Solvent Effect on the Kinetics of the Reaction of 2,3-[9,10-Dihydroanthracene-*endo*-9,10-diyl]-*N*-(2,4-dinitrophenoxy)succinimide with Piperidine

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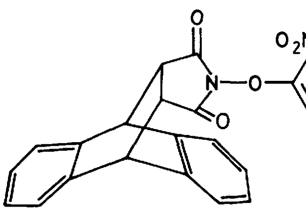
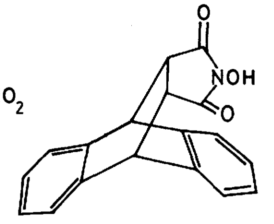
The kinetics of the reaction between 2,3-(9,10-dihydroanthracene-*endo*-9,10-diyl)-*N*-(2,4-dinitrophenoxy)succinimide and piperidine have been studied in acetonitrile, ethyl acetate, benzene, dioxane, and methanol at 35 ± 0.1 °C. The second-order rate coefficient increases with increased piperidine concentration in all cases except for methanol. The observed base catalysis in acetonitrile, ethyl acetate, benzene and dioxane is explained in terms of the rate-limiting nucleofuge detachment. For the case of methanol, due to its high hydrogen-bond donating property, the formation of the intermediate is rate determining.

The mechanism of base-catalysed aromatic substitution reactions often changes when the solvent is changed from protic to aprotic or dipolar aprotic.[1,2] Recently, Nudelman *et al.*[3] reported efficient base catalysis in trichloroethane, dioxane, benzene, toluene, dichloromethane, acetone, THF, chlorobenzene, and ethyl acetate for reactions of 1-fluoro-2,4-dinitrobenzene with piperidine. However, no base catalysis was observed in chloroform, acetonitrile, or nitromethane. The electronic and structural nature of the nucleofuge plays a key role in deciding whether base catalysis will occur or not. In order to confirm further this view the present study of the kinetics of the reactions of 2,3-(9,10-dihydroanthracene-*endo*-9,10-diyl)-*N*-(2,4-dinitrophenoxy)succinimide (**1**) with piperidine in dioxane, benzene, ethyl acetate, acetonitrile, and methanol at 35 ± 0.1 °C, discusses this result.



(**1**)



(**2**)

Results

The reaction of (**1**) with piperidine was carried out in acetonitrile, ethyl acetate, dioxane, and benzene using six different amine concentrations in the range (0.5–2.5) × 10^{-3} mol dm^{-3} under pseudo-first-order conditions at 35 ± 0.1 °C. The coloured product obtained in each case was *N*-(2,4-dinitrophenyl)piperidine. The second-order rate coefficient, k_A (obtained by dividing the first-order rate constant, k_o by [amine]) increased with increased piperidine concentration. The plots of k_A *versus* [piperidine] were linear with positive intercepts and slopes. The reactions are, therefore, base catalysed.[4,5] The well established relation [equation (1)] interrelating rate coefficients was obeyed in each case.

$$k_A = k' + k''[B] \qquad (1)$$

where k' (the intercept) is the non-catalytic and k'' (the slope) is the catalytic rate coefficient. A comparison of k' values obtained in anhydrous acetonitrile and in aqueous acetonitrile [1:4 (v/v)] showed that k' is higher in anhydrous acetonitrile, (k' = 2.54 and 0.85, respectively).

The reaction has also been studied in anhydrous methanol using different piperidine concentrations in the range (2–8) × 10^{-3} mol dm^{-3}. The second-order rate coefficients obtained under these conditions were, however, almost constant, reflecting the absence of base catalysis. The relevant data are given in Table 1.

