

## Base Catalysis in Nucleophilic Aromatic Substitution Reactions: Evidence for Cyclic Transition State Mechanism over the Dimer Mechanism in a Non-polar Aprotic Solvent

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The reactions of X-phenyl 2,4,6-trinitrophenyl ethers [X = 2-NO<sub>2</sub>, 3-NO<sub>2</sub>, 4-NO<sub>2</sub>, 2,4-(NO<sub>2</sub>)<sub>2</sub>, 3,4-(NO<sub>2</sub>)<sub>2</sub>, 2,5-(NO<sub>2</sub>)<sub>2</sub>, and 2,6-(NO<sub>2</sub>)<sub>2</sub>] with aniline in benzene display three distinct mechanisms even though all except the 2,6-dinitrophenyl ether are base catalysed. The catalysis of the mononitro-substituted ethers involves two aniline molecules and proceeds at a temperature-independent rate in the temperature range 5–35 °C while that of the dinitro-substituted ones involves only one aniline molecule and proceeds at a temperature-dependent rate over the same temperature range. The results are interpreted in terms of a cyclic mechanism involving four-, six-, and eight-membered rings in the transition state.

Much of the evidence for the now well established S<sub>N</sub>Ar mechanism for nucleophilic aromatic substitution reactions has come from studies of base catalysis<sup>1</sup> in the reactions involving nitro-activated substrates such as aryl halides and aryl ethers and amine nucleophiles, both primary and secondary. While the mechanism by which base catalysis occurs in these reactions in protic solvents is fairly well established,<sup>2</sup> that in non-polar aprotic solvents is still a subject of controversy.<sup>2,3</sup>

The occurrence of base catalysis in the above reactions is usually manifested by a linear dependence of the experimental second-order rate constant  $k_A$  on the base concentration [B], i.e.  $k_A = k' + k''[B]$  where  $k'$  is the intercept and  $k''$  the slope, or in some cases by a downward curvilinear dependence that terminates at a plateau at high base concentration. Sometimes, upward curvature is observed.<sup>4,5</sup>

One of the reported cases of upward curvature in the plot of  $k_A$  against amine concentration was by Bamkole and Hirst<sup>5</sup> for the reaction of bis-2,4-dinitrophenyl ether with morpholine in benzene. They explained their observation as being due to a medium effect superposed on base catalysis by the nucleophile. They also offered an alternative explanation that at least part of the electrophilic catalysis of the second step could be due to the homoconjugate acid  $\overset{+}{H}Nu$  (where Nu stands for nucleophile). A straight line was indeed obtained when another base different from Nu was added.

We have, however, found in our reactions of phenyl 2,4,6-trinitrophenyl ether with aniline<sup>6</sup> and substituted anilines<sup>7</sup> in benzene a quadratic dependence of the observed second-order rate constant  $k_A$  on the amine concentration, i.e.  $k_A = k' + k''[B]^2$  where  $k'$  and  $k''$  have the usual connotations.

Nudelman and Palleros have also recently reported a similar finding in the reactions of 2,4- and 2,6-dinitroanisoles<sup>8,9</sup> and 2,4-dinitrofluorobenzene<sup>10</sup> with several amines in aprotic solvents. They interpreted their results in terms of an aggregate (dimer) BB of the amine or of the amine with a present base (mixed dimer). They suggested that the dimer should be a better nucleophile than the monomer.

We, on the other hand, interpreted our results in terms of a cyclic mechanism involving an eight-membered ring comprising the zwitterionic intermediate and two amine molecules in the transition state. We also related the experimental results to observed temperature effects,<sup>7</sup> a fact which was then unknown to Nudelman and Palleros.<sup>9</sup> We report here some additional data which provide further evidence for the cyclic mechanism

involving single amine molecules. We have examined the reactions of aniline in benzene with a number of nitro-activated substrate with varying nucleofugicity at different temperatures. The reactions were studied spectrophotometrically in the presence of a varying excess of the amine to ensure pseudo-first-order kinetics. The observed second-order rate constants,  $k_A$ , were calculated from the pseudo-first-order rate constants and are listed in Table 1.

