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Steric and Repeated-collision Effects in Diffusion-controlled Reactions in Solution: Kinetics of Formation of some Iodine Donor–Acceptor Complexes of Sulphur Compounds

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Rates of formation of electron donor–electron acceptor complexes of iodine with some compounds of the general formula R_2CS with iodine ($R_2CS\cdots I{-}I$) in 1-chlorobutane have been determined by means of a microwave temperature-jump apparatus. For each of these reactions, the observed forward rate constant (k_f) is proportional to the theoretical diffusion-controlled value (k_D^*) over a range of temperatures, but somewhat smaller. The values of k_f/k_D^* for the various reactions are approximately inversely proportional to the estimated surface areas of the R_2CS molecules. Assuming that the area of the reactive site is constant, this suggests that k_f/k_D^* is proportional to the fraction of the molecule surface area that is reactive, *i.e.* that k_f is subject to a geometrical steric factor. The observed values of k_f/k_D^* are, however, *ca.* four times larger than would be expected on this basis from molecular models, if one took into account only the frequency with which first-time collisions occur between reactant molecules with the correct orientation. This discrepancy can be removed by taking into account the fact that repeated collisions during an encounter will increase the chance of a successful collision. A hard-sphere model of encounters between molecules with limited reaction sites, reorienting by rotation between collisions, suggests that repeated collisions may contribute to k_f/k_D^* a factor in the region of 4, in line with our experimental results.

Steric effects on reaction rates, *i.e.* effects attributable to the bulk of atoms or groups, may be distinguished as due either to the limited size of the reactive site in a molecule, or to the obstruction by neighbouring atoms of access to the reactive site. The former is a geometric effect,[1–4] and will depend (according to the simplest model) on the fraction of the 'surface area' of each reactant molecule that is occupied by the reaction site, or more accurately on the solid angle over which the reactive site is accessible, on which depends the chance that when the reactant molecules collide they will be correctly oriented for reaction; this will affect the activation entropy but not the activation energy. The latter effect has a quite different origin; if the reactive site on one molecule is crowded by bulky neighbouring atoms which hinder access of the other reactants, the transition state can only be formed if these atoms are moved aside, and the necessary bending of bonds will contribute both to the energy and to the entropy of activation.[5]

We wish to study geometric effects on the kinetics of reactions in solution, in order to put these effects of molecular size and shape on a quantitative basis. There have been a number of theoretical investigations, especially in connection with reactions of large molecules such as proteins, but except for thorough studies of radical recombination reactions by Russian workers[6] little systematic experimental work appears to have been done. In order to study geometric effects in isolation, free from complications due to bond-bending or other bond changes, we are investigating reactions that proceed without activation energy, *i.e.* diffusion-controlled reactions, using the criterion (derived from the Smoluchowski treatment[7,8]) that for such reactions the rate constant $k_D \propto T/\eta$, where η is the viscosity. To avoid strong interactions and large solvation changes, we require neutral reactants of low polarity in low-polarity solvents. To avoid bond-bending we need reactive sites that are not crowded or obstructed by bulky neighbouring groups.

A suitable series of related reactions in which the size of one reactant can be systematically varied is provided by the formation of electron donor–electron acceptor complexes[9] between iodine and thiocarbonyl compounds (R_2CS) such as substituted thioureas and thiones, for which the equilibria and kinetics are in accord with the simple mechanism

$$R_2CS + I_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R_2CS\cdots I_2.$$

The structural formulae of the thio-compounds used are shown in fig. 1. The complexes show an intense absorption ($\varepsilon > 10^4$ dm^3 mol^{-1} cm^{-1}) in the region of 350 nm, which allows the use of low concentrations (*ca.* 10^{-5} mol dm^{-3}). The microwave temperature-jump technique with spectrophotometric detection[10] and signal-averaging is well suited to such systems. The corresponding complex with imidazole has

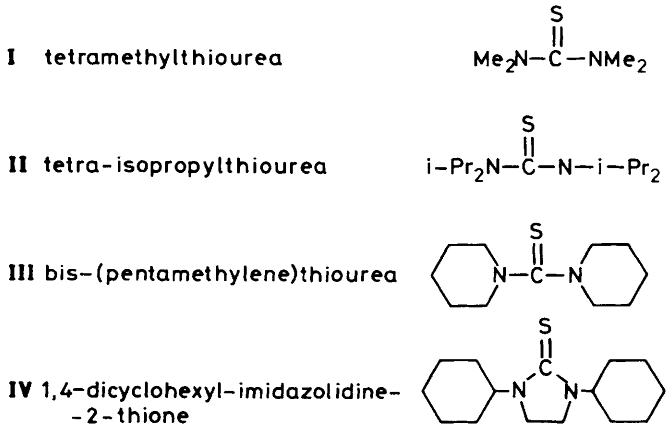

Fig. 1. Thiocompounds used in the present study.

