

Although this is the desired form of the rate expression, this particular mechanism may be ruled out by the change in  $pH$  which occurs during the loss of optical activity. If the loss of optical activity is accompanied by dissociation as it is here, then it seems more probable that an alternative mechanism will be more satisfactory since here the dissociation and racemization are probably *concurrent* processes.

Three additional mechanisms can be invoked which are consistent with the information which is presently on hand for this system. The first would be merely a reaction in which the racemization process of the free acid mentioned above is a dissociative one which results in the release of ligand to the solution. The second is one in which a rate-determining attack by a hydronium ion produces a seven-coördinate  $sp^3d^3$  intermediate which subsequently undergoes rapid dissociation. Arsenic(V) has empty  $d$  orbitals of the same energy as those involved in the octahedral hybridization. This would lead to an intermediate with the  $ZrF_7^{-3}$  structure.<sup>13</sup> A *trans* attack by  $H_3O^+$  on the parent complex will then lead to racemization by loss of  $C_6H_4(OH)O^-$  and a proton. The proton simultaneously or subsequently is taken up by  $C_6H_4(OH)O^-$  to form  $C_6H_4(OH)_2$ . Following this the complex breaks up completely at a rate more rapid than this initial step. This mechanism will also yield the rate expression found. If the complex only loses one molecule of catechol in the racemization, the product with two chelated catechols may or may not be of sufficient stability to be isolated. The third possible mechanism is one in which the rate-determining step involves the transfer of a proton from hydronium ion to one of the coördinated catechol chelate oxygens. The resulting complex in which two catechols are coördinated through a single oxygen atom then can racemize readily by rearrangement to a symmetrical configuration more readily attacked by protons than the initial complex. The catechols then all leave the arsenic at some rate faster than this rate of rearrangement.

The rather large entropy of activation observed

here demands some comment. This large positive value indicates that the constituents of the activated complex enjoy a greater degree of freedom in the activated state than they do before forming it. Such might be the result of a very considerable loosening of the bonds in the activated complex. The value observed is close to the entropies of activation observed<sup>13</sup> for the racemization of  $Fe(o-phen)_3^{+2}$ . In the case of the  $Fe(II)$  complexes however, this large entropy of activation is explained in terms of crystal field theory, *viz.*, the higher energy, spin-free state of the complex which has larger ion-ligand distances and weaker bonding.

It is of some interest to compare the results of this study with the only other comparable study of an octahedral complex of a non-transition element: that of Dhar, Doron and Kirschner<sup>18</sup> on  $l(-)[Si(acac)_3]Cl$ . In this case the rate of racemization is equal to the rate of aquation and both are *independent* of the  $pH$  below a  $pH$  of 9.25. Above this  $pH$ , a rapid alkaline hydrolysis occurs. Thus there is every reason to believe that the detailed mechanisms of these two processes are different. It should also be noted that the racemization of the silicon complex involves an irreversible dissociation in which the acetylacetonate groups are all split off. Furthermore, the silicon complex cannot be formed in aqueous solution from its constituents. In the case of the arsenic(V) complex this reaction is a reversible one, although slowly so, and appreciable amounts of the complex can be obtained if the concentrations of the constituents are increased as in the preparative method used.

We wish to acknowledge, with thanks, the assistance of Mr. John Breinig and Mr. David Vickroy in carrying out the polarimetric studies. We also wish to thank Drs. K. K. Innes, L. Cunningham, R. Lageman and R. E. Rummel for loan of or assistance with apparatus.

This study was supported by a grant from the U.S. Atomic Energy Commission, AT-(40-1)-2576.

(18) S. K. Dhar, V. Doron and S. Kirschner, *J. Am. Chem. Soc.*, **81**, 6372 (1959).

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## Iodine Atom Combination in Hexamethylbenzene-Carbon Tetrachloride Solutions. The Iodine Atom-Hexamethylbenzene Complex

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RECEIVED DECEMBER 17, 1960

Kinetic studies have been made spectrophotometrically following the flash photolysis of  $I_2$  in hexamethylbenzene-carbon tetrachloride solutions at room temperature. The second order rate constant for the formation of  $I_2$  ( $7.9 \times 10^9$  l. mole<sup>-1</sup> sec.<sup>-1</sup>) is obtained from data taken at 489  $m\mu$ , where observed absorbance changes are due to changes in  $I_2$  concentration alone. By combining these data with data taken at 605 or 646  $m\mu$  (where most of the change in absorbance is due to the iodine atom-hexamethylbenzene charge-transfer complex) at different hexamethylbenzene concentrations, an equilibrium constant for the complex of *ca.* 2.7 l. mole<sup>-1</sup> is estimated. Observed kinetics at 605 and 646  $m\mu$  are explained.