### Discussion

The reaction between each ether and aniline yielded the expected 2,4,6-trinitrophenylaniline and phenol with no side-products detected. Table 1 shows that the reactions except that of the 2,6-(NO<sub>2</sub>)<sub>2</sub> substituted ether are very sensitive to the concentration of aniline in the reaction medium. If the rate coefficients  $k_A$  for the mononitro-substituted ethers are plotted against aniline concentration [B] a straight line with a negative intercept is obtained in all cases instead of the expected positive intercept if the conventional base catalysis law<sup>1</sup> were operating. The fact that this rather unusual linear increase is not due to a simple medium effect superposed on base catalysis is borne out by a plot of the observed second-order rate constant  $k_A$  against the square of the amine concentration [B]<sup>2</sup> which then gives a straight line with a positive (and thus meaningful) intercept, indicating a different mechanism involving a second-order dependence of  $k_A$  on the amine concentration. The rate data for this set of ethers thus fit an earlier observed<sup>7</sup> equation (1) where

$$\text{Rate}/[\text{Substrate}][\text{Amine}] = k_A = k' + k''_m[B]^2 \quad (1)$$

$k'/l \text{ mol}^{-1} \text{ s}^{-1}$ , the intercept, is the non-catalytic rate coefficient and  $k''_m/l^3 \text{ mol}^{-3} \text{ s}^{-1}$ , the slope, represents the catalytic rate coefficient for the mononitro-substituted phenyl ethers (Table 2).

The base-catalysed dinitro-substituted phenyl ethers on the other hand present quite a different picture from the above as a plot of their observed second-order rate coefficient  $k_A$  with the amine concentration [B] gives the conventional linear plot with positive intercept. The rate data for this set of ethers thus fit equation (2) where  $k''_d/l^2 \text{ mol}^{-2} \text{ s}^{-1}$  represents the catalytic rate

$$\text{Rate}/[\text{Substrate}][\text{Amine}] = k_A = k' + k''_d[B] \quad (2)$$

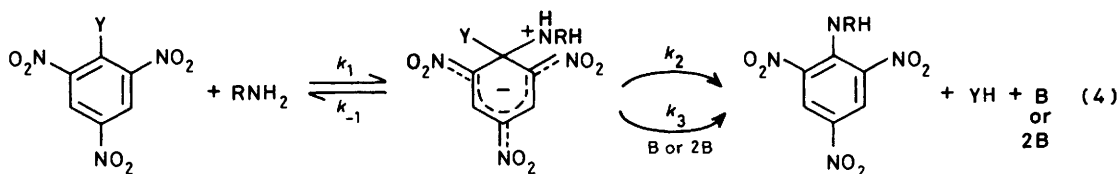
coefficient for the dinitro-substituted phenyl ethers (Table 3).

The 2,6-dinitrophenyl 2,4,6-trinitrophenyl ether was not base-catalysed and so was first-order in both substrate and nucleophile and hence its rate data fitted the simple second-order equation (3).

$$\text{Rate}/[\text{Substrate}][\text{Amine}] = k_A = k' \quad (3)$$

The rates were also investigated over a range of temperatures (5–35 °C) at a constant ratio between concentration of substrate and amine (Table 1). The rates were observed to fall into two distinct categories, depending on whether the phenoxide component of the ether is mono- or di-nitro-substituted. For the mononitro-substituted phenyl ethers, X = 2-NO<sub>2</sub>, 3-NO<sub>2</sub>, and 4-NO<sub>2</sub>, the rates were found to be constant with increasing temperature while for the dinitro-substituted ethers, X = 2,4-(NO<sub>2</sub>)<sub>2</sub>, 3,4-(NO<sub>2</sub>)<sub>2</sub>, 2,5-(NO<sub>2</sub>)<sub>2</sub>, and 2,6-(NO<sub>2</sub>)<sub>2</sub>, the rates increased conventionally with increasing temperature over the entire temperature range investigated.

These results can be satisfactorily accommodated by a modified form [equation (4)] of the intermediate complex mechanism.