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been shown[11] to have a rate constant at −64 °C, agreeing with an approximate theoretical value for diffusion control ($k_D^* = 4RT/\eta$).

We wish to compare experimental rate constants with values calculated from theoretical models for diffusion-controlled reactions that occur without either geometric or activation constraints. We therefore need a simple expression for the rate constant (k_D) of such reactions. The simplest model, based on that of Smoluchowski,[7,8] envisages spherical reactant molecules, undergoing random diffusive motions in a uniform fluid, and reacting at every encounter. For reactants of equal size, this treatment leads to the well known expression $k_D = 4RT/\eta$. The numerical factor 4 is a consequence of the assumption that the translational diffusion coefficient for each reactant (radius r) is given by the Stokes–Einstein expression for 'slip' conditions, $D^{tr} = k_B T/4\pi\eta r$. It is well known, however, that this expression underestimates D^{tr} for moderate-sized molecules in common solvents; experimental values[12–14] are often in better agreement with $D^{tr} \approx k_B T/3\pi\eta r$, which leads to $k_D \approx 5RT/\eta$. For large solute molecules, however, D^{tr} is nearer the Stokes–Einstein value for 'non-slip' conditions, $D^{tr} = k_B T/6\pi\eta r$, which leads to $k_D = (8/3)RT/\eta$, *ca.* half the preceding value. In presenting our results we have made comparisons with the intermediate value $4RT/\eta$, which we designate as k_D^*. Comparisons with other values can then easily be made.

Experimental and Results

Materials

Tetramethylthiourea was a commercial sample (Aldrich). 1,3-Dicyclohexyl-imidazolidine-2-thione was prepared by thermal decomposition of *N*,*N*′-dicyclohexylethylenediamine dithiocarbonate.[15,16] The other thioureas were prepared from thiophosgene and the corresponding secondary amines.[17] Solids were recrystallised from acetone or methanol, while liquids were purified by low-pressure fractional distillation. Data are summarised in table 1. In all cases mass spectra run at low energy gave peaks corresponding to the parent compound only. Iodine was purified by sublimation. 1-Cholorobutane was purified as previously described.[4]

Table 1. Physical constants for substituted thiocompounds SCR_2

compound[a]	m.pt/°C	b.pt/°C	λ_{max}/nm		ref.
			thiocomp.	complex	
I	78	—	216	333	
II	—	144/3 mm[b]	283	346	17
III	53	154/0.4 mm[b]	268	335	[c]
IV	224–226	—	247	324	15, 16

[a] Compounds are numbered as in fig. 1. [b] mm = pressure at which b.pt measured, in mmHg (1 mmHg = 101 325/760 Pa). [c] This work.

Spectra

Absorption maxima for the various thiocompounds and the charge-transfer bands with iodine are listed in table 1. Spectra were run in 1-chlorobutane in the range 210–500 nm using either a Cary 219 or a Pye-Unicam PU 8800 spectrophotometer. In the cases of compounds I, III and IV, but not II, isosbestic points were observed (I, 248 and 269 nm; III, 265 and 276 nm; IV, 246 and 266 nm). Spectra were stable over several hours, provided that certain makes of glassware were avoided.

Equilibrium Constants

Equilibrium constants, *K*, were determined from absorbance measurements at the maxima of the charge-transfer bands. Values of *K* and the extinction coefficients of the complexes were obtained using a microcomputer-aided iterative procedure and the Lang equation.[18] Thermodynamic quantities were calculated from least-squares fits to the van't Hoff equation, using data obtained for at least four temperatures. Results are listed in table 2.

Rate Constants

The apparatus and methods were essentially as described in earlier papers.[10,11] The microwave temperature-jump apparatus produced 1.5 μs pulses up to 20 times a second. Signal-averaging over 500–1000 pulses was employed; the oscilloscope trace was then exponential after an initial period of a few μs. The relaxation time (τ) for each trace was determined within ±5% by matching with an adjustable exponential curve; 5–10 traces were replicated. Relaxation times below 8 μs were corrected for the response time of the detector by the equation of Sirs.[19] Relaxation times τ were measured for 5–7 reaction solutions for each donor at each temperature. Typical ranges of initial concentrations were, for iodine, $a_0 \approx 10^{-5}$ (0.6–2) mol dm^{-3} for donors, $b_0 \approx 10^{-5}$ (1–4) mol dm^{-3}. Corrections were made for change of solvent volume with temperature. Reproducible results were obtained when the bath temperature was raised and then lowered or *vice versa*. The forward rate constant k_f at each temperature was obtained by using the usual equation for the process $A + B \rightleftharpoons AB$, plotting τ^{-1} against $(\bar{a} + \bar{b} + K^{-1})$; here $\bar{a}$ and $\bar{b}$ are the equilibrium concentrations. The points lay within experimental error on a straight line through the origin, whose slope gave the value of k_f. Measurements were made over the whole temperature range that was usable, given that as the temperature is increased the reaction eventually becomes too fast, while as it is decreased *K* increases and the amplitude of the absorption change eventually becomes too small.

