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Kinetics of Formation of the Electron Donor–Acceptor Complex between Iodine and Imidazole in Chlorobutane Solution

By Edward F. Caldin* and John P. Field

University Chemical Laboratory, University of Kent, Canterbury, Kent CT2 7NH

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The kinetics of the formation of the electron donor–acceptor complex between iodine and imidazole in 1-chlorobutane at −64 °C have been investigated by an improved microwave temperature-jump apparatus. The forward rate constant k_f is $(3.3 \pm 0.4) \times 10^9$ $dm^3\ mol^{-1}\ s^{-1}$. This is nearly the same as the diffusion-controlled value k_D calculated from the simple Smoluchowski model for reaction at every encounter between spherical molecules, without geometrical requirements, in a homogeneous fluid ($k_f/k_D = 0.8$).

Molecular complexes of the electron donor–acceptor (or charge-transfer) type[1] between neutral molecules are of special interest for chemical kinetics. In aprotic solvents of low polarity, many of these systems give 1:1 complexes according to the simple scheme

$$A + B \rightleftharpoons C \tag{1}$$

and the equilibria and spectra have been well studied. The structures of a considerable number of these complexes in the crystalline state have been determined by X-ray crystallography[2,3] and the bonding in solution has been studied by far-infrared spectroscopy.[4] The general picture is that the new bond is abnormally long and weak, so that the role of repulsion in the reaction $A + B \rightarrow C$ will be much less than is usual in chemical reactions; while at the same time the complex is easily detected by u.v. or visible spectroscopy, because of the intense absorption of the charge-transfer band. Substituents and solvent can be varied. These systems therefore offer the possibility of learning about the effects of molecular size and shape on reaction rates, with much less interference from other factors than is normal in chemical reactions. Factors influencing diffusion-controlled rates could be investigated.

The formation of these complexes in solution is very rapid, and little has been published on their kinetics. This is no doubt due to the special difficulty of following very fast reactions in non-conducting solutions, when the standard type of temperature-jump apparatus, for instance, cannot be used, because it uses Joule heating to effect the rise in temperature. Dielectric-relaxation measurements of rotational relaxation times have been made for solutions of iodine in benzene and in dioxan,[5] and of tetracyanoethylene in mesitylene and similar systems;[6] they showed that the rate constants for complex formation are very high. Measurements of deuterium quadrupolar relaxation[7] for the complex formation between 1,3,5-trinitrobenzene and various fluorenes in chloroform solution gave rate constants in the range 0.6×10^{10}–1.7×10^{10} $dm^3\ mol^{-1}\ s^{-1}$ at 33 °C. These are comparable with the value calculated for diffusion control (k_D), which according to the simple Smoluchowski model of spherical molecules with uniformly reactive surfaces in a homogeneous viscous fluid is $4\boldsymbol{R}T/\eta$ (where η = viscosity), and in this case has the value 2.05×10^{10} $dm^3\ mol^{-1}\ s^{-1}$.

A study by the microwave temperature-jump technique, which can be used with non-conducting solutions in any polar solvent, on the system tetracyanoethylene + hexamethylbenzene in 1-chlorobutane at −83 °C, gave a rate constant smaller than the corresponding value of k_D by an order of magnitude.[8] This system is one of the most favourable ones from the point of view of the temperature-jump method, as regards its equilibrium constant and enthalpy of reaction, but the measurements were near the limit of the capability of the single-pulse technique then in use. Recent improvements in our microwave temperature-jump apparatus, especially the use of signal-averaging,[9, 10] have greatly improved the sensitivity; together with the use of low-temperature thermostats, they have extended the measurable range to include many more very fast reactions. We have accordingly been able to begin a study of the complexes formed by iodine with organic donor molecules in low-polar solvents such as 1-chlorobutane.[11]