Application of the steady-state hypothesis to this simplified equation results in equation (5) or (6) depending on whether catalysis is by one or two amine molecules respectively.

$$k_A = \frac{k_1 k_2 + k_1 k_3 [\text{B}]}{k_{-1} + k_2 + k_3 [\text{B}]} \quad (5)$$

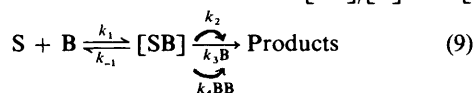
$$k_A = \frac{k_1 k_2 + k_1 k_3 [\text{B}]^2}{k_{-1} + k_2 + k_3 [\text{B}]^2} \quad (6)$$

In the reactions of amines with poor nucleofuges like F, OCH<sub>3</sub>, and OPh, the second step is usually rate-determining, and the inequality  $k_{-1} \gg (k_2 + k_3 [\text{B}])$  or  $(k_2 + k_3 [\text{B}]^2)$ , as the case may be, holds and equations (5) and (6) can then be simplified to equations (7) and (8), respectively with  $k' = k_1 k_2 / k_{-1}$  and  $k'' = k_1 k_3 / k_{-1}$ .

$$k_A = k_1 k_2 / k_{-1} + k_1 k_3 [\text{B}] / k_{-1} \quad (7)$$

$$k_A = k_1 k_2 / k_{-1} + k_1 k_3 [\text{B}]^2 / k_{-1} \quad (8)$$

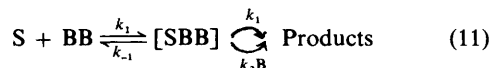
Equations (7) and (8) fit the results of Table 1 and show a linear dependence of  $k_A$  on either  $[\text{B}]$  or  $[\text{B}]^2$  as the case may be and are, in fact, the same as equations (2) and (1), respectively. To explain the above observations Bamkole and Hirst's proposal [equation (9), dimer mechanism] would require that the dimer of the amine acts along with the monomer in the second step. If we take BB to represent the dimer of the amine B, S the substrate, and SB the zwitterionic intermediate resulting from the first encounter of amine with the substrate then the derived kinetic expression for  $k_A$  should be given by equation (10) where  $K$  is the dimerization constant =  $[\text{BB}] / [\text{B}]^2$  and  $[\text{B}]$



$$k_A = \frac{k_1 k_2 + k_1 k_3 [\text{B}] + k_1 k_4 K [\text{B}]^2}{k_{-1} + k_2 + k_3 [\text{B}] + k_4 K [\text{B}]^2} \quad (10)$$

the free monomeric concentration of base.

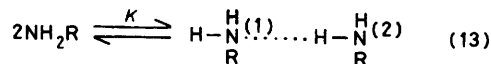
Nudelman and Palleros' proposal on the other hand [equation (11)] would require that the dimer of the amine acts in the first step and the monomer in the second step resulting in a kinetic expression for  $k_A$  given by equation (12). These are no



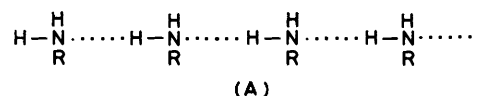
$$k_A = \frac{k_1 k_2 K [\text{B}] + k_1 k_3 K [\text{B}]^2}{k_{-1} + k_2 + k_3 [\text{B}]} \quad (12)$$

doubt three different ways of explaining the same set of observations. Though the dimer mechanism is able to account for the quadratic dependence of  $k_A$  with the amine concentration, it failed to explain the factors that determine con-

clusively whether it is the dimer or the monomer that acts in any one step of the proposed two-step mechanism. The choice so far seems to be that which catches the fancy of the proponent as demonstrated by the two cited dimer mechanisms. Surely the choice can't be that arbitrary. The proponents have also failed to explain why the dimer mechanism is sometimes not observable,<sup>11</sup> though presumably both the dimer and monomer coexist. The preponderance or otherwise of the dimer itself rests on the value of the dimerization constant  $K$  of the amine in the aprotic solvents, a value which none of the proponents of the mechanism have determined so far, but which Bernasconi and Zollinger have estimated to be extremely small<sup>12</sup> judging by the association constants of similar systems. Besides, there is no reason to believe that the association of the amines through hydrogen bonding stops at the dimer stage as proposed by Nudelman and Palleros<sup>9</sup> [equation (13)] as nitrogen (2) could



also be hydrogen bonded to another amine molecule and the process repeated thus resulting in a long association complex (A) and this chain has to be broken before it could react in