The data on the forward rate constants k_f for each reaction are given in table 3, which also includes values of k_f/k_D^*; in each case this ratio is constant within experimental error over the accessible temperature-range. In table 4 are collected the

Table 2. Thermodynamic data for complexes of iodine with thiocompounds in 1-chlorobutane

donor	*K* (298 K)/10^4 dm^3 mol^{-1}	ε (298 K)/10^4 dm^3 mol^{-1} cm^{-1}	$-\Delta H^0$/kJ mol^{-1}	$-\Delta S^0$/J mol^{-1} K^{-1}
I	5.8 ± 0.06	3.7	52.8 ± 4	85.8 ± 0.4
II	1.57 ± 0.03	2.1	47.8 ± 12	80.0 ± 8
111	13.13 ± 0.10	3.6	59.3 ± 5	100.8 ± 3
IV	2.00 ± 0.05	4.4	35.6 ± 6	36.8 ± 4

Donors are numbered as in fig. 1. *K* = equilibrium constant; ε = molecular absorption. Initial solute concentration ranges: for iodine, $a_0 = 10^{-5}$(2–4) mol dm^{-3}, for donors I, III and IV, $b_0 = 10^{-5}$(1–9) mol dm^{-3}; for II, $b_0 = 10^{-5}$(2–20) mol dm^{-3}. Corrections are made for change of solvent volume with temperature. The correlation coefficient for the Lang plots of ($a_0 b_0$/absorbance) against ($a_0 + b_0$ − absorbance/ε) was usually in the range 0.9998–0.9990, minimum 0.9983. Uncertainties are standard deviations.

Table 3. Determination of rate constants for reactions $I_2 + SCR_2 \rightarrow$ complex in 1-BuCl

donor[a]	T/K	τ^b/μs	$k_f^c/10^9$ dm^3 mol^{-1} s^{-1}	$k_D^{*d}/10^9$ dm^3 mol^{-1} s^{-1}	k_f/k_D^*
I	256.3	16–50	6.00 ± 0.20	12.41	0.48_3
	260.1	15–35	6.44 ± 0.13	13.30	0.48_4
	263.6	12–27	6.80 ± 0.17	14.16	0.48_8
	275.3	8–13	8.02 ± 0.08	17.22	0.46_6
	284.3	3–7	9.70 ± 0.32	19.81	0.49_0
II	246.9	30–60	2.57 ± 0.04	10.35	0.24_0
	252.2	21–40	2.95 ± 0.04	11.48	0.25_7
	257.9	13–25	3.17 ± 0.02	12.78	0.24_8
	262.7	10–21	3.54 ± 0.02	13.93	0.25_4
	267.5	7–13	4.00 ± 0.06	15.14	0.26_4
III	252.9	25–80	4.30 ± 0.18	11.65	0.36_9
	258.0	26–55	4.93 ± 0.11	12.70	0.38_8
	263.7	20–35	5.53 ± 0.13	14.2	0.38_9
	269.1	14–37	6.23 ± 0.08	15.5	0.40_2
	273.8	12–24	6.83 ± 0.16	16.8	0.40_6
IV	253.2	13–35	2.88 ± 0.18	11.71	0.24_6
	257.9	10–21	3.49 ± 0.21	12.78	0.27_3
	266.2	7–14	3.98 ± 0.03	14.81	0.26_9
	271.9	5–8	4.80 ± 0.09	16.30	0.29_4

[a] Donors numbered as in fig. 1. [b] τ = measured relaxation time. [c] k_f = observed forward rate constant, with standard deviation. [d] $k_D^* \equiv 4RT/\eta$.