The strong complexes of iodine with tertiary amines are of particular interest. A good deal is known about their structures. In the trimethylamine complex, for instance, the iodine molecule is collinear with the N atom in the solid state;[12] in solution there may well be some flexibility but it seems likely that the geometry of the product is fairly well defined. The N—I distance is longer than a normal covalent bond by *ca.* 20 pm. In solution, the analogous system iodine + triethylamine is easier to handle; in n-heptane the u.v.–visible spectrum shows, besides the absorption due to free iodine, a peak at 414 nm due to the complexed iodine, and an intense 'charge-transfer' peak in the near-u.v.[13] Equilibrium measurements give a good isosbestic point, indicating formation of a 1:1 complex only, and the equilibrium parameters are in the range suitable for temperature-jump experiments ($K = 4.6 \times 10^3$ dm^{-3} mol^{-1} at 25 °C; $\Delta H^{\ominus} = -12$ kcal mol^{-1}). The microwave technique, however, requires a polar solvent; where a low-melting, non-aromatic solvent is needed, as here, 1-chlorobutane is suitable (dielectric constant 7.39 at 20 °C, m.p. −123 °C). In this solvent, unfortunately, the iodine + triethylamine solutions are not stable enough. The analogous iodine + pyridine system is stable in 1-chlorobutane solution, but it is formed too fast for a quantitative study. Imidazole, a stronger base than pyridine, provides a suitable system. The reaction is similar to that with pyridine, but has a higher equilibrium constant, enthalpy change, and change of molar absorbance in the visible region; these lead to measurable absorbance changes in temperature-jumps at *ca.* −65 °C, where the reaction is not too fast to be followed. Solutions are stable for several days. The structure of the complex in the solid state does not appear to have been determined. By analogy with that of other amine–iodine complexes, we might expect a preference for a geometry with N · · · I—I approximately collinear, but since imidazole is a π-donor with an aromatic sextet the structure may be more closely related to that of the benzene–iodine complex, in which there is less steric constraint. A study of a series of substituted imidazoles can be envisaged. (Among these are histamine and histidine, which may be of interest in view of the possible biological importance of charge-transfer complexes.) Our present interest is in the effects of repulsion, desolvation and the geometry of reactants and complex, on the rates of reactions where the activation barrier is low or non-existent.

EXPERIMENTAL AND RESULTS

MATERIALS

Iodine (A.R.) was resublimed twice from KI + KOH. Imidazole and 1-chlorobutane were purified as before.[9]

SPECTRA

Absorbance measurements were made on a Cary 219 spectrophotometer. The visible spectrum of a solution of iodine + imidazole in 1-chlorobutane consists of (*a*) a peak due to free iodine at *ca.* 500 nm and (*b*) a 'shifted-iodine' peak at *ca.* 390 nm due to the iodine species in the complex. A single isosbestic was observed, in agreement with formation of a 1 : 1 complex [eqn (1)], and the variation of the absorbance with concentration gave constant values for the equilibrium constant K. No change in the spectrum occurred during several hours, provided that large concentrations of imidazole were avoided. No anomalies attributable to water, which would produce I_3^-, were observed.[13, 14]

EQUILIBRIUM CONSTANTS

Equilibrium constants were determined from absorbance measurements at 500 nm. The iodine concentration was 4.3×10^{-4} mol dm^{-3}. At each temperature, five different concentrations of imidazole in the range 2×10^{-5}-2×10^{-4} mol dm^{-3} were used, the molar absorbance of the complex being determined by adding excess. The value of K was determined from the expression $K = c/ab$, when a, b and c are, respectively, the concentrations of A, B and C in the solution [eqn (1)], and c is given by $(A-\varepsilon_A a_0)/(\varepsilon_C-\varepsilon_A)$, where A is the observed absorbance and a_0 the formal concentration of A. The range of temperature was 11-38 °C. The results are shown in table 1. The Van't Hoff plot is a good straight line (correlation coefficient 0.999). The slope of the best straight line, determined by a weighted-least-squares computer program, gives $\Delta H^\ominus = -7.4\pm0.45$ kcal mol^{-1}. Extrapolation gives $K = 2.1\times10^5$ dm^3 mol^{-1} at -64 °C.

TABLE 1.—REACTION OF IODINE WITH IMIDAZOLE IN 1-CHLOROBUTANE. EQUILIBRIUM CONSTANT AT VARIOUS TEMPERATURES.

temperature /°C	K/dm^3 mol^{-1}
11.3	1895 ± 75
20.4	1303 ± 20
29.6	847 ± 13
38.2	630 ± 20

$-\Delta G^\ominus = 4.12\pm0.02$ kcal mol^{-1} ($17._2\pm0.1$ kJ mol^{-1}) at 298 K.
$-\Delta H^\ominus = 7.4\pm0.45$ kcal mol^{-1} (31 ± 2 kJ mol^{-1}).
$-\Delta S^\ominus = 11\pm1.5$ cal K^{-1} mol^{-1} (46 ± 6 J K^{-1} mol^{-1}).