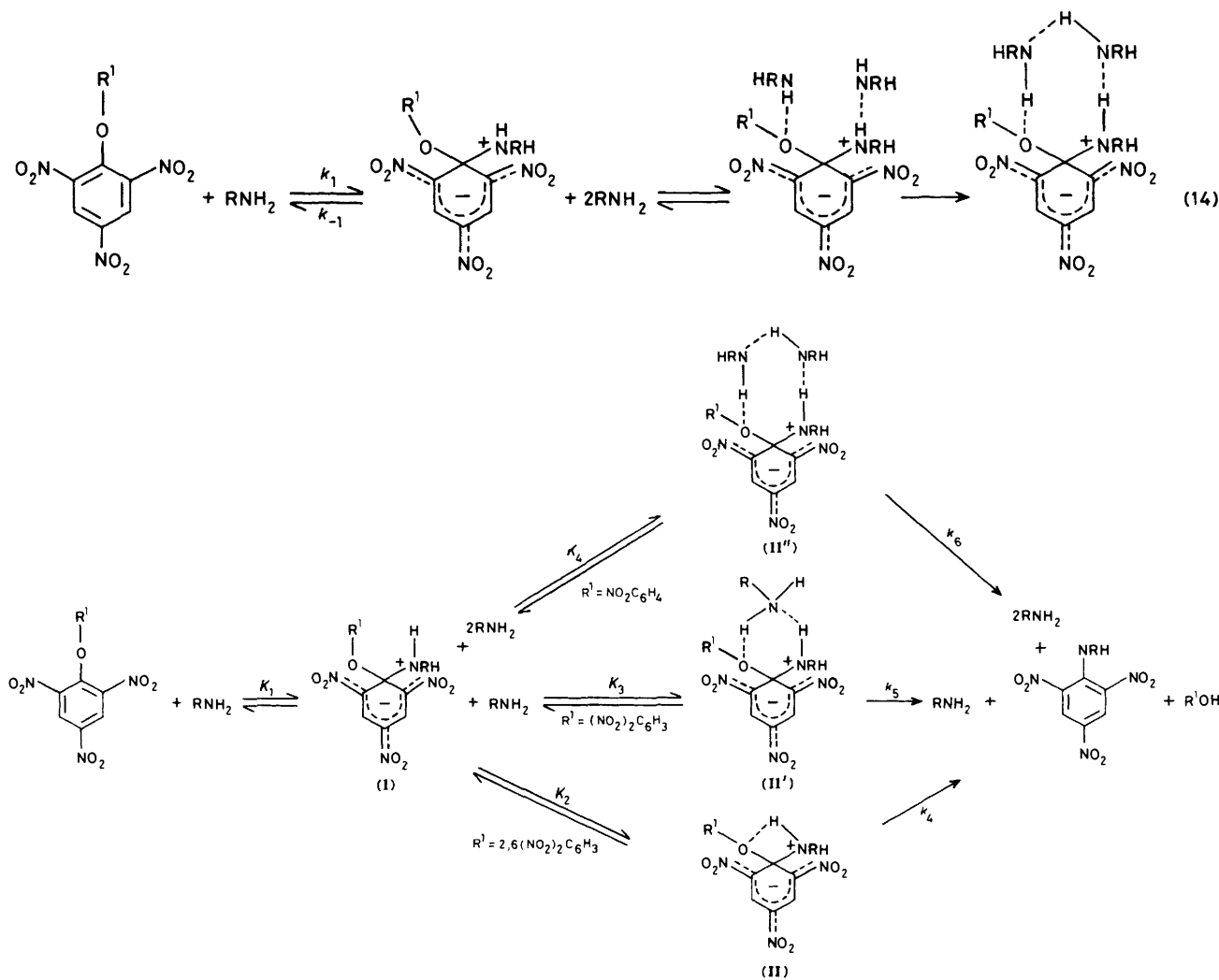


whatever form. Not that we entirely rule out the possibility of this happening but we feel that, from the evidence available, the equilibrium lies more to the left in which case the preponderance of the monomer makes it the active nucleophile and catalyst.

Nudelman and Palleros' criticism of our mechanism as requiring the encounter of three molecules in the second step does not hold as it cannot be regarded as a conventional three-

body collision since the two catalysing amine molecules are not attacking one centre (or atom) but are bonded to the zwitterion intermediate at two separate points, one at the oxygen of the phenoxide moiety and the second at the hydrogen of the zwitterion intermediate as shown in equation (14) (each thus being a two-body collision). Hydrogen bonding between these hooked amine molecules then results in ring closure as shown in equation (14).

it is and hence the less assistance it needs from the available aniline molecules for breaking away from the zwitterionic intermediate. Empirically, a fairly activated phenoxide needs the assistance of only one aniline molecule for its catalysis while a less activated one needs two. The observed order of nucleofugicity  $\text{NO}_2\text{C}_6\text{H}_4\text{O} < (\text{NO}_2)_2\text{C}_6\text{H}_3\text{O}$  thus accords with the decreasing order  $7.14 > 4.09$  of the respective  $\text{p}K_a$  of their conjugate acids.