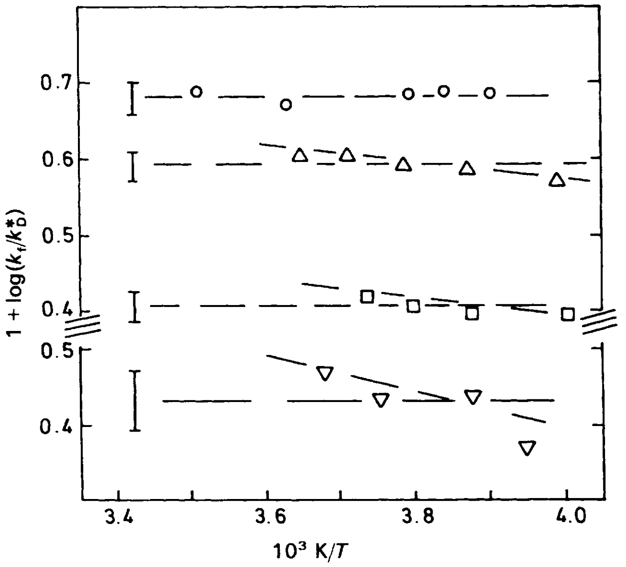

Fig. 2. Plots of [1 + log(k_f/k_D^*)] against T^{-1} for reactions $R_2CS + I_2$ in 1-chlorobutane. Experimental data in table 3. $k_D^* = 4RT/\eta$. The plot for compound IV has been displaced for clarity. ○, I; □, II; △, III; ▽, IV.

mean values of k_f/k_D^* for the various donors, and the extrapolated values of k_f at 25 °C. Arrhenius-type plots of log(k_f/k_D^*) against $1/T$ are shown in fig. 2. With the possible exception of that for the reaction of compound IV, these plots are satisfactorily close to horizontal straight lines, as is shown by the dashed lines for which the slopes correspond to less than 4 kJ mol^{-1} (1 kcal mol^{-1}) in E_A, an amount comparable with $k_B T$. Horizontal lines imply that $k_f \propto k_D^* \propto T/\eta$.

Discussion

Geometric Steric Effect

For each of the reactions investigated, the observed forward rate constant k_f is proportional within experimental error to k_D^*, and therefore to T/η. The simplest interpretation is that the rate of each of these reactions is diffusion-limited and that the energy-barrier is negligible. In each case, however, $k_f < k_D^*$; this may be taken to indicate that there is a geometric steric effect, which will reduce k_f below k_D^* without introducing an activation energy. It is natural to ask whether the ratio k_f/k_D^* can be correlated with the dimensions of the molecules. The simplest parameter to consider is the ratio (ϕ) of the area of the reactive site to that of the molecule as a whole. For the iodine molecule we assume uniform reactivity over the whole surface ($\phi_A = 1$). To estimate ϕ for the donor molecule (ϕ_B), we have to adopt a model. The volume (V) of an organic molecule can be approximately estimated by summing the atomic van der Waals increments listed by Edward;[20] but the area (A) depends also on the shape. In fig. 3 are shown drawings of the structures of (a) tetramethylthiourea and (b) tetraisopropylthiourea, generated by molecular-graphics calculations; these were kindly suggested by Dr M. J. Blandamer and carried out by Mr A. Hakin at the University of Leicester. Inspection of these diagrams, and of space-filling models of other related compounds, led us to adopt the model shown in fig. 3(c), in which the sulphur atom is treated as a projecting hemisphere at the centre of the flat face of a larger hemisphere representing the organic moiety ($R_2C{=}$) of the molecules; it is 'screened' only by this larger hemisphere, not by adjacent protecting groups. The area, a, of the active site is taken as that of the sulphur hemisphere. The values of a and A and of ϕ_B ($= a/A$) for the various donors, calculated with the aid of Edward's data[20] (which give the area of the sulphur hemisphere as 19 Å^2) are given in table 4. (This calculation of the geometrical factor omits consideration of the possibility that a successful collision may require the iodine molecule to approach the donor molecule from a particular direction; this seems unlikely in the present instance.) The values of (k_f/k_D^*)/ϕ_B, also given, are all in the region of 4, the mean value being 3.7. A plot of k_f/k_D^* against ϕ_B is shown in fig. 4. The straight line is drawn with slope 3.7; it must pass through the origin, since there will be no reaction if $\phi_B = 0$. It represents the data fairly well, the only

Table 4. Kinetic data *etc.* for reactions $I_2 + SCR_2$ in 1-BuCl

donor	$A_B{}^a$/Å^2 per molecule	$\phi_B{}^b$	k_f/k_D^{*c}	k_f (298 K)^d/10^9 dm^3 mol^{-1} s^{-1}	(k_f/k_D^*)ϕ_B	$E_A{}^e$/kJ mol^{-1}	log A^e
I	126	0.127	0.480 ± 0.003	11.0	3.8	10.9 ± 0.8	11.95 ± 0.17
III	172	0.092	0.39 ± 0.01	9.0	4.2	12.1 ± 1.7	12.24 ± 0.17
II	202	0.078	0.254 ± 0.005	5.8	3.3	12.6 ± 0.8	11.99 ± 0.35
IV	207	0.077	0.27 ± 0.01	6.2	3.5	13.1 ± 0.8	12.18 ± 0.24