### Introduction

The formation of a transient charge-transfer complex involving an iodine atom and an aromatic molecule following the flash photolysis of iodine in

several pure aromatic solvents has been demonstrated.<sup>1,2</sup> In all systems studied the  $I_2$  and com-

- (1) S. J. Rand and R. L. Strong, *J. Am. Chem. Soc.*, **82**, 5 (1960).
- (2) R. L. Strong, S. J. Rand and J. A. Britt, *ibid.*, **82**, 5053 (1960).

plex charge-transfer spectra overlap in the visible region. Relative molar extinction coefficients ( $\epsilon_c/k$ , where  $\epsilon_c$  is the molar extinction coefficient of the complex and  $k$  is the second-order combination rate constant) were calculated for a given solvent by assuming that changes in transmittancy at all wave lengths studied resulting from the change in  $I_2$  concentration following the flash were negligible compared to those due to charge-transfer absorption by the complex. Long wave length shifts in the charge-transfer absorption maxima ( $\lambda_{\max}$ ) relative to the maximum of benzene (in e.v.) with increasing methylation of the donor molecule were approximately the same as those for comparable  $I_2$ ,  $ICl$ , and  $Br_2$  molecular complexes.<sup>2</sup>

On this basis, maximum shift for the methylated benzene series should occur when hexamethylbenzene is the donor molecule, with  $\lambda_{\max}$  ca. 770  $m\mu$ , since  $\lambda_{\max}$  for the corresponding  $I_2$  complex is 371  $m\mu$ .<sup>3</sup> Although 770  $m\mu$  is considerably above the upper wave length limit for which reliable data can be obtained with the flash apparatus used, it was presumed that this shift might provide sufficient separation of the two visible spectra to permit an estimation of the absolute rate of formation of  $I_2$  by atom combination from measurements on the  $I_2$  absorption spectrum alone.

In this paper are presented the results of this investigation at 489  $m\mu$  for various hexamethylbenzene concentrations in carbon tetrachloride. Also given are results obtained at 605 and 646  $m\mu$ , where most of the absorbance change is due to the complex (although below  $\lambda_{\max}$ ). Using these spectrophotometric data from the two spectral regions, an equilibrium constant for the complex is estimated by a modification of the method of Benesi and Hildebrand<sup>4</sup> for the treatment of complexes involving molecular halogens.

### Experimental

The spectrophotometric flash photolysis apparatus and techniques used in this work for obtaining rapid changes in transmittancy as a function of time at a single wave length have been described.<sup>1</sup> Characteristics of the three Bausch and Lomb interference filters used are given in ref. 2; as in that work, each cell was filled in air and was completely surrounded with a Wratten K2 filter to limit absorbed radiation to wave lengths greater than approximately 470  $m\mu$ .

Baker and Adamson Reagent carbon tetrachloride was purified by adding to it a small amount of chlorine and illuminating in a Pyrex bottle for at least 24 hr. with a 200-watt tungsten lamp. Excess chlorine was washed out with 0.02  $M$   $Na_2SO_3$ , and the  $CCl_4$  was washed three times with distilled water and distilled twice over  $P_2O_5$  through a 24-inch Vigreux column, only the middle fraction finally being used. Fisher resublimed iodine and Eastman highest purity hexamethylbenzene were used without further purification. There was no dark reaction between the iodine and hexamethylbenzene, but (as reported below) a small amount of photochemical reaction occurred at each flash. No attempt was made to identify the products of this reaction.

Various stock iodine solutions were prepared at different times by dissolving a weighed amount of iodine in a small amount of carbon tetrachloride and making up to volume in a calibrated 100-ml. volumetric flask. A 0.30-ml. aliquot of this stock solution was added with a calibrated pipet to a known volume of a given hexamethylbenzene-carbon tetrachloride solution (usually 100 ml.) to make up the final solution. Spectra of all solutions were taken with a Beck-

man Model DU Spectrophotometer from 340 to 605  $m\mu$  before and after each series of flash experiments.

