The Reaction of Imidazole with some 1-Halogeno-2,4-dinitrobenzenes in Aprotic Solvents

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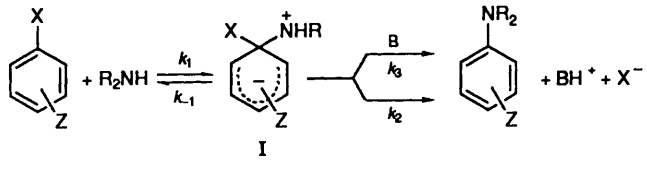
The reactions of imidazole with 1-chloro- and 1-fluoro-2,4-dinitrobenzenes in dimethyl sulfoxide are not catalysed by imidazole, DABCO or imidazolium perchlorate. In acetonitrile these reactions are not catalysed by the nucleophile or DABCO but the second-order rate constant k_A has a linear dependence on the concentration of tetrabutylammonium chloride and is depressed by the addition of imidazolium perchlorate. In this solvent the reaction of imidazole with 1-bromo-2,4-dinitrobenzene is not catalysed by the nucleophile and the k_A^{Br}/k_A^{Cl} ratio is 0.90. These results are rationalised in terms of the conventional mechanism of aromatic nucleophilic substitution reactions in aprotic solvents of high relative permittivity, with chloride ion catalysing the formation of the intermediate in acetonitrile solution.

In benzene the reaction of imidazole with 1-chloro-2,4-dinitrobenzene is strongly catalysed by the nucleophile and by tetrabutylammonium chloride and weakly by pyridine. The corresponding reaction with 1-bromo-2,4-dinitrobenzene is also strongly catalysed by imidazole and there is little difference in the reactivity of the two substrates. The catalysis of the reactions by amines observed here, and that previously reported in the literature, is explained as being due to reaction taking place *via* complexes formed from the reactants and catalysts.

The nucleophilic substitution reactions of primary and secondary amines with activated aromatic substrates are often base catalysed. This observation is rationalized in terms of the intermediate complex mechanism given in Scheme 1. Applic-



I

Scheme 1

ation of the steady state hypothesis to Scheme 1 gives eqn. (1) where k_A is the observed second-order rate constant and B is

$$k_A = \frac{k_1(k_2 + k_3[B])}{k_{-1} + k_2 + k_3[B]} \quad (1)$$

either a second molecule of the nucleophile or an added base. For the condition $k_{-1} \ll k_2 + k_3[B]$ the formation of the intermediate is rate limiting and the reaction is not base catalysed. If this condition is not satisfied the decomposition of the intermediate to products is rate limiting and base catalysis is observed. If eqn. (1) cannot be simplified, k_A has a curvilinear (concave downward) dependence on base concentration, but when $k_{-1} \gg k_2 + k_3[B]$, the equation has the form $k_A = k' + k''[B]$ (when B = nucleophile, $k''/k' = k_3/k_2$).

In many reactions small linear increases of k_A with increasing base concentration are observed. The values of k''/k' are small and the accelerating effect of the bases bears no relationship to their base strength. According to Bunnett and Garst[1] this does not represent true base catalysis; the formation of the intermediate is rate limiting and the accelerations are due to some unspecified effect. In other reactions the addition of base has a powerful accelerating effect and k''/k' is high (> 50). These reactions are regarded as base catalysed and decomposition of the intermediate is rate limiting.

Chloride ion is a good leaving group, and only a very few cases of base-catalysed nucleophilic substitution of aromatic chloro compounds are known. With the exception of reactions involving imidazole, the catalysis can be ascribed to causes other than a rate limiting decomposition of the initially formed intermediate.[2,3] Pietra and del Cima[4] found that the reaction of 1-chloro-2,4-dinitrobenzene with imidazole in benzene was accelerated by imidazole, but did not regard the acceleration as being due to base-catalysed decomposition of the intermediate to products. Minetti and Bruylants[5] have shown that the reaction of imidazole with picryl chloride in chloroform is catalysed by both imidazole and 1,4-diaza[2.2.2]octane (DABCO) and when the substrate is 1-chloro-2,4-dinitrobenzene, de Rossi *et al.*[6] have demonstrated catalysis by the same two reagents in both benzene and chloroform. Both sets of authors interpreted the results in terms of the mechanism given in Scheme 1 with a rate-limiting breakdown of the intermediate to products.