Scheme.

This cyclic transition state mechanism earlier proposed by us<sup>6,7</sup> is, however, devoid of the above shortcomings of the dimer mechanism and appears a more plausible alternative. It identifies the amine as reacting with the substrate in the first step to form the intermediate complex. Whether it is one or two amine molecules that are involved in the catalysis of the second step is determined by the nucleofugacity of the leaving group which increases with the decreasing  $\text{p}K_a$  of its conjugate acid.<sup>13-15</sup> This contention is borne out by the results of our present investigation in which it is found that the mononitro-substituted phenyl 2,4,6-trinitrophenyl ethers are catalysed by two aniline molecules while the dinitro-substituted ones are catalysed by only one. We attribute this to the activating role of the nitro group on the phenoxide portion of the ether.

The more the number of the nitro groups the more activated the phenoxide becomes, consequently the better a leaving group

The apparent absence of energy of activation over a fairly wide temperature range for the rate coefficients  $k'$  and  $k_m''$  (Table 2) in the reactions of the mononitro-substituted phenyl ethers is indicative of a reaction occurring stepwise,<sup>16,17</sup> the rate-determining step being preceded by at least one fast equilibrium, whereby the expected increase in rate for the slow step with increasing temperature would be neutralized by a shift of the preceding equilibrium (or equilibria) towards the reactants. It also indicates that the rate-determining step is not just the final transfer of a proton from the zwitterionic intermediate to the catalysing amine, but that this is preceded by a process controlled by some geometric factors, presumably the formation of a hydrogen-bonded or a somewhat properly oriented complex. The observed zero activation energies (or negative activation enthalpies) require that the formation of the weak complex is exothermic to the extent of some  $\text{kJ mol}^{-1}$ .

**Table 1.** Influence of concentration and temperature on the reactions of X-phenyl 2,4,6-trinitrophenyl ethers with aniline in benzene

X	$10^2[\text{C}_6\text{H}_5\text{NH}_2]/\text{M}$	$10^3 k_A/\text{l mol}^{-1} \text{s}^{-1}$			
		5 °C	15 °C	25 °C	35 °C
2-NO <sub>2</sub> <sup>a</sup>	2.0	20.5	20.5	20.5	20.5
	4.0	33.0	33.0	33.0	33.0
	6.0	53.3	53.3	53.3	53.3
	8.0	81.4	81.4	81.4	81.4
3-NO <sub>2</sub> <sup>a</sup>	18.0	5.18	5.18	5.18	5.18
	20.0	6.20	6.20	6.20	6.20
	22.5	7.69	7.69	7.69	7.69
	25.0	9.32	9.32	9.32	9.32
4-NO <sub>2</sub> <sup>a</sup>	18.0	4.75	4.75	4.75	4.75
	20.0	5.70	5.70	5.70	5.70
	22.5	7.07	7.07	7.07	7.07
	25.0	8.60	8.60	8.60	8.60
2,4-(NO <sub>2</sub> ) <sub>2</sub> <sup>b</sup>	1.0	27.0	35.6	44.5	54.3
	2.0	47.0	64.5	82.5	100.9
	3.0	67.0	93.0	120.0	148.5
	4.0	86.8	121.5	157.5	195.3
3,4-(NO <sub>2</sub> ) <sub>2</sub> <sup>b</sup>	8.0	8.3	11.7	14.9	18.3
	10.0	10.1	14.4	18.4	22.6
	12.0	12.1	17.2	22.0	27.2
	14.0	14.1	20.1	25.7	31.6
2,5-(NO <sub>2</sub> ) <sub>2</sub> <sup>b</sup>	4.0	25.8	31.1	36.0	41.0
	6.0	37.0	44.5	52.2	59.8
	8.0	47.8	57.8	68.0	78.2
	10.0	58.5	71.5	84.0	96.5
2,6-(NO <sub>2</sub> ) <sub>2</sub> <sup>c</sup>	0.25	448.0	724.0	996.0	1411.0
	0.50	448.0	724.0	996.0	1411.0
	0.75	448.0	724.0	996.0	1411.0
	1.0	448.0	724.0	996.0	1411.0

<sup>a</sup> [Substrate]  $5.0 \times 10^{-4}\text{M}$ . <sup>b</sup> [Substrate]  $2.5 \times 10^{-4}\text{M}$ . <sup>c</sup> [Substrate]  $1.25 \times 10^{-4}\text{M}$ .