### Results

The changes in transmittancy as a function of time following the flash photolysis of the iodine in carbon tetrachloride solutions of hexamethylbenzene (from 0.062 to 0.434  $M$ , a concentration slightly less than the solubility of hexamethylbenzene in  $CCl_4$  at room temperature) were measured at 489, 605 and 646  $m\mu$ . As expected, at 489  $m\mu$  there was a transient increase in transmittancy after the flash corresponding to a decrease in molecular iodine concentration, whereas at each of the two higher wave lengths there was a decrease in transmittancy, representative of the formation of a charge-transfer spectrum. In all cases the return of the absorbance to approximately its value prior to the flash was kinetically second order, as shown by consistent linear plots of the reciprocal of the change in absorbance,  $1/\Delta A$  ( $= -2.3 I/\Delta I$  for small changes in transmittancy,<sup>1</sup> where  $I$  is the transmitted light intensity) against time over at least a fivefold change in  $A$ . (Since there was a slight amount of photochemical reaction—ca. 0.02% per flash—the oscilloscope trace failed to return exactly to the original base line on oscillograms taken at 489  $m\mu$ . This relatively small amount of "undershoot," corresponding to the permanent change in  $I_2$  concentration, was measured at long times and subtracted from all oscilloscope deflection values on the assumption that most of the photochemical reaction occurred rapidly during the period the flash lamp was the most intense, and therefore in the region that scattered light prevented measurements being taken.)

Assuming that the iodine atom-hexamethylbenzene complex,  $DI$ , does not absorb at 489  $m\mu$ , the change in absorbance at this wave length,  $\Delta A^0$ , is

$$\Delta A^0 = \epsilon_{I_2}^0 d \Delta [I_2] = -1/2 \epsilon_{I_2}^0 d [I]_{\text{total}} \quad (1)$$

where  $d$  is the absorbing path length,  $\epsilon_{I_2}^0$  is the molar extinction coefficient of  $I_2$  at 489  $m\mu$ , and  $[I]_{\text{total}}$  ( $= -2\Delta [I_2]$ ) is the total iodine atom concentration—either as free iodine atoms, or complexed with hexamethylbenzene. (There is considerable overlapping of the  $I_2$  and hexamethylbenzene- $I_2$  charge-transfer spectra at 489  $m\mu$ , so that  $\epsilon_{I_2}^0$  is a function of both hexamethylbenzene and iodine concentrations. It was calculated in this work for each hexamethylbenzene concentration used; since the actual further change in  $I_2$  concentration after the scattered light from the flash has decayed to a negligible value is small,<sup>1</sup> the assumption that  $\epsilon_{I_2}^0$  is constant over this range is valid.) If it is further assumed that the rate of formation of  $I_2$  is the same regardless of the form of the iodine atoms (*i.e.*, either as  $I$  or  $DI$ ; this assumption is discussed below), then



$$2 \frac{d[I_2]}{dt} = - \frac{d[I]_{\text{total}}}{dt} = 2k[I]_{\text{total}}^2 \quad (3)$$

and the rate constant,  $k$ , can be calculated from the linear second order plots of  $1/\Delta A^0$  vs. time.

(3) M. Tamres, D. R. Virzi and S. Searles, *J. Am. Chem. Soc.*, **75**, 4358 (1953).

(4) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

TABLE I  
RATES OF COMBINATION AND ABSORBANCE DATA FOR  
IODINE ATOMS IN HEXAMETHYLBENZENE-CARBON TETRA-  
CHLORIDE SOLUTIONS AT ROOM TEMPERATURE