The uncatalysed decomposition of the intermediate is believed[7] to take place unimolecularly *via* the internally-hydrogen-bonded transition state shown in Fig. 1. De Rossi[6]

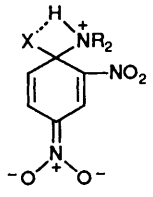


Fig. 1 Transition state for the uncatalysed decomposition of the intermediate I to products

has proposed that when imidazole is the nucleophile, the intermediate may be represented by Fig. 2. Here the proton is not at a bonding distance to the leaving group and hence is not available for intramolecular assistance to the nucleofuge, resulting in a reduction in the rate at which the uncatalysed path takes place. If this is the case the reaction should be susceptible to electrophilic catalysis, in particular by the imidazolium ion. The reaction of the corresponding fluoride should be even more susceptible to electrophilic catalysis owing

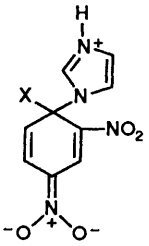
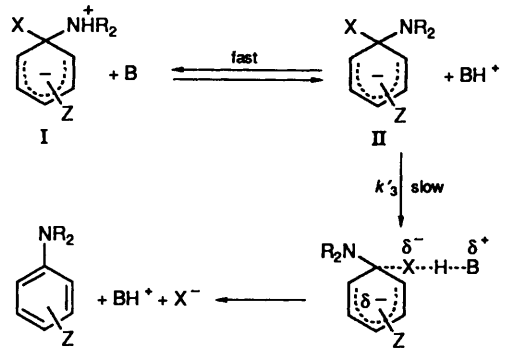


Fig. 2 Proposed transition state for the uncatalysed decomposition of the intermediate **I** to products when imidazole is the nucleophile

to the greater strength of the C–F bond. As the same type of intermediate is formed irrespective of the solvent, it was decided to study the reactions of imidazole with 1-fluoro- and 1-chloro-2,4-dinitrobenzenes in acetonitrile and dimethyl sulfoxide, two solvents in which a previous search[8] for electrophilic catalysis of aromatic nucleophilic substitution reactions had been unsuccessful. With other amines catalysis by the conjugate acid of the nucleophile would not be expected to be observed. The generally accepted mechanism for the catalysed decomposition of the intermediate in dipolar aprotic solvents of high relative permittivity is that of Bunnett and Davies[9] and given in Scheme 2. For this mechanism $d[\text{products}]/dt = k'_3[\mathbf{II}][BH^+] = k'_3K[\mathbf{I}][B]$ where $K = [\mathbf{II}][BH^+]/[\mathbf{I}][B]$.



Scheme 2

For the uncatalysed route, electrophilic catalysis by a weak acid cannot compete successfully with the intramolecular process shown in Fig. 1, which is favoured on entropy grounds.[10] Only the unique structural feature of the intermediate postulated by de Rossi gives electrophilic catalysis by the imidazolium ion the possibility of being observed.

Results and Discussion

The results are given in Tables 1–3. From Table 2 the second-order rate constant k_A for the reaction of 1-chloro-2,4-dinitrobenzene with imidazole in dimethyl sulfoxide does not increase with increasing imidazole concentration. It does however increase linearly with increasing DABCO concentration. In the presence of this reagent the experimental and theoretical infinity values did not agree. A solution containing only the substrate and DABCO gave rise to an absorbance at 330 nm, the wavelength at which these measurements were made. Hence the observed increments of k_A with increasing DABCO concentration are not due to its catalytic effect as a base but to its competition as a nucleophile with imidazole. We conclude that the reaction of 1-chloro-2,4-dinitrobenzene with imidazole in dimethyl sulfoxide is not base catalysed.