**Table 2.** Values of intercepts and slopes of the plot of  $k_A$  versus [aniline]<sup>2</sup> for the reactions of mono-substituted phenyl 2,4,6-trinitrophenyl ethers in benzene at different temperatures

X	$r^a$	$10^4 k' b/\text{l mol}^{-1} \text{s}^{-1}$	$10 k_m'' b/\text{l}^3 \text{mol}^{-3} \text{s}^{-1}$
2-NO <sub>2</sub>	0.9999	166	101
3-NO <sub>2</sub>	0.9999	7.02	1.38
4-NO <sub>2</sub>	0.9999	5.89	1.28

<sup>a</sup> Linear correlation coefficient. <sup>b</sup> Same for all four temperatures 5, 15, 25, and 35 °C.

Nudelman's mechanism on the other hand explains the zero (or negative) activation energies simply in terms of a pre-equilibrium ( $2\text{B} \rightleftharpoons \text{BB}$ ) involving the monomer and the dimer, which is regarded as being affected by temperature in an inverse manner, but what happens to this equilibrium in cases where the dimer mechanism is not observable is a point still to be explained. Our present and previous results<sup>6,7,18,\*</sup> are satisfactorily explained in terms of the intermediate formation of a weak complex (involving the zwitterion intermediate and

\* In ref. 7, the  $k_A$  values at 35 °C for X = *m*-OMe were mistakenly recorded in Table 1 as 12.3, 16.0, 20.3, and 25.0 (the squares of the amine concentrations used) in place of the observed values of 15.75, 20.50, 25.90, and 31.90 respectively. This error is regretted. However, in all calculations involving the amine, the correct values were used.

one or two amine molecules as the case may be) within which the reactant molecules can rotate into a suitable orientation where inter- or intra-hydrogen bonding is possible, thus resulting in a cyclic transition state. The need for the cyclic mechanism is that non-polar aprotic solvents are unable to stabilize highly ionic transition states present in Bunnett's mechanism<sup>2</sup> but are suitable to promote a cyclic mechanism which allows a non-ion generating decomposition of the zwitterionic intermediate into products. The mechanism is similar to that proposed by Capon and Rees<sup>19</sup> for the reaction of piperidine with 2,4-dinitrofluorobenzene in benzene. It is also related to bifunctional catalysis described by Bitter and Zollinger<sup>20</sup> for the reaction of 2,4,6-trichloro-1,3,5-triazine with aniline in benzene. Our results show that in a non-polar aprotic solvent like benzene nucleophilic aromatic substitution involving primary amines and substrates with fairly poor leaving groups will proceed predominantly by a catalysed path through a cyclic transition state involving an eight-membered ring (II'') (Scheme) formed by inter-hydrogen bonding between the zwitterionic intermediate (I) and two amine molecules acting bifunctionally, one as a proton donor to the leaving group (electrophilic catalysis) and the other as a proton acceptor from the positively charged nitrogen of the zwitterion (base catalysis). With a not specially good leaving group, the reactions still proceed by the catalysed path but now through a cyclic transition state involving a six-membered ring (II') (Scheme) formed by a similar inter-hydrogen bonding between the zwitterion intermediate (I) and only one amine molecule also acting bifunctionally.

With a fairly good leaving group, however, the reaction is not likely to be base-catalysed and will proceed through a cyclic transition state involving a four-membered ring (II) (Scheme) formed only by the zwitterion intermediate (I) through intra-hydrogen bonding. These three cases are typified by the reactions of 3-nitro-, 3,4-dinitro-, and 2,6-dinitrophenyl 2,4,6-trinitrophenyl ethers, respectively, in which the phenoxide portion becomes progressively a better leaving group due to the increasing activating effects of the nitro groups in the respective positions of the phenoxide component of the ether.