[D] (moles/ l.)	[I <sub>2</sub> ] × 10 <sup>5</sup> (moles/ l.)	k × 10 <sup>-9</sup> (l. mole <sup>-1</sup> sec. <sup>-1</sup> )	k <sub>obsd.</sub> × 10 <sup>-6</sup> (sec. <sup>-1</sup> )		-ΔA <sup>0</sup> × 10 <sup>4</sup> at		ΔA <sub>λ</sub> × 10 <sup>3</sup> at	
			605 mμ	646 mμ	t = 250 μsec.	t = 250 μsec. 605 mμ	605 mμ	646 mμ
0.434	2.8	7.6	1.9	1.7	9.03	1.31	1.47	
.434	3.0	7.0	1.6	2.2	10.4	1.72	1.46	
.434	2.7	6.6	1.5	1.6	9.87	1.52	1.44	
.372	3.7	6.2	1.9	1.7	9.77	1.45	1.71	
.310	3.3	7.1	1.8	1.7	8.70	1.42	1.59	
.310	3.7	9.0	2.4	1.8	9.19	1.40	1.88	
.248	2.7	8.6	3.3	2.6	8.51	1.01	1.04	
.186	3.3	10.1	3.1	3.1	7.50	0.88	0.81	
.186	3.7	7.8	3.7	3.2	7.62	.80	.95	
.124	2.7	10.4	4.6	3.3	7.88	.61	.55	
.062	4.1	6.9	5.8	..	9.24	.43	..	

At 605 and 646 mμ, the concentration of the absorbing substance is not known (if in fact it is a single substance), so that the combination rate constant cannot be calculated. However, an observed rate constant,  $k_{\text{obsd.}}$ , defined by

$$-\frac{d\Delta A_{\lambda}}{dt} = k_{\text{obsd.}} (\Delta A_{\lambda})^2 \quad (4)$$

where  $\Delta A_{\lambda}$  is the change in absorbance at either 605 or 646 mμ, can be calculated from the second order plots, as above.

Values of  $k$  and  $k_{\text{obsd.}}$  are summarized in Table I for the seven different hexamethylbenzene concentrations [D] used. Also included are values of  $\Delta A^0$  and  $\Delta A_{\lambda}$  at 250 μsec. after initiation of the flash. Each value represents the average from at least 15 oscillograms of the same cell, with standard deviations approximately ±8%.

### Discussion

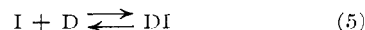
**Rate of Combination at 489 mμ.**—It is evident from the values of  $k$  given in Table I that, although somewhat scattered, they indicate no definite trend as a function of hexamethylbenzene concentration. Therefore, the assumption that the charge-transfer absorption by the DI complex is insignificant at 489 mμ compared to the change in absorbance resulting from the change in I<sub>2</sub> concentration is presumed to be valid. The average value of  $k$  for all concentrations,  $7.9 \times 10^9$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, is in fair agreement with the values obtained for the recombination of iodine in pure carbon tetrachloride in earlier flash work ( $7.2 \times 10^9$  l. mole<sup>-1</sup> sec.<sup>-1</sup><sup>5</sup> and  $5.7 \times 10^9$  l. mole<sup>-1</sup> sec.<sup>-1</sup><sup>6</sup>) and in work involving the combination of mean iodine atom lifetime and quantum yield measurements ( $8.2 \times 10^9$  l. mole<sup>-1</sup> sec.<sup>-1</sup>).<sup>7</sup> Apparently complexing of the atoms has very little effect on the rate of combination to form I<sub>2</sub>, which is in disagreement with the results calculated previously in an indirect manner for the iodine-benzene system<sup>1</sup> and other donor aromatic solvents.<sup>2</sup> A possible explanation for the discrepancy is that the complex is not formed at exactly the same rate that flash light is absorbed, an assumption required in the computer calculation of  $k$  in the other systems.<sup>1</sup>

(5) R. Marshall and N. Davidson, *J. Chem. Phys.*, **21**, 2086 (1953).

(6) R. L. Strong and J. E. Willard, *J. Am. Chem. Soc.*, **79**, 2098 (1957).

(7) H. Rosman and R. M. Noyes, *ibid.*, **80**, 2410 (1958).

**The Equilibrium Constant for the Hexamethylbenzene-Iodine Atom System.**—On the basis that only a 1:1 complex is formed between I atoms and hexamethylbenzene (D), then



It seems probable that the forward and reverse rates contributing to this equilibrium are much faster than the rate of combination to form I<sub>2</sub>, so that the equilibrium constant in concentration units,  $K_c$ , is

$$K_c = \frac{C_c}{C_I C_D} = \frac{C_c}{([I]_{\text{total}} - C_c)([D] - C_c)} \quad (6)$$

where  $C_c$ ,  $C_I$  and  $C_D$  are equilibrium concentrations of the complex, iodine atoms and D, respectively, [D] is the initial concentration of D, and [I]<sub>total</sub> is the total concentration of iodine atoms not present as I<sub>2</sub>. Assuming that  $C_D \gg \gg C_c$  and therefore constant,<sup>8</sup>  $C_D = [D]$  and

$$K_c = \frac{C_c}{[D]([I]_{\text{total}} - C_c)} = \frac{C_c}{[D](-2\Delta[I_2] - C_c)} \quad (7)$$

where  $\Delta[I_2]$  is the transient change in molecular iodine concentration.