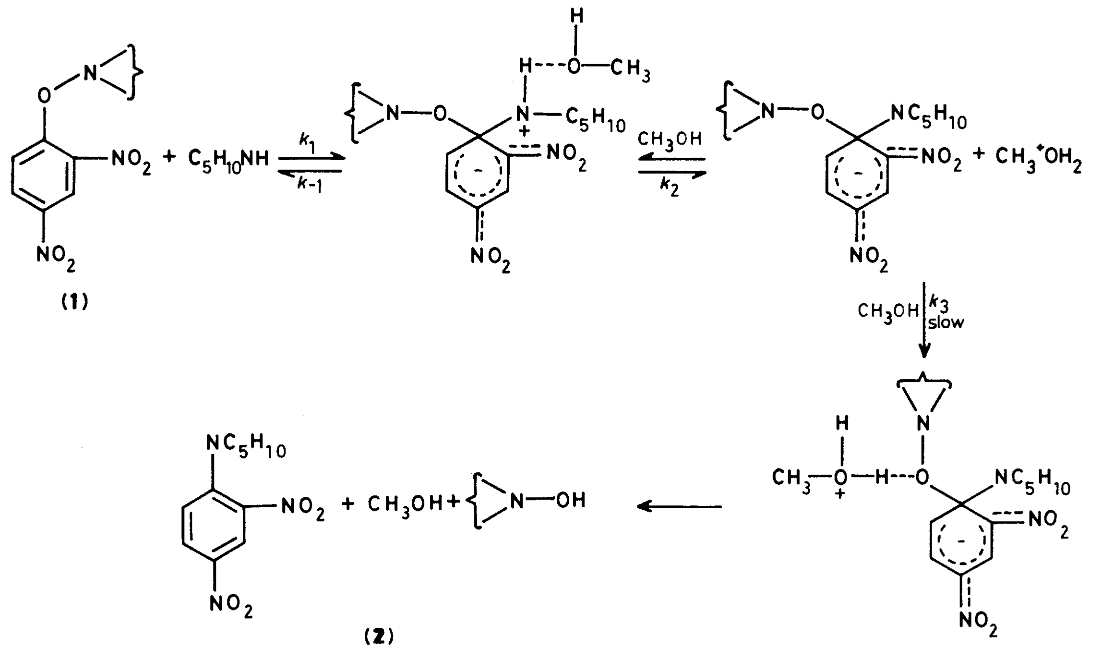
Discussion

The k' value observed in anhydrous acetonitrile was higher than that in 1:4 (v/v) aqueous acetonitrile and this may be due to an increase in the basicity (pK_a of piperidine in anhydrous acetonitrile is 18.9, whereas it is 10.2 in 1:4 (v/v) aqueous acetonitrile). Moreover, the absence of water frees the amine further and enhances its nucleophilicity. In solvents of low dielectric constant such as benzene many authors [2,6,7] observed

Table 1. Reaction of (**1**) with piperidine in various solvents at 35 ± 0.1 °C. Second-order rate coefficients.[a]

	[Piperidine]/10^{-4} mol dm^{-3}									
Solvent	5	7.5	10	12.5	15	20	30	40	60	80
Acetonitrile	274	—	303	310	320	343	—	—	—	—
Ethyl acetate	122	128	131	—	141	148	—	—	—	—
Dioxane	74	79	81	—	87	93	—	—	—	—
Benzene	74	80	85	—	94	101	—	—	—	—
Methanol	—	—	—	—	—	24	23	22	22	21

[a] $k_A/10^{-2}$ dm^3 mol^{-1} s^{-1}; [Substrate] = 4 × 10^{-5} mol dm^{-3}.



Scheme.

Table 2. Rate coefficients for various solvents.

Solvent	$k'/10^{-2}$ dm^3 mol^{-1} s^{-1}	ε^a
Acetonitrile	254	37.5
Ethyl acetate	115	5.96
Dioxane	70	2.2
Benzene	66	2.3
Methanol	22	31.5

[a] At 25 °C.

a quadratic dependence of the observed second-order rate coefficient, k_A on [amine] in the equation. This was explained on the basis of the formation of a cyclic transition state. In the present case, however, no such possibility exists. A comparison of the non-catalytic rate coefficients obtained in different solvents is shown in Table 2.

The importance of the dielectric constant of the medium is apparent from Table 2. However, the rate markedly diminished in methanol. Nudelman *et al.*[8] referred to it as a specific hydroxylic-solvent effect. In the presence of piperidine, alcohols are known to act as hydrogen-bond donors.[8] Methanol exhibits the largest self-association energy and hydrogen-bond-donating ability among various alcohols.[9] Nudelman *et al.*[8] also observed that the rate of reaction of 1-chloro-2,4-dinitrobenzene was at a minimum with piperidine in methanol, compared with other alcohols, clearly supporting the hypothesis that strong solvation of piperidine in methanol is responsible for the observed decrease in rate. In the light of earlier observation,[10] the mechanism of the reaction of piperidine with (**1**) may be as shown in the Scheme. As mentioned earlier Nudelman[3] *et al.* did not observe any indication of a base catalysis in acetonitrile for reaction of 1-fluoro-2,4-dinitrobenzene with piperidine, however, in the present study we have a clear indication of base catalysis in the same solvent when a sterically rigid nucleofuge constituted the bulk of the substrate. This reflects the importance of the nature of the nucleofuge in nucleophilic aromatic substitution reactions.

Experimental

Materials.—Compound (**1**) was prepared and characterised by literature methods.[11] Piperidine (Fluka) and acetonitrile (Merck, GR grade) were used as received. Dioxane, benzene, ethyl acetate, and methanol were purified by literature methods.[12]

Kinetics were followed at 370 nm with a Unicam SP-500 spectrophotometer under pseudo-first-order conditions at 35 ± 0.1 °C. The substrate concentration was maintained at 4×10^{-5} mol dm^{-3}. The products obtained were *N*-(2,4-dinitrophenyl)piperidine and the parent *N*-hydroxy compound (**2**) in each case.

Acknowledgements

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