The rate constants for the reaction of 1-fluoro-2,4-dinitrobenzene with imidazole in dimethyl sulfoxide have a linear dependence on the imidazole concentration giving a k''/k' value of 33. This is below the value recognized by Bunnett[1] as

Table 1 Effect of various additives on the rate constants ($dm^3\ mol^{-1}\ s^{-1}$) for the reactions of imidazole with 1-chloro-, 1-bromo and 1-fluoro-2,4-dinitrobenzenes in acetonitrile

Substrate	Additive	Concentration/ mol dm^{-3}	k_A
1-Chloro-2,4-dinitrobenzene[a,b]	Imidazole	4.02×10^{-2}	1.18×10^{-5}
		6.03×10^{-2}	1.11×10^{-5}
		8.04×10^{-2}	1.04×10^{-5}
		10.0×10^{-2}	1.18×10^{-5}
		15.0×10^{-2}	1.16×10^{-5}
	DABCO[c]	0.5×10^{-2}	1.24×10^{-5}
		1.0×10^{-2}	1.24×10^{-5}
		3.0×10^{-2}	1.25×10^{-5}
		5.0×10^{-2}	1.28×10^{-5}
	Bu_4NClO_4[c]	1.0×10^{-2}	1.01×10^{-5}
		3.0×10^{-2}	1.07×10^{-5}
		6.0×10^{-2}	1.16×10^{-5}
		10.0×10^{-2}	1.14×10^{-5}
		20.0×10^{-2}	1.02×10^{-5}
	Bu_4NCl[c]	0	1.18×10^{-5}
		1.0×10^{-2}	1.36×10^{-5}
		3.0×10^{-2}	2.13×10^{-5}
		6.0×10^{-2}	3.02×10^{-5}
		10.0×10^{-2}	4.38×10^{-5}
		20.0×10^{-2}	6.02×10^{-5}
	Imidazolium perchlorate[c]	0	11.8×10^{-6}
		0.609×10^{-2}	9.33×10^{-6}
		1.2×10^{-2}	7.64×10^{-6}
		2.4×10^{-2}	7.36×10^{-6}
		4.2×10^{-2}	5.99×10^{-6}
		6.23×10^{-2}	4.94×10^{-6}
		10.0×10^{-2}	3.67×10^{-6}
1-Fluoro-2,4-dinitrobenzene[d,e]	Imidazole	2.50×10^{-3}	2.08×10^{-2}
		5.0×10^{-3}	2.10×10^{-2}
		7.5×10^{-3}	2.33×10^{-2}
		10.0×10^{-3}	2.41×10^{-2}
		15.0×10^{-3}	2.54×10^{-2}
		20.0×10^{-3}	2.56×10^{-2}
	DABCO[f]	0	2.33×10^{-2}
		0.516×10^{-2}	2.51×10^{-2}
		1.032×10^{-2}	2.82×10^{-2}
		2.064×10^{-2}	3.22×10^{-2}
		3.0×10^{-2}	3.75×10^{-2}
		5.16×10^{-2}	4.19×10^{-2}
		6.0×10^{-2}	5.19×10^{-2}
	Bu_4NClO_4[f]	1.0×10^{-2}	2.35×10^{-2}
		3.0×10^{-2}	2.38×10^{-2}
		10.0×10^{-2}	2.51×10^{-2}
		20.0×10^{-2}	2.56×10^{-2}
	Bu_4NCl[f]	5.0×10^{-3}	3.84×10^{-2}
		10.0×10^{-3}	5.04×10^{-2}
		30.0×10^{-3}	8.35×10^{-2}
		50.0×10^{-3}	10.6×10^{-2}
		80.0×10^{-3}	13.9×10^{-2}
		100.0×10^{-3}	16.9×10^{-2}
	Imidazolium perchlorate[f]	0.677×10^{-2}	2.05×10^{-2}
		2.03×10^{-2}	1.48×10^{-2}
		4.06×10^{-2}	1.06×10^{-2}
		6.0×10^{-2}	0.723×10^{-2}
1-Bromo-2,4-dinitrobenzene[b,g]	Imidazole	4.0×10^{-2}	1.08×10^{-5}
		6.0×10^{-2}	0.97×10^{-5}
		8.0×10^{-2}	1.01×10^{-5}

[a] $[\text{substrate}]_0\ 2.04 \times 10^{-3}$ mol dm^{-3}. [b] $T = 30.8$ °C. [c] $[\text{Im}]_0 = 1.0 \times 10^{-1}$ mol dm^{-3}. [d] $[\text{substrate}]_0\ 2.05 \times 10^{-4}$ mol dm^{-3}. [e] $T = 25.0$ °C. [f] $[\text{Im}]_0\ 7.5 \times 10^{-3}$ mol dm^{-3}. [g] $[\text{substrate}]_0\ 2.0 \times 10^{-3}$ mol dm^{-3}.