Both DI and (to a lesser extent) I<sub>2</sub> contribute to the absorbance at 605 and 646 mμ. Therefore, the change in absorbance,  $\Delta A_{\lambda}$ , is

$$\Delta A_{\lambda} = \epsilon_{\lambda,c} C_c d + \epsilon_{\lambda,I_2} \Delta[I_2] d \quad (8)$$

and

$$C_c = \frac{\Delta A_{\lambda} - \epsilon_{\lambda,I_2} \Delta[I_2] d}{\epsilon_{\lambda,c} d} \quad (9)$$

In equations 8 and 9,  $\epsilon_{\lambda,c}$  and  $\epsilon_{\lambda,I_2}$  are, respectively, the molar extinction coefficients of DI and I<sub>2</sub> at wave length  $\lambda$ , which is either 605 or 646 mμ. Substituting for  $C_c$  in equation 7 and rearranging gives

$$K_c [D] (\epsilon_{\lambda,I_2} \Delta[I_2] d - \Delta A_{\lambda} - 2\epsilon_{\lambda,c} \Delta[I_2] d) = \Delta A_{\lambda} - \epsilon_{\lambda,I_2} \Delta[I_2] d \quad (10)$$

As discussed above, the fact that  $k$ , the rate of combination measured at 489 mμ, is (approximately) constant indicates that light absorption by DI at this wave length occurs only to a minor extent—if indeed at all—and  $\Delta[I_2]$  is given by rearrangement of equation 1. Substituting this expression into equation 10 and rearranging leads to

$$Y \equiv \frac{2\Delta A^0 [D]}{\epsilon_{\lambda,I_2} \Delta A^0 - \epsilon_{I_2} \Delta A_{\lambda}} = \frac{[D]}{\epsilon_{\lambda,c}} + \frac{1}{K_c \epsilon_{\lambda,c}} \quad (11)$$

This equation is similar in form to that obtained by Scott.<sup>9</sup> The two unknowns,  $\epsilon_{\lambda,c}$  and  $K_c$ , can be obtained from the  $Y$ -intercept and slope of the plot of the left-hand side of equation 11,  $Y$ , against the hexamethylbenzene concentration. Calculated values of  $Y$  at 250 μsec. after initiation of the flash (using  $\Delta A^0$  and  $\Delta A_{\lambda}$  values from Table I) at 605 and 646 mμ, with measured values of  $\epsilon_{I_2}^0$ , at each hexamethylbenzene concentration are given in Table II. In Fig. 1 values of  $Y$  at 605 mμ are plotted vs. [D]; from the slope and  $Y$ -intercept of the best straight line through the points (obtained by least squares analysis of the data) an equilibrium constant of  $K_c = 2.7$  l.

(8) For a critical discussion on the validity of this assumption, see R. S. Drago and N. J. Rose, *ibid.*, **81**, 6141 (1959).

(9) R. L. Scott, *Rec. trav. chim.*, **75**, 787 (1956).

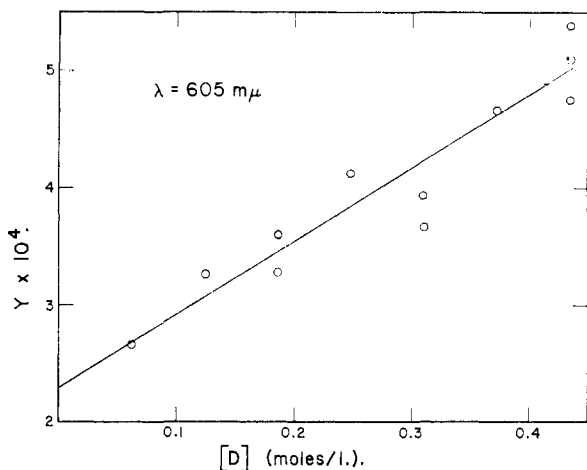


Fig. 1.—Data obtained at 605  $m\mu$  plotted according to equation 11.

