k_1/P	
1·111	3	2°	0·269	136·0	Average 121·0
1·090	1	2	0·112	114·5	
1·090	2	2	0·252	117·4	
1·090	3	2	0·304	117·1	
1·106	2	21	0·493	110·7	Average 95·0
1·659	3	21	0·961	93·7	
2·212	1	21	0·518	94·0	
2·766	2	21	0·729	75·7	
3·319	3	21	1·017	125·0	
3·872	1	21	0·430	77·4	
1·569	4	40	0·656	82·9	Average 96·0
1·678	2	40	0·292	98·1	
1·678	4	40	0·846	74·1	
1·678	8	40	1·122	127·4	

The irreversibility of the first step cannot be tested because M is approximately 2×10^{-5} mole per pellet while the concentration of the surrounding liquid is at least 10^{-3} mole/l. However, the consistency of the mathematical analysis clearly shows that a desorption process, if present, must be negligible in comparison with the adsorption process.

A search for alternative models to describe these data was unsuccessful.

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