[a] A_B = area of donor molecule, calculated from its volume V_B computed from atomic increments [ref. (20)], according to the model in fig. 3(c). [b] ϕ_B = (area of reactive site)/(total area of molecule) = (area of S hemisphere)/A_B = (19 Å^2)/A_B. [c] Mean of the values of (k_f/k_D^*) at the several temperatures (table 3), with mean deviation. $k_D^* = 4RT/\eta$. [d] Extrapolated value of k_f at 25 °C assuming k_f/k_D has the same value at 25 °C as in preceding column. At this temperature, $\eta = 4.27 \times 10^{-4}$ kg m^{-1} s^{-1} (0.427 cP) and $k_D^* = 23 \times 10^9$ dm^3 mol^{-1} s^{-1}. [e] E_A and A are the Arrhenius parameters. The calculated value corresponding to k_D^* is $(E_A)_D$ = 10.1 kJ mol^{-1}.

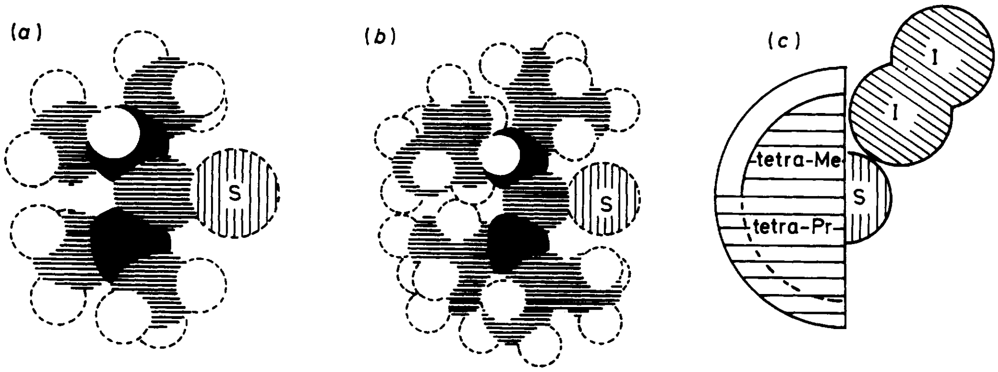

Fig. 3. Molecular models: constructed by molecular graphics for (*a*) tetramethylthiourea and (*b*) tetraisopropylthiourea; (*c*) assumed for the calculation of reactive molecular surface fractions ϕ_B (see text); iodine molecule also shown.

large deviation being +20% for compound III. We conclude that, despite the crudeness of the molecular model, the forward rate constant is approximately proportional to the fraction of the molecular surface occupied by the reactive site, in accordance with what would be expected for a purely geometric steric effect.

It is of interest that the rate constants are almost identical for the reactions of compounds II and IV, which have nearly the same molecular volumes, but differ in that the carbon chains are 'tied back' in IV but not in II. This supports the view that in this series of reactions the variations in k_f are not due to varying shielding of the reactive centre by the adjacent substituents, but are related simply to the size of the non-reactive part of the molecule.

It is theoretically possible that the variations in k_f are attributable to small variations in activation energy; a variation of *ca.* 2 kJ mol^{-1} (0.5 kcal mol^{-1}) would be enough. The picture presented in fig. 2 and 4, while it does not entirely exclude this suggestion, does nevertheless appear to be more coherently interpreted in terms of a geometric steric effect.

Role of repeated Collisions during Encounter

A second conclusion is that k_f/k_D^* is *ca.* 4 times larger than it would be if k_f were determined by the chance of the *first* collision of each encounter being successful, *i.e.* if $k_f/k_D^* = \phi_B$, or in general if $k_f/k_D^* = \phi_A\phi_B$. An explanation may be sought in the fact that a pair of reactant molecules in solution, once they have met, will remain close to each other in an encounter complex for a time long enough to allow a number of collisions between which the molecules may rotate and so reorientate themselves before the next collision, thus increasing the chance of a correctly oriented collision occurring before the molecules separate permanently. The effect on k_f of these repeated collisions will depend on the duration of the encounter, the number of collisions possible before break-up, and the rates of rotation of the molecules, as well as ϕ_A and ϕ_B.