RATE CONSTANTS

Rate constants at -64 °C were determined by means of the microwave temperature-jump apparatus and low-temperature thermostat described in the preceding paper.[9] The wavelength of the monitoring light-beam was 400 nm, at which the molar absorbance is 3560 mol dm^{-3} cm^{-1}; it corresponds approximately to $\lambda_{\max}$ for the shifted-iodine peak (390 nm). The temperature-jump produces a decrease of absorbance at this wavelength, and a corresponding increase at a wavelength characteristic of free iodine (500 nm). Five solutions were used (see table 2). The equilibrium concentrations ($\bar{a}$ and $\bar{b}$) at -64 °C were calculated from the extrapolated value of K and corrected for the change in density of the solvent with temperature. Signal-averaging was used, since a single pulse produced a trace with no discernible trend; it was normal to replicate the pulse *ca.* 2000 times (in 100 s) to produce an acceptable trace. All such traces were exponential within experimental error, and the relaxation time τ for each could be determined within $\pm10\%$ by matching with an adjustable exponential curve; 3-4 traces were measured and the average taken. The observed relaxation times were in the range 3-5 μs; they were corrected for the response time of the detector (1.5 μs) by the

TABLE 2.—RELAXATION TIMES FOR THE REACTION OF IODINE WITH IMIDAZOLE IN 1-CHLOROBUTANE AT −64 °C.

$[I_2]$ and [imid] are formal concs in columns 2 and 3, equilibrium concentrations in column 4. τ = mean relaxation time/s.

solution no.	$[I_2]/10^{-4}$ mol dm^{-3}	[imid]/10^{-4} mol dm^{-3}	($[I_2]$+[imid]) at equilibrium /10^{-4} mol dm^{-3}	10^6 τ(obsd)	10^6 τ(corr)
1	2.365	0.953	1.475	3.47	2.07
2	2.365	1.188	1.270	3.60	2.25
3	2.365	1.430	1.07	3.86	2.56
4	2.365	1.672	0.89	4.54	3.43
5	2.365	1.903	0.75	4.94	3.95

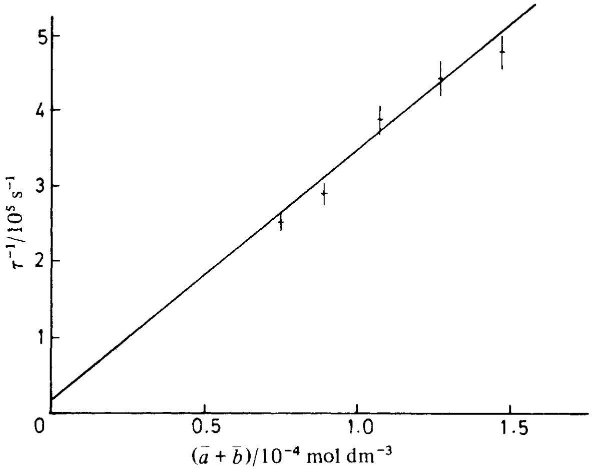

FIG. 1.—Reaction of iodine with imidazole in 1-chlorobutane at −64 °C. Plot of the reciprocal relaxation time (τ^{-1}) against the sum of the equilibrium concentrations of reagents ($\bar{a}+\bar{b}$). The error bars correspond to ±5%.

equation given by Sirs.[15] The overall uncertainty in the corrected values is around ±5%. The results are in table 2.

To obtain the rate constants, we have used the usual equation for a simple process $A+B \rightleftharpoons AB$ with rate constant k_f for the forward reaction and k_b for the back reaction:

$$\tau^{-1} = k_f(\bar{a}+\bar{b})+k_b. \tag{2}$$

The plot, shown in fig. 1, is linear within experimental error (correlation coefficient 0.982). The line is drawn so that the ratio of slope to intercept (k_f/k_b) agrees with the value of K derived from the spectroscopic results; the slope (k_f) is 3.3×10^9 dm^3 mol^{-1} s^{-1} and the intercept (k_b) is 1.6×10^4 s^{-1}. These values agree within experimental error with the values for the best line obtained by a least-squares method: this confirms that our value of K is reasonable.