Table 2 Effect of various additives on the rate constants (dm^3 mol^{-1} s^{-1}) for the reactions of imidazole with 1-chloro- and 1-fluoro-2,4-dinitrobenzenes in dimethyl sulfoxide

Substrate	Additive	Concentration/ mol dm^{-3}	k_A
1-Chloro-2,4-dinitrobenzene[a,b]	Imidazole	4.0×10^{-2}	4.86×10^{-5}
		6.0×10^{-2}	5.11×10^{-5}
		8.54×10^{-2}	5.49×10^{-5}
		10.0×10^{-2}	5.24×10^{-5}
	DABCO[c]	5.02×10^{-3}	7.62×10^{-5}
		10.0×10^{-3}	14.4×10^{-5}
		20.0×10^{-3}	27.8×10^{-5}
		30.0×10^{-3}	40.5×10^{-5}
		50.2×10^{-3}	55.7×10^{-5}
	Imidazolium perchlorate[d]	0.609×10^{-2}	5.44×10^{-5}
		1.22×10^{-2}	5.47×10^{-5}
		2.44×10^{-2}	5.38×10^{-5}
1-Fluoro-2,4-dinitrobenzene[e,f]	Imidazole	2.51×10^{-3}	1.29×10^{-1}
		5.01×10^{-3}	1.31×10^{-1}
		7.52×10^{-3}	1.49×10^{-1}
		10.02×10^{-3}	1.58×10^{-1}
		12.57×10^{-3}	1.59×10^{-1}
		15.1×10^{-3}	1.79×10^{-1}
	DABCO[g]	0.50×10^{-2}	0.165
		1.0×10^{-2}	0.158
		2.0×10^{-2}	0.134
		4.0×10^{-2}	0.140
	Imidazolium perchlorate[g,h]	0	0.187
		0.682×10^{-2}	0.188
		2.04×10^{-2}	0.184
		4.08×10^{-2}	0.181

[a] $[substrate]_0$ 2.04×10^{-3} mol dm^{-3}. [b] $T = 30.8$ °C. [c] $[Im]_0$ 6.0×10^{-2} mol dm^{-3}. [d] $[Im]_0$ 2.0×10^{-2} mol dm^{-3}. [e] $[substrate]_0$ 2.05×10^{-4} mol dm^{-3}. [f] 25.0 °C. [g] $[Im]_0$ 7.55×10^{-3} mol dm^{-3}. [h] $T = 28.0$ °C.

Table 3 Effect of various additives on the rate constants (dm^3 mol^{-1} s^{-1}) for the reactions of imidazole with 1-chloro- and 1-bromo-2,4-dinitrobenzenes in benzene

Substrate	Additive	Concentration/ mol dm^{-3}	k_A
1-Chloro-2,4-dinitrobenzene[a,b]	Imidazole	1.01×10^{-2}	1.19×10^{-5}
		1.51×10^{-2}	1.65×10^{-5}
		2.02×10^{-2}	2.12×10^{-5}
		2.50×10^{-2}	2.70×10^{-5}
	Pyridine[c]	0.10	5.03×10^{-5}
		0.20	7.89×10^{-5}
		0.35	11.26×10^{-5}
		0.50	13.8×10^{-5}
	Bu_4NCl[c]	1.17×10^{-3}	4.61×10^{-5}
		2.35×10^{-3}	6.98×10^{-5}
		4.70×10^{-3}	11.0×10^{-5}
		9.40×10^{-3}	20.2×10^{-5}
		18.8×10^{-3}	41.1×10^{-5}
	Bu_4NClO_4[c]	1.0×10^{-3}	2.71×10^{-5}
		5.0×10^{-3}	2.83×10^{-5}
1-Bromo-2,4-dinitrobenzene[b,d]	Imidazole	1.01×10^{-2}	1.27×10^{-5}
		1.52×10^{-2}	2.06×10^{-5}
		2.00×10^{-2}	2.62×10^{-5}