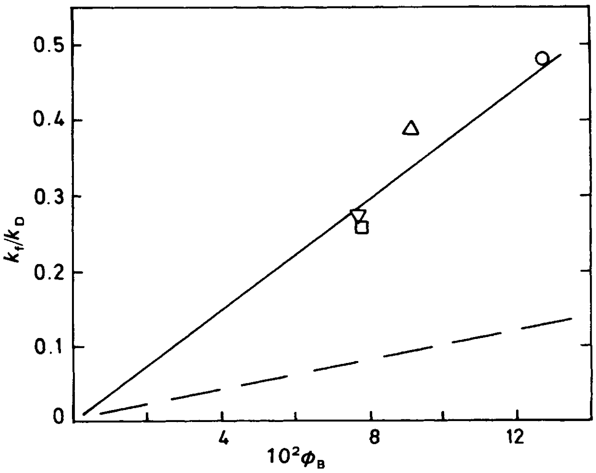

Fig. 4. Plot of k_f/k_D^* against fraction of reactive surface ϕ_B for reactions $R_2CS + I_2$. Thiocompounds numbered as in fig. 1. The full line has slope 3.7. (---) calcd for $k_f/k_D = \phi_B$.

This aspect of diffusion-controlled reactions in solution (which has no parallel in the gas phase) has been the subject of some recent theoretical treatments.[6,21–23] The simplest to apply is that of López-Quintela *et al.*,[23] which adopts a model of hard-sphere reactant molecules undergoing random translational and rotational diffusive motions in a continuous fluid, with diffusion coefficients D^{tr} and D^R. Application of random-walk theory leads to an expression for k_f/k_D in terms of (*a*) the geometric factor $\phi_A\phi_B$, which we will write as Φ; (*b*) the average duration of the encounter in the absence of reaction (τ_{enc}), which is related to D^{tr}, and (*c*) a rotational time-constant τ_{rot} related to D^R. For equal-sized reactant molecules, it may be put in the form:

$$k_f/k_D = \Phi[1 + (\tau_{enc}/\tau_{rot})]. \tag{1}$$

Eqn (1), according to our calculations, may be used as an approximation accurate within 10% for moderate-sized molecules (radius 2–5 Å) for values of Φ up to *ca.* 0.1. If one assumes that D^{tr} and D^R are given by the Stokes–Einstein-type expressions $D^{tr} = k_B T/n\pi\eta r$ and $D^R = k_B T/m\pi\eta r^3$, where m and n are constants to be determined by experiment, one eventually obtains

$$k_f/k_D \approx \Phi[1 + (8/3)(n/m)]. \tag{2}$$

Experimental values suggest $n \approx 3$–4 (*cf.* Introduction) and $m \approx 3$–4 (*cf.* Appendix). Substituting these values in eqn (2), one obtains

$$k_f/k_D^* \approx \Phi(4 \pm 1) \approx 4\Phi. \tag{3}$$

Comparing our results with eqn (3), it appears that the model can account both for the near-linearity of the plot of k_f/k_D^* against ϕ_B, and for the figure of *ca.* 4 for $(k_f/k_D^*)/\phi_B$ derived from its slope.

This simple hard-sphere model indicates that, in calculating the effect of a geometrical steric factor on the rate constant of a diffusion-limited reaction, it is not sufficient to multiply k_D by the geometric factor Φ; it is necessary also to multiply by a numerical factor due to the repeated collisions during encounter. The upper limit for this factor may well be higher than the value *ca.* 4 derived above. For instance, if the critical distance for escape were taken as twice the molecular diameter, it would be *ca.* 7. If the life of the encounter complex is prolonged, *e.g.* by non-specific interactions between the reactants allowing re-orientation but not escape, the factor will again be larger.

An alternative treatment developed by Benesi[21,22] likewise adopts a hard-sphere model but does not envisage a specific picture of the encounter complex. It expresses the effects of rotational diffusion in determining the rate of reorientation of molecules (and hence the average number of times that the reactive spots make contact in an encounter) by means of a parameter Ω, which is a function of the sizes of the molecules and their reactive spots and of their translational and rotational diffusion coefficients (for which Stokes–Einstein expressions are used); it must be calculated by computer. The resulting equation relating $(k_\mathrm{f}/k_\mathrm{D})/\Phi$ to diffusional properties [eqn (6) of ref. (22)] may be approximated within a few per cent, in the range with which we are concerned, by the following equation, which may be compared with eqn (3):

$$k_\mathrm{f}/k_\mathrm{D} \approx \Phi[N_\mathrm{enc}/(1+\Omega)]. \qquad (4)$$

