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Catalytic effects of hydrogen-bond acceptor solvent on nucleophilic aromatic substitution reactions in non-polar aprotic solvent: reactions of phenyl 2,4,6-trinitrophenyl ether with amines in benzene-acetonitrile mixtures

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Abstract—The effect of addition of small amounts of hydrogen-bond acceptor solvent, acetonitrile, to the benzene medium of the reactions of phenyl 2,4,6-trinitrophenyl ether with aniline and cyclohexylamine, respectively have been investigated. The addition produced similar effects in the two reactions—continuous rate increase with increasing amounts of acetonitrile. The results are interpreted in terms of the effect of amine–solvent interaction on the nucleophilicity of the amines and are in accord with our expectations based on the effects observed for hydrogen-bond donor solvent, methanol on the same reactions. It is also established from the results that the role of hydrogen-bond acceptor co-solvent could be played by an added more basic non-nucleophilic amine.

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1. Introduction

Some unusual findings in the kinetics of aromatic nucleophilic substitution reactions in non-polar aprotic solvents reported in the literature in recent times include the sometimes observed third-order dependence of the second-order rate constant, k_A , on amine concentrations.^{1–7} As a result of this, a number of mechanisms have been proposed. Attempts have thus been made by some authors to provide support for their proposed mechanisms. Remarkable among these attempts is the study of the effects of added hydrogen-bond donor and hydrogen-bond acceptor co-solvents on such reactions in benzene⁸⁻¹¹ and toluene.^{12,13} Having successfully studied and rationalised the sometimes conflicting effects of hydrogen-bond donor co-solvent, methanol, on S_NAr reactions in non-polar aprotic solvent, benzene,^{8,9} and toluene,^{12,13} we found it necessary to investigate also the effect of hydrogen-bond acceptor solvent on these reactions so as to have an overall view of the mechanisms of the reactions involving these two different types of solvents in non-polar aprotic medium. Examination of the literature reveals that only few cases of the effect of hydrogen-bond acceptor (hba) co-solvent on

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 S_NAr reactions in non-polar aprotic solvents have been reported. Surh¹⁴ studied the reaction of p-fluoronitrobenzene with piperidine in benzene–DMSO mixtures while Bernasconi and Zollinger¹⁵ studied the reaction of 2,4-dinitrochloro- and 2,4,-dinitrifluorobenzene in benzene– DMSO mixtures. The latest report was by Nudelman and Palleros¹⁶ on the reaction of 2,6-dinitroanisole with cyclohexylamine in toluene–DMSO mixtures. As in the case of hydrogen-bond donor co-solvent methanol, treated in our last paper,⁸ we have decided to investigate in detail the effects of addition of small amounts of another hydrogen bond acceptor co-solvent, acetonitrile, on the reaction of 2,4,6-trinitrophenyl ether (PTPE) with aniline and cyclohexylamine, respectively, the two reactions that have been previously studied by us^{4,9} in pure benzene.

2. Results and discussion

The reaction of aniline is third order in amine,⁴ being catalysed by two aniline molecules while that of cyclohexylamine is first order in amine, as it is not base-catalysed.⁸ Addition of small amounts of acetonitrile to the benzene medium of the respective reactions produced remarkable increases in the rates of the reactions (Tables 1 and 2). Similar observations in the literature include the reactions of 2,4-dinitrofluoro- and 2,4-dinitrochlorobenzenes with piperidine in benzene–dimethyl sulfoxide

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Table 1. Second-order rate constants, k_A for the reaction of phenyl-2,4,6-trinitrophenyl ether with aniline in benzene and benzene–acetonitrile mixtures at 25 °C

[Amine]/mol dm ³	% Acetonitrile (v/v)	$10^3 k_{\rm A} {\rm dm}^3 {\rm mol}^{-1} {\rm s}^{-1}$
0.15	0	5.20
	0.1	6.27
	0.2	7.00
	0.3	7.87
	0.4	8.73
	0.6	10.04
	0.8	12.15
0.20	0	8.40
	0.1	9.85
	0.2	10.95
	0.3	12.05
	0.4	13.40
	0.6	15.80
	0.8	18.15
0.25	0	13.10
	0.1	15.22
	0.2	16.72
	0.3	18.50
	0.4	20.04
	0.6	23.92
	0.8	26.70
0.30	0	19.00
	0.1	21.30
	0.2	23.50
	0.3	25.90
	0.4	28.53
	0.6	32.12
	0.8	36.50

 $[Substrate] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}.$

Table 2. Second-order rate constants, k_A for the reaction of phenyl-2,4,6-trinitrophenyl ether with cyclohexylamine in benzene–acetonitrile mixtures at 25 °C

[Amine]/mol dm ³	% Acetonitrile (v/v)	$10^3 k_{\rm A} {\rm dm}^3 {\rm mol}^{-1} {\rm s}^{-1}$		
25×10^{-4}	0	12.84		
	0.1	13.96		
	0.2	14.92		
	0.3	15.96		
	0.4	16.88		
	0.6	17.88		
	0.8	18.80		

 $[Substrate] = 2.5 \times 10^{-5} \text{ mol dm}^{-3}.$

(DMSO) mixtures by Bernasconi and Zollinger.¹⁵ The reaction of the fluoro-substrate is second order in amine while that of the chloro is first order. Nudelman and Palleros¹⁶ also observed similar increases in the rate of the reaction of 2,6-dinitroanisole with cyclohexylamine in toluene–DMSO mixtures. The above observations show that added hydrogen-bond