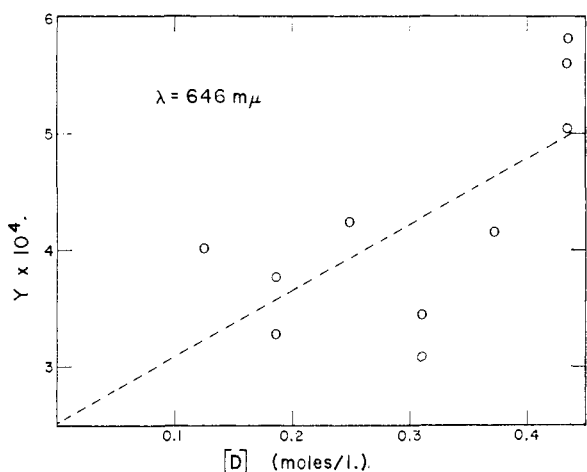


Fig. 2.—Data obtained at 646  $m\mu$  plotted according to equation 11.

mole<sup>-1</sup>, and a molar extinction coefficient of  $\epsilon_{605,c} = 1600$  l. mole<sup>-1</sup> cm.<sup>-1</sup> were obtained.

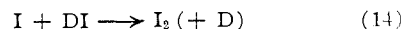
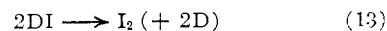
TABLE II			
[D] (moles/l.)	FOR I <sub>2</sub> : $\epsilon_{605} = 122$ $\epsilon_{646} = 50$		Y × 10 <sup>4</sup> (from eq. 11)
	$\epsilon_{12}^0$ (489 $m\mu$ ) (l. mole <sup>-1</sup> cm. <sup>-1</sup> )		
0.434	1027	605 $m\mu$	5.39
		646 $m\mu$	5.04
.372	995	605 $m\mu$	4.75
		646 $m\mu$	5.82
.310	958	605 $m\mu$	5.10
		646 $m\mu$	5.61
.248	916	605 $m\mu$	4.66
		646 $m\mu$	4.15
.186	868	605 $m\mu$	3.67
		646 $m\mu$	3.44
.124	813	605 $m\mu$	3.93
		646 $m\mu$	3.08
.062	747	605 $m\mu$	4.12
		646 $m\mu$	4.24
		605 $m\mu$	3.28
		646 $m\mu$	3.77
		605 $m\mu$	3.63
		646 $m\mu$	3.28
		605 $m\mu$	3.27
		646 $m\mu$	4.02

The data at 646  $m\mu$ , plotted in Fig. 2, are much more scattered than those at 605  $m\mu$ —so much so that the least squares fit (dotted line, which gives  $K_c = 2.2$  l. mole<sup>-1</sup> and  $\epsilon_{646,c} = 1800$  l. mole<sup>-1</sup> cm.<sup>-1</sup>) is probably unjustified. This value of  $\epsilon_{646,c}$  relative to that at 605  $m\mu$  is, however, in agreement with the assumption made above that the I atom-hexamethylbenzene charge-transfer

maximum should be at a still higher wave length. These large experimental deviations at 646  $m\mu$  are probably due to the relatively small oscilloscope deflections and large noise-to-signal ratios resulting from the lower sensitivity of the 931-A photo-multiplier tube to this wave length.

The value for  $K_c$  is greater than that for the comparable I<sub>2</sub>-hexamethylbenzene complex<sup>3,3</sup> (1.5 l. mole<sup>-1</sup>), indicative of the stronger acidic nature of the iodine atom relative to I<sub>2</sub>. The difference between the two is not large though, certainly not of the order of magnitude found for various acceptor halogen and interhalogen molecules with benzene or other aromatic donors,<sup>10-12</sup> or the differences between comparable complexes of I<sub>2</sub> and chloranil.<sup>13</sup> This is in marked contrast to the fact that there is a large shift in  $\lambda_{max}$  from the ultraviolet region for I<sub>2</sub> to the visible region for each iodine atom-aromatic complex<sup>2</sup> (of the order of 300  $m\mu$ ), whereas shifts for other quite different acceptor molecules are generally less than 20  $m\mu$ .<sup>14</sup> Indeed, some acceptors apparently give more stable complexes than I<sub>2</sub> but shift  $\lambda_{max}$  towards shorter wave lengths (for example, ICl with various polyalkylbenzenes<sup>12</sup>).