A few experiments were done with pyridine in place of imidazole, at the same temperature. An increase of absorbance at 400 nm associated with the shifted-iodine peak of the complex, and a corresponding decrease at 500 nm associated with free iodine, were observed. Higher concentrations were needed than with imidazole because of the lower molar absorbance; in consequence the relaxation times were shorter and less accurate. It appeared, however, that the rate constant k_f is in the same region as for imidazole.

DISCUSSION

The equilibrium and kinetic results are in agreement with the simple scheme represented by eqn (1) for the overall process of complex formation. The observed forward rate constant k_f for the formation of the complex is $(3.3 \pm 0.4) \times 10^9$ dm^3 mol^{-1} s^{-1}. This may be compared with the diffusion-controlled value k_D calculated from the Smoluchowski model of reaction at every encounter between spherical molecules, without geometrical requirements, in a homogeneous fluid ($k_D = 4\boldsymbol{R}T/\eta$ where η = viscosity); in l-chlorobutane at -64 °C, $k_D = 4.1 \times 10^9$ dm^3 mol^{-1} s^{-1}. The ratio k_f/k_D is 0.8, remarkably close to unity. This close agreement of k_f with k_D is in contrast with the twelve-fold difference found for the formation of the π–π complex between tetracyanoethylene and hexamethylbenzene in the same solvent[8] (as well as for the formation of the σ-complexes of zinc *meso*-tetraphenylporphyrin with tertiary amines[9]), but is in agreement with the results on the π–π complexes of trinitrobenzene with fluorenes[7]. These comparisons suggest two considerations.

(*a*) If the complex is supposed to have a preferred orientation N···I—I, like the analogous complexes with triethylamine or pyridine,[12] it may appear surprising that the value of k_f is not reduced below k_D by a factor related to the fraction of the surface of the imidazole molecules that constitutes the reaction site (as the treatment of Schmitz and Schurr would suggest[16]). The explanation may be that an encounter in solution lasts (at room temperature) for a time of the order of 10^{-10} s, during which the reactant molecules in the solvent cage have time to rotate perhaps 10 times, and may therefore come into a suitable orientation for reaction. The fraction of reactant pairs that react in an encounter despite restrictive geometrical requirements is thus much larger than the fraction that would react in a single collision, the more so when the temperature is reduced and the viscosity increases. If, alternatively, the charge-transfer interaction involves electron-donation from the π-orbitals of imidazole, the orientational constraint may be much less. In the first case, it is only necessary that the imidazole–solvent 'bond' should be directional (*e.g.* a hydrogen bond[9, 17]), so that the incoming iodine molecule can approach without the need to break it; in the second case, even this condition is unnecessary.

(*b*) The question arises why k_f is an order of magnitude larger for the formation of the iodine–imidazole complex than for that of the π–π TCNE–HMB complex in the same solvent. The agreement of k_f with k_D for the iodine+imidazole reaction suggests not only that the geometrical restrictions are unimportant but also that the energy barrier is negligible. The lower rate for TCNE+HMB was tentatively attributed[8] to an energy barrier of the order of 1 kcal mol^{-1}, which might be due to a need for desolvation of reactants; another possibility is that despite the weakness of the bonding there is some contribution from repulsion. Solvation may well be less for iodine (which is known to have a positive heat of solution in low-polarity solvents) than for TCNE, and for imidazole it may be unimportant, for the reasons given above. Repulsion is less easy to estimate, but calculations[11] suggest that for TCNE systems it is appreciable. It is difficult to come to a more specific conclusion until experiments have been done on both systems at different temperatures and in different solvents, but we may suppose that for iodine+imidazole the repulsion energy is small and the geometrical constraints are overcome by the repeated collisions during an encounter.

Our general conclusion is that the rate constant for the bimolecular complex-formation is strikingly close to that calculated from the simplest model of diffusion control, and suggests that the energy barrier is negligible and also that reorientation of the molecules within the encounter cage is fast enough for a favourable orientation to be reached in the majority of encounters.

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