[a] $[substrate]_0$ 5.03×10^{-4} mol dm^{-3}. [b] $T = 30.8$ °C. [c] $[Im]_0$ 2.50×10^{-2} mol dm^{-3}. [d] $[substrate]_0$ 5.0×10^{-4} mol dm^{-3}.

indicating true base catalysis and the reaction is not catalysed by the much stronger base DABCO. Hence in this reaction the decomposition to products of the intermediate is not rate limiting. This conclusion is strengthened by the very high k_A^F/k_A^{CL} value of 2.25×10^3 which according to Bunnett[11] indicates that breaking of the C–F bond cannot have made any significant progress in the rate-determining transition state* and is in agreement with the results of Zima *et al.*[12] for their system. For both the chloro and fluorosubstrates, the addition of imidazolium perchlorate has no effect on the rate.

In acetonitrile the reaction of the chloro substrate with imidazole is not catalysed by either imidazole or DABCO, hence the formation of the intermediate is rate limiting. This conclusion is reinforced by the element effect. Measurement of k_A for the corresponding bromo compound gives a value of k_A^{Br}/k_A^{Cl} of 0.90. This is in agreement with a rate-limiting formation of the intermediate. If the breaking of the C–halogen bond were involved in the rate-limiting step the ratio would be considerably higher.[14] The rate constant does however increase with increasing concentration of tetrabutylammonium chloride. This is not a salt effect as tetrabutylammonium perchlorate has no effect on the reaction. The results are completely analogous to those obtained for the reaction of 1-chloro-2,4-dinitrobenzene with aniline in this solvent.[15] This reaction is not catalysed by either the nucleophile or DABCO, but is strongly catalysed by tetrabutylammonium chloride. It was shown[15,16] that this catalysis is due to the anion of the salt stabilizing the transition state for the formation of the intermediate by hydrogen bonding as shown in Fig. 3, and we believe that a similar phenomenon is

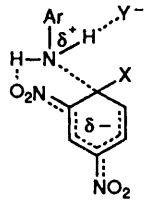


Fig. 3 Stabilisation of the transition state for the formation of the intermediate **I** by hydrogen-bonding

occurring here. This mechanism occurring concurrently with that given in Scheme 1 (with $k_{-1} \ll k_2 + k_3[B]$) gives a rate equation of the form given in eqn. (2) which requires a linear

$$k_A = k_0 + k[Y^-] \quad (2)$$

dependence of the measured rate constant on the anion concentration, as is found experimentally.†

The value of k_A for the reaction of 1-fluoro-2,4-dinitrobenzene in acetonitrile increases linearly with increase in concentration of both imidazole and DABCO giving values of k''/k' of 14.7 (imidazole) and 18.6 (DABCO). The values of these ratios, though substantial, are well below the minimum of 50 recognized by Bunnett[1] as indicating true base catalysis, and although DABCO is a much stronger base than imidazole

* This criterion may not always hold. Thus Pietra and Vitali[13] have shown that the rate constants for the reactions of butyl-, *sec*-butyl- and *tert*-butyl-amine with 1-fluoro-2,4-dinitrobenzene in benzene have a *curvilinear* (concave downward) dependence on the nucleophile concentration, whereas the reactions of the corresponding chlorosubstrate are not base catalysed. The authors have rationalized their results in terms of Scheme 1 and give the k^F/k^{CL} ratios at zero nucleophile concentration for the fluorosubstrate as 400, 1800 and 1000 for butyl-, *sec*-butyl- and *tert*-butyl-amines respectively.

† A plot of k_A against Bu_4NCl concentration is linear with the last point (at $[Bu_4NCl] = 0.2$ mol dm^{-3}) showing considerable deviation below the line. When this point is omitted the correlation coefficient is 0.9990. It is known[17] that at concentrations in acetonitrile of 10^{-3} mol dm^{-3} no association of Bu_4NCl occurs. At higher concentrations appreciable association does take place.

[pK_a (acetonitrile) imidazole,[18] 13.8; DABCO,[19] 18.3], it is only approximately 1.5 times as effective as a 'catalyst'. The k_A^F/k_A^{Cl} value of 1.81×10^3 obtained at zero imidazole concentration for the fluoro substrate is high and of similar magnitude to that in DMSO and the $k_A^{piperidine}/k_A^{imidazole}$ ratio of 6.9×10^3 obtained using Hirst's[20] value of $k_A = 140$ for the reaction with piperidine in acetonitrile is comparable with that of 3.6×10^3 calculated from the results of Zima[12] in DMSO. We conclude that the formation of the intermediate in Scheme 1 is rate limiting in this reaction.