Here Ω includes all the effects of rotational diffusion, while N_enc is the average number of collisions per (non-reactive) encounter, and is calculated as the ratio of the Maxwell rate constant for gas-phase collisions $[\pi(r_\mathrm{A}+r_\mathrm{B})^2(8k_\mathrm{B}T/\pi\mu)^{1/2}$ where μ = reduced mass] to the diffusion-controlled rate constant [commonly approximated by the Smoluchowski expression[7] $k_\mathrm{D} = 4\pi(D_\mathrm{A}+D_\mathrm{B})(r_\mathrm{A}+r_\mathrm{B})$, but given more exactly by Noyes' expression[8]]; thus N_enc depends only on the molecular masses, radii and diffusion coefficients. Benesi has computed Ω as a function of ϕ_A for several reactions of small molecules, including reactions I and II of the present paper and the recombinations of methyl and n-butyl radicals in cyclohexane.[24] The resulting values of $(k_\mathrm{f}/k_\mathrm{D}^*)/\Phi$ for reactions I and II (with the values of Φ that we have assumed) are 2.6 and 3.2 respectively, and so are comparable with our experimental figure of *ca.* 4. For the radical recombination reactions they are in the range 2–7, depending on the values of Φ assumed. All this evidence is compatible with the view that $k_\mathrm{f}/k_\mathrm{D}$ in such reactions is several times larger than would be expected from consideration of the fraction of reactive area alone. Moreover, the calculated values of k_f all agree with the experimental values within a factor of two. Considering the simplicity of the model, and the uncertainties in Φ, the agreement is encouraging. The disadvantage of the treatment is that there is no simple expression for Ω.

Implications for the Study of Geometrical Steric Effects

The general result that the rate constant for a reaction limited both by diffusion and by a geometrical steric factor Φ may be considerably greater than $k_\mathrm{D}\Phi$ has implications for the study both of steric effects and of diffusion control. (*a*) What can be concluded if the observed k_f is diffusion-limited (*i.e.* if $k_\mathrm{f} \propto T/\eta$) but is markedly less than the calculated k_D? Qualitatively, the difference may be attributed to geometric steric limitation of k_f, but the magnitude of the geometrical factor is not given by $\Phi = k_\mathrm{f}/k_\mathrm{D}$; it may be considerably smaller, according to eqn (3). Values of k/k_D not much smaller than unity may conceal an appreciable geometric factor, which may thus escape experimental detection. (*b*) What can be concluded if the observed k_f at some one temperature is not far below $4RT/\eta$, *e.g.* half this value? In the absence of further evidence, such a factor $\frac{1}{2}$ could be attributed either to a geometric steric factor, or to an activation energy of *ca.* 1.6 kJ mol^{-1} (0.4 kcal mol^{-1}). To establish which of these is the more likely, it would be necessary to determine k_f over a range of temperatures. If $k_\mathrm{f} \propto T/\eta$, *i.e.* if the Arrhenius plots for k_f and k_D against $1/T$ are parallel, then the explanation in terms of a geometric factor is to that extent favoured. (*c*) Even if the observed k_f is equal to $4RT/\eta$ within experimental error, it cannot be concluded that reaction occurs in every encounter, since the true encounter rate for many reactions is probably nearer $5RT/\eta$, and there could be either a geometric factor or a small activation energy. Care must be taken, therefore, in interpreting the data when k_f is in the region of $4RT/\eta$.

Comparison with some other Very Fast Reactions

A preliminary search for other series of reactions in simple non-ionic systems for which k_f is proportional to T/η but is dominated by geometrical steric effects has yielded a disappointingly small amount of quantitative evidence, although various examples of individual reactions have been found [ref. (25)–(37)]. The extensive and systematic Russian work[6] on radical recombinations has taken account of geometrical effects, but the rates appear to be much influenced by screening of the reaction sites by bulky neighbouring groups.

Conclusions

For the series of related reactions studied, where the donor molecules have limited (but not crowded) reaction sites and the rate constant appears to be diffusion-limited, the rate constant is approximately proportional to the fraction of reactive surface, as calculated according to simple models of the donor molecules. The rate constants are *ca.* four times larger than would be expected from this geometric factor alone. The discrepancy is resolved by taking into account the repeated collisions that occur in an encounter and the reorientations that can occur by rotation between collisions, which increase the chance of a successful collision. Calculations of these effects appear to be of general importance in the investigation both of diffusion effects and of steric effects.