Taking the respective equilibria in the Scheme into consideration the rates of the three classes of reactants are given by equations (15) ( $k''_m = k_6 K_4 K_4$ ), (16) ( $k''_d = k_5 K_1 K_3$ ), and (17) ( $k' = k_4 K_1 K_2$ ).

base-catalysed mononitro-substituted phenyl ethers

$$\begin{aligned} \text{Rate} &= k_6[(\text{II}'')] = k_6 K_4 (\text{I}) [\text{RNH}_2]^2 \\ &= k_6 K_1 K_4 [\text{Ether}] [\text{RNH}_2]^3 \\ &= k''_m [\text{Ether}] [\text{RNH}_2]^3 \end{aligned} \quad (15)$$

base-catalysed dinitro-substituted phenyl ethers

$$\begin{aligned} \text{Rate} &= k_5[(\text{II}')] = k_5 K_3 (\text{I}) [\text{RNH}_2] \\ &= k_5 K_1 K_3 [\text{Ether}] [\text{RNH}_2]^2 \\ &= k''_d [\text{Ether}] [\text{RNH}_2]^2 \end{aligned} \quad (16)$$

uncatalysed ether

$$\begin{aligned} \text{Rate} &= k_4[(\text{II})] = k_4 K_1 K_2 [\text{Ether}] [\text{RNH}_2] \\ &= k' [\text{Ether}] [\text{RNH}_2] \end{aligned} \quad (17)$$

The situation with secondary amines like morpholine and piperidine with substrate with a fairly poor leaving group had been found by us to be somewhat different<sup>18</sup> as the catalysis of their reactions involves only one amine molecule in the cyclic transition state.

The fact that the phenoxide group of the 2,6-dinitro substituted phenyl ether is a fairly good leaving group is partly attributable to the steric compressions in the intermediate complex (I)<sup>11,21</sup> when this ether is the substrate thus facilitating

**Table 3.** Values of intercepts and slopes of the plot of  $k_A$  versus [aniline] for the reactions of disubstituted phenyl 2,4,6-trinitrophenyl ethers in benzene at different temperatures

X	$r^a$	$10^4 k' / \text{l mol}^{-1} \text{ s}^{-1}$	$10^2 k_A' / \text{l}^2 \text{ mol}^{-2} \text{ s}^{-1}$			
			5 °C	15 °C	25 °C	35 °C
2,4-(NO <sub>2</sub> ) <sub>2</sub>	0.9999	71.0	199	286	377	471
3,4-(NO <sub>2</sub> ) <sub>2</sub>	0.9999	4.5	9.72	14.0	18.0	22.3
2,5-(NO <sub>2</sub> ) <sub>2</sub>	0.9999	41.6	54.5	67.3	79.9	92.5

<sup>a</sup> Linear correlation coefficient. <sup>b</sup> Same for all four temperatures.

**Table 4.** Activation parameters for the reactions of nitro-substituted phenyl 2,4,6-trinitrophenyl ethers with aniline in benzene

Substituent	$r^a$	$E_A / \text{kJ mol}^{-1}$	$\Delta H^\ddagger / \text{kJ mol}^{-1}$	$\Delta S^\ddagger / \text{J mol}^{-1}$
2-NO <sub>2</sub>		0	-2.48	-234 ± 0.51 <sup>b</sup>
3-NO <sub>2</sub>		0	-2.48	-270 ± 0.03
4-NO <sub>2</sub>		0	-2.48	-270 ± 0.03
2,4-(NO <sub>2</sub> ) <sub>2</sub>	0.9961	20.30 ± 0.16 <sup>b</sup>	17.82 ± 0.16 <sup>b</sup>	-174 ± 3.06
3,4-(NO <sub>2</sub> ) <sub>2</sub>	0.9957	19.72 ± 0.16	17.24 ± 0.16	-201 ± 3.06
2,5-(NO <sub>2</sub> ) <sub>2</sub>	0.9998	12.56 ± 0.10	10.08 ± 0.10	-213 ± 1.91
2,6-(NO <sub>2</sub> ) <sub>2</sub>	0.9986	27.19 ± 0.21	24.71 ± 0.21	-168 ± 4.02

<sup>a</sup> Linear correlation coefficient. <sup>b</sup> Standard deviations. <sup>c</sup> At 25 °C.

conversion into products. This steric factor could also be partly responsible apart from the large  $-I$  effect of the NO<sub>2</sub> group for the faster rate of the 2-nitro-substituted phenoxide over those of the other monosubstituted ones and also the faster rates of the 2,4- and 2,5-dinitro-substituted phenyl ethers over that of the 3,4-dinitro-substituted ether (Table 1).