The rate constant for this reaction increases linearly with increase in tetrabutylammonium chloride concentration and comparison with the effect of tetrabutylammonium perchlorate shows that this is not a salt effect. By analogy with the chloro substrate we interpret the accelerations as being due to catalysis of the formation of the intermediate by chloride ion. This raises the question of the origins of the accelerations produced by imidazole and DABCO. They could be due to similar catalysis of the formation of the intermediate or be further examples of Bunnett's[1] accelerations of unknown origin.

The addition of imidazolium perchlorate inhibits the reactions of both chloro and fluoro substrates as is shown in Fig. 4. A

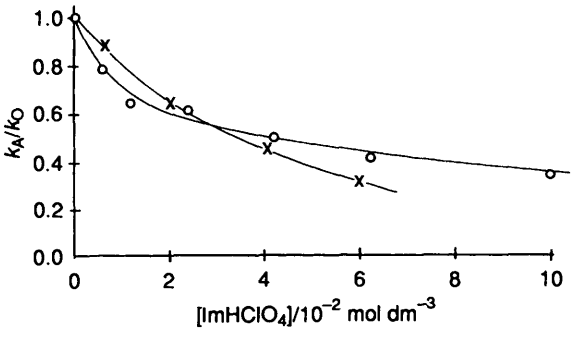
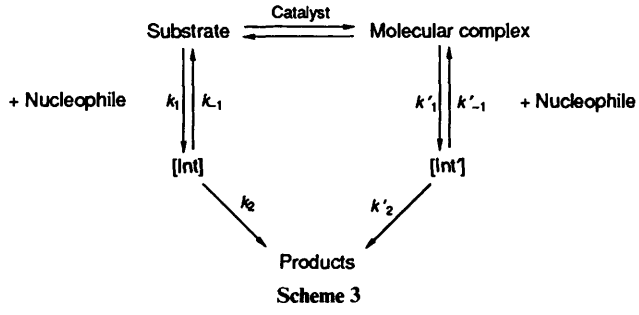


Fig. 4 Plots illustrating the influence of imidazolium perchlorate on the reactions of 1-chloro- and 1-fluoro-2,4-dinitrobenzene with imidazole in acetonitrile: O, chloro substrate; X, fluoro substrate

similar retardation has been observed by Menger[21] by pyrrolidinium perchlorate on the reaction of *p*-cyanophenyl *p*-nitrobenzoate with pyrrolidine in acetonitrile and ascribed to the formation of a complex between the nucleophile and its conjugate acid. A similar explanation is advanced for the present results.

The absence of conventional catalysis in these reactions prompted us to reinvestigate the reaction of the chloro substrate with imidazole in benzene. At 30.8 °C the second-order rate constant has a strong linear dependence on imidazole (k''/k', 671) and tetrabutylammonium chloride (k''/k' 1.2×10^3) and a mild one on pyridine (k''/k' 6.8). Addition of tetrabutylammonium perchlorate showed that the accelerations observed with the chloride were not due to a salt effect. The results in Table 3 show that there is very little difference in the rates of reaction of 1-bromo- and 1-chloro-2,4-dinitrobenzenes, hence breaking of the carbon–halogen bond is not involved in the rate-limiting stage. These observations can be accommodated by postulating catalysis of the formation of the intermediate, as in acetonitrile, and as is also the case in the reaction of 1-chloro-2,4-dinitrobenzene with *p*-anisidine in this solvent.[2] This is most probably the explanation when chloride ion is the catalyst. When the reaction is carried out at 100 °C, de Rossi[6] has found a curvilinear dependence of the rate constant on both pyridine and DABCO concentrations and a similar dependence on both imidazole and DABCO concentrations when the reaction is carried out in chloroform. In benzene the rate appears to level off at high base concentrations, the value of k_A at which this occurs is lower for pyridine than DABCO. This kinetic form is not compatible with the proposed catalysis and additional effects must be operating.