Appendix

Rotational Reorientation Times of Solute Molecules in Low-polarity Solvents

The simplified hard-sphere model of an encounter used above led to the conclusion [eqn (1)] that the contribution of repeated collisions to the rate constant of a geometrically limited reaction depends upon $\tau_\mathrm{enc}/\tau_\mathrm{rot}$, which depends upon $D^\mathrm{R}/D^\mathrm{tr}$. The uncertainty about the value to be attached to τ_enc, reflecting in part the uncertainty in D^tr, has already been mentioned. There is also uncertainty about D^R since experimental values have been determined for relatively few systems. Since the molecular volume, V, can be estimated for many organic molecules by simply summing the van der Waals increments given by Edward,[20] it is tempting to make use of the theoretical Debye expression $\tau_\mathrm{R} = V\eta/k_\mathrm{B}T$. Here τ_R is the reorientation time calculated for rotational diffusion of a spherical particle in a uniform fluid of viscosity η, on the assumption that at the surface the fluid rotates with the particle without slipping (the 'no-slip' or 'stick' condition), so that the frictional resistance to rotation is attributable to the circular motion imposed on the fluid, which (like the solute molecule) is assumed to rotate without being radially displaced. Similar equations are available for ellipsoidal particles. Analysis of the data in ref. (12)–(14) and (38)–(40) shows, however, that the experimental values of τ_R (determined by light-scattering or dielectric-relaxation methods) in a given solvent are not accurately proportional to V; deviation from sphericity increases the value of τ_R. Treating the solvent molecules as ellipsoids rather than spheres[38] does not remove the discrepancies. The theoretical estimates of τ_R are moreover 2–3 times larger than the experimental, although this difference is reduced by taking into account the discontinuous nature of the solvent and the consequent effect of the solvent shell next to the solute molecule on the friction factor.[13]

The root defect of the Debye model appears to be its use of the 'no-slip' assumption. The alternative 'slip' model assumes that the friction accompanying rotation of the solvent molecule arises from the displacement of the fluid due to non-sphericity of the rotating molecule. The hydrodynamic equations for this model have been solved for ellipsoidal solute molecules.[41] Reorientation times for various organic solutes with moderate-sized molecules whose shape can be approximated by ellipsoids have been determined by light-scattering experiments, in several organic solvents.[39,40] They show a linear dependence of τ_R on viscosity; no other solvent property seems to be involved. They are found to agree with the theoretical values calculated from the 'slip' model, in contrast with the large discrepancies found with the 'no-slip' model.[40] The 'slip' model thus succeeds in taking quantitative account both of volume and of shape for these molecules.

Given that both these variables are important, a simple relation between τ_R and V alone is not to be expected. Nonetheless, an approximate empirical relation of the form $\tau_R = \alpha(V\eta/k_B T)$, where α is a numerical constant, is useful. A plot of the experimental values of τ_R against V is shown in fig. 5; the line representing the Debye equation ($\alpha = 1$) is shown for comparison. It is seen that, apart from some exceptionally small molecules, the general trend of the plot justifies the use of the relation $\tau_R = \alpha(V\eta/k_B T)$ with α in the range 0.3–0.6, as an approximation for moderate-sized molecules. With larger molecules, or strong solute–solvent interactions, the reorientation times are closer to the values calculated on the 'no-slip' model. These findings are important in calculating the effects of repeated collisions (see Discussion).

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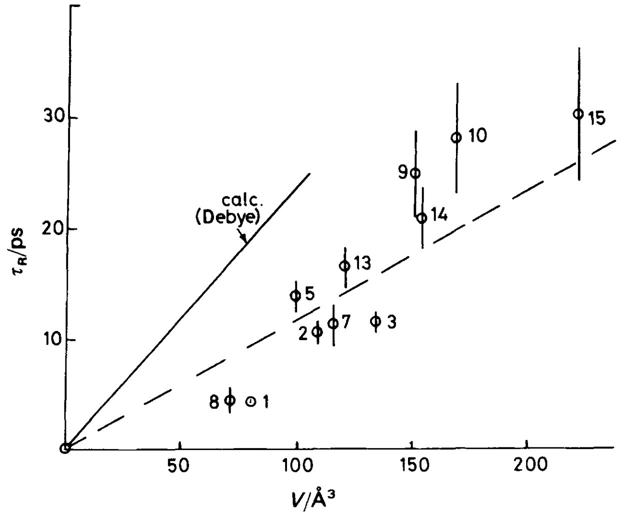

Fig. 5. Rotational reorientation times (τ^R) for solute molecules, from light-scattering experiments, plotted against molecular volume (V) of solute. Data on τ^R from ref. (40). Viscosity assumed 1 cP; T = 298 K. Molecular volumes V calculated according to ref. (20). Full line refers to the Debye equation ($\tau^R = V\eta/k_B T$). 1, benzene; 2 C_6F_6; 3, mesitylene; 5, toluene; 7, p-xylene; 8, methyl acetate; 9, biphenyl; 10, fluorene; 12, benzoic acid; 13, acetic acid; 14, propanoic acid; 15, valeric acid. (Acids assumed completely dimerised.)

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