**Effect of Hexamethylbenzene Concentration on  $k_{obsd}$ .**—Combination to form molecular iodine can occur by reaction between two I atoms, between two DI complexes or between an I atom and a DI complex



where I<sub>2</sub> represents total molecular iodine—either as free I<sub>2</sub> or as the charge-transfer complex with the hexamethylbenzene. Undoubtedly the rate constants for the individual steps are different, for these presumably are diffusion-controlled<sup>7</sup> and therefore will be a function of the encounter diameters of the reacting species. However, the differences are probably not great, and for ease of calculation the individual rate constants are assumed—as in the section above—to be equal ( $k$ ).

Thus

$$-\frac{dC_c}{dt} = 2k(C_c^2 + C_c C_I) = k_a C_c^2 \quad (15)$$

where

$$k_a = 2k \left( 1 + \frac{1}{K_c [D]} \right) \quad (16)$$

and, as above

$$K_c = \frac{C_c}{C_I [D]} \quad (17)$$

In equation 8,  $\Delta[I_2]$  gives the total I atom concentration at time  $t$  following the flash and equals  $-1/2(C_I + C_c)$ , so that

$$\Delta A \lambda = d[(\epsilon_{\lambda,c} - 1/2\epsilon_{\lambda,I_2})C_c - 1/2\epsilon_{\lambda,I_2} C_I] \quad (18)$$

Combining (17) and (18) leads to

$$\Delta A \lambda = d \left[ \epsilon_{\lambda,c} - 1/2\epsilon_{\lambda,I_2} \left( 1 + \frac{1}{K_c [D]} \right) \right] C_c \quad (19)$$

(10) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **73**, 462 (1951).

(11) M. W. Blake, H. Winston and J. A. Patterson, *ibid.*, **73**, 4437 (1951).

(12) L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952).

(13) J. N. Murrell, *ibid.*, **81**, 5037 (1959).

(14) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

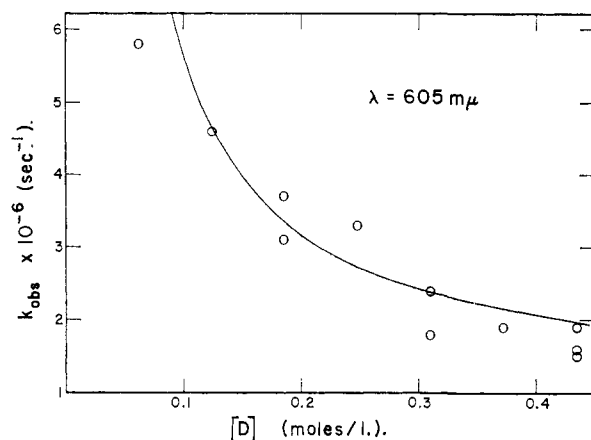


Fig. 3.—Plot of  $k_{\text{obsd.}}$  at 605  $m\mu$  vs. hexamethylbenzene concentration. Open circles represent experimental values; solid line calculated from equation 21.

Differentiation of this expression with respect to time gives

$$\frac{d\Delta A_{\lambda}}{dt} = d \left[ \epsilon_{\lambda, c} - \frac{1}{2} \epsilon_{\lambda, I_2} \left( 1 + \frac{1}{K_c [D]} \right) \right] \frac{dC_c}{dt} \quad (20)$$

which, by equation 4, equals  $-k_{\text{obsd.}} (\Delta A_{\lambda})^2$ .

Thus, by combining equation 20 with the rate of disappearance of the complex (equation 15), the observed rate constant becomes

$$k_{\text{obsd.}} = \frac{2k_c (K_c [D] + 1)}{d [K_c [D] (\epsilon_{\lambda, c} - \frac{1}{2} \epsilon_{\lambda, I_2}) - \frac{1}{2} \epsilon_{\lambda, I_2}]} \quad (21)$$

Values of  $k_{\text{obsd.}}$  calculated from this expression are compared in Figs. 3 and 4 (solid lines) with the experimentally determined values (open circles) at 605 and 646  $m\mu$ , respectively. For the calculations, the more reliable value of  $K_c$  from Fig. 1 (2.7 l. mole<sup>-1</sup>) was used for both wave lengths, although the particular value of  $\epsilon_{\lambda, c}$  used was that determined for the specific wave length.