Save for this aberration, the reactivity of these ethers follows the normal order for substituents in the benzene ring, the 3'-nitro- being faster than the 4'-nitro-substituted phenyl ether due to the greater  $-I$  effect while the dinitro-substituted phenyl ethers are generally faster than the mononitro-substituted ones.

The activation parameters for the reactions are reported in Table 4 with their linear correlation coefficients and standard deviations. The figures for the  $E_A$  values were obtained from the temperature-dependent catalytic rate coefficients  $k_A'$  (Table 3) except that for the uncatalysed ether which was obtained from its  $k_A$  values (Table 1). The reactions as in the previous case<sup>7</sup> are accompanied by negative activation entropies since the formation of an encounter complex and of a defined aggregate is usually accompanied by a loss in entropy. It can be seen that the negative values for the mononitro-substituted phenyl ethers are greater than those of the dinitro-substituted ones, the value for the uncatalysed 2,6-dinitro-substituted phenyl ether being the smallest. This no doubt follows the order of the size of the cyclic transition state involving the ethers, those ethers proceeding through the eight-membered-ring transition state having the most negative values for the activation entropies while that proceeding through a four-membered ring has the least negative value. The negative value is dependent on the number of reactant molecules brought into an orderly arrangement in the transition state.

## Experimental

**Materials.**—The nitro-substituted phenyl 2,4,6-trinitrophenyl ethers were prepared by methods similar to that earlier reported<sup>7</sup> for phenyl 2,4,6-trinitrophenyl ether by using the appropriate substituted phenol in place of phenol. The m.p. in each case agreed with literature values. Data for new ethers (crystallized from glacial acetic acid) are as follows: 3,4-dinitrophenyl 2,4,6-trinitrophenyl ether, m.p. 202 °C (Found: C, 36.4; H, 1.3; N, 17.75. C<sub>12</sub>H<sub>5</sub>N<sub>5</sub>O<sub>11</sub> requires C, 36.5; H, 1.3; N,

17.7%); 2,5-dinitrophenyl 2,4,6-trinitrophenyl ether, m.p. 243 °C (Found: C, 36.4; H, 1.3; N, 17.8%); 2,6-dinitrophenyl 2,4,6-trinitrophenyl ether, m.p. 207–208 °C (Found: C, 36.5; H, 1.25; N, 17.6%). AnalaR benzene and aniline were also purified by standard methods.

**Kinetic Measurements.**—The kinetics were followed spectrophotometrically by the pipette procedure previously described.<sup>7</sup> With all the ethers, excellent pseudo-first-order plots were obtained up to at least 70% reaction and the absorption spectrum of each reaction mixture at 'infinite time' corresponded within 2% to the 'mock infinity' prepared by using 2,4,6-trinitrophenylaniline obtained as product. The second-order rate constants  $k_A$  were obtained by dividing the pseudo-first-order rate constants by the aniline concentration. All rates were usually run in duplicate but in quadruplicate (for exactness) in cases where the rates were found to be constant either with increasing concentration or temperature. The rate constants are accurate to within ±2%. Though the substrate concentrations were kept constant for the reactions of each substrate, it was found necessary either for reasons of solubility or exceedingly fast rates to use different values for some of the substrates (see Table 1). At temperatures other than 25 °C, the rate constants were corrected for thermal expansion or contraction of the solvent. The activation parameters were calculated from a least-squares treatment of  $\log k_A$  against  $1/T$ .

**Product Analysis.**—Each nitro-activated ether was treated with about twice its molar quantity of aniline in benzene at room temperature until t.l.c. showed the complete disappearance of the starting ether. Besides phenol and 2,4,6-trinitrophenyl aniline, no other product was detected in the reaction either by t.l.c. or u.v. spectroscopy.

The volume of each solution was reduced to about a third (by removing the solvent under reduced pressure at ca. 30 °C) to allow for the precipitation of one of the products, 2,4,6-trinitrophenylaniline. This was then crystallized from glacial acetic acid and then toluene and dried, m.p. 181–182 °C (lit.,<sup>22</sup> 182 °C).

The remaining solution was boiled with 2% HCl for ca. 10 min then filtered through a preheated Buchner funnel and the filtrate allowed to crystallize overnight. The phenols were

recrystallized from alcohol and dried to constant melting points. The m.p.s of the phenols agreed with literature values.

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