When the decomposition to products of the intermediate in Scheme 1 is not rate limiting, a curvilinear dependence of the rate constant on base concentration can be rationalized by reaction involving a molecular complex of the base with one of the reactants. While we are not aware of any report of a complex between DABCO and the chloro substrate, Forlani[22] has reported one with the very similar compound 1-fluoro-2,4-dinitrobenzene in benzene and has advocated[22,23,24] a model in which the catalytic phenomenon is an effect of substrate/nucleophile (or substrate/catalyst) interaction in a rapidly established equilibrium preceding the substitution process, as shown in Scheme 3. The catalyst can be either the nucleophile



Scheme 3

or an added base, and [In] is the zwitterionic intermediate. On this scheme the variation of the second order rate constant k_A with base concentration has the form of eqn. (3) where K is the

$$k_A(1 + K[B]) = k_0 + k_3[B] \quad (3)$$

association constant and B is the catalyst (base or nucleophile).

In principle, the observed curvatures could also be due to reaction of the substrate with a complex formed by the nucleophile with a base, a system which has a similar rate law as that of eqn. (3). The reaction of 1-fluoro-2,4-dinitrobenzene with butylamine in benzene[13] and 1,2-dinitrobenzene with piperidine in hexane[25] are catalysed by pyridine, and the rate constant has a curvilinear (concave downward) dependence on the pyridine concentration. Cattana *et al.*[25] have suggested that this is due to an association between pyridine and the nucleophile, the complex catalysing the rate-limiting breakdown of the intermediates formed in these reactions. Although imidazole forms linear oligomers in solution (in carbon tetrachloride the dimerization constant has the high value of 234)[26] there is no evidence that any of these participate in its nucleophile reactions in benzene. Thus its reaction with phenacyl chloride in this solvent has a first-order dependence on the imidazole concentration.[27,28]

The concept of the reactions of imidazole with 1-halogeno-2,4-dinitrobenzenes in benzene taking place *via* reaction of complexes formed from the reactants and catalysts is not new. It was used by Pietra and del Cima[4] to explain their observations of the catalysis of the reaction of imidazole with 1-fluoro-2,4-dinitrobenzene by imidazole and quinuclidine in this solvent.

Experimental

The purification of acetonitrile,[29] dimethyl sulfoxide[30] 1-fluoro- and 1-chloro-2,4-dinitrobenzenes,[31] tetrabutylammonium perchlorate,[30] pyridine[32] and benzene[32] have already been described. Tetrabutylammonium chloride was purified by azeotropic distillation with benzene and dried over phosphorus pentoxide. Imidazole was recrystallised from benzene and then sublimed under vacuum, m.p. 90°. *N*-2,4-Dinitrophenylimidazole was prepared by refluxing 10 mmol of imidazole and

5 mmol of 1-chloro-2,4-dinitrobenzene in 4 cm^3 of dry benzene for 30 min. The benzene was distilled off and the residue recrystallised from methanol, m.p. 146–147 °C (lit.,[33] 146–148 °C). The product was protected from light throughout its preparation. Imidazolium perchlorate was prepared by adding 0.01 mol of concentrated perchloric to 0.01 mol of imidazole dissolved in ethanol. The precipitate was recrystallised from ethanol.

Kinetics.—The spectrum of *N*-2,4-dinitrophenylimidazole is very broad with no definite maximum in the region useful for examination in the three solvents employed. The following wavelengths were chosen for monitoring the product: benzene, 324 nm; acetonitrile, 306 nm; dimethyl sulfoxide, 330 nm. All reactions were carried out with imidazole present in large excess. The kinetics of the chloro and bromo substrates were investigated using a pipette technique in which aliquots of the reaction mixture were diluted with the respective solvent and the absorbance measured on a HP 8451A Diode Array Spectrophotometer. For the fluoro substrate, calculated amounts of the reagents were added from stock solutions to a cuvette containing the appropriate amount of solvent. After rapid mixing the cuvette was placed in the spectrophotometer and the production of product monitored directly. In all cases good first-order kinetics were observed and with the exception of the reaction of the chloro substrate in the presence of DABCO (see Discussion) the absorbances of the reaction mixtures at infinite time agreed with the calculated ones.

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