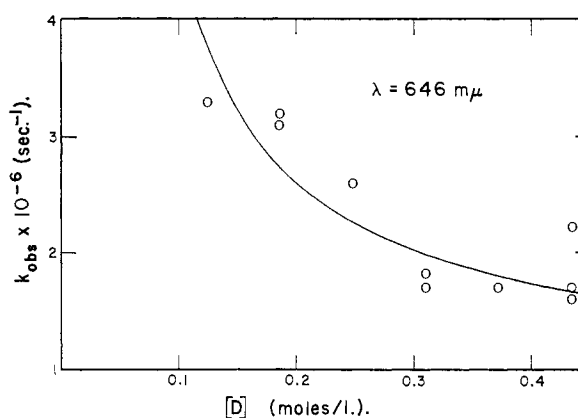


Fig. 4.—Plot of  $k_{\text{obsd.}}$  at 646  $m\mu$  vs. hexamethylbenzene concentration. Open circles represent experimental values; solid line calculated from equation 21.

It is clear that equation 21 correctly gives the observed qualitative behavior of  $k_{\text{obsd.}}$  with varying hexamethylbenzene concentration and appears to deviate badly only at the lowest concentrations of D, where experimental errors are quite large. It is concluded, therefore, that this interpretation in terms of a very rapid attainment of equilibrium between iodine atoms and D molecules to form DI complexes, together with the several simultaneous combination processes leading to  $I_2$ , provides a satisfactory and consistent picture of the observed kinetics. As pointed out, though, the assumption that all of the combination rate constants are the same can only be considered approximate, and more accurate measurements on  $k$  should show deviations from second order kinetics.

**Acknowledgment.**—The authors gratefully acknowledge support by the National Science Foundation through grant No. NSF G-9988.

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## Alumina: Catalyst and Support. IX.<sup>1</sup> The Alumina Catalyzed Dehydration of Alcohols<sup>2,3</sup>

BY HERMAN PINES AND WERNER O. HAAG<sup>4</sup>

RECEIVED DECEMBER 19, 1960

There is no agreement in the literature with regard to the mechanism of catalytic dehydration of alcohols over alumina and not even with respect to the nature of olefinic hydrocarbons. It was demonstrated that the discrepancies result from different catalytic properties of the alumina catalysts used. Alumina catalysts can vary widely in their activity for double bond shift and for skeletal isomerization of olefinic hydrocarbons. These differences also influence the product distribution in the dehydration of alcohols. Dehydration was studied with aluminas having a whole spectrum of isomerization properties. The following alcohols were used: cyclohexanol, 2-butanol, 2-pentanol, 3-pentanol, 3,3-dimethyl-2-butanol (pinacol alcohol). The mechanism of the dehydration and of the accompanying isomerization is discussed.

Alumina is an excellent and widely used catalyst for the dehydration of alcohols.<sup>5</sup> In spite of this

(1) For paper VIII of these series see H. Pines and C. T. Chen, *Proceeding of the 2nd International Congress in Catalysis*, Paris, July 4-9, 1960.

(2) Paper 11 of the series "Dehydration of Alcohols." For paper I, see H. Pines and C. N. Pillai, *J. Am. Chem. Soc.*, **82**, 2401 (1960).

(3) Presented in part before the Division of Colloid Chemistry, American Society Meeting, San Francisco, April 13-18, 1958; and

fact there is no agreement in the literature with regard to the mechanism of this reaction or the nature of the olefinic products. For example, pure before the Gordon Research Conferences in Catalysis, June 23-27, 1958, New London, N. H.

(4) Predoctoral Fellow, Universal Oil Products Company, 1956-1957; Tony Company, Chicago, Illinois 1957-1958.

(5) (a) A. A. Gregorieff, *J. Russ. Phys. Chem. Soc.*, **33**, 173 (1901). (b) V. N. Ipatieff, *ibid.*, **33**, 182 (1901); *Ber.*, **34**, 596, 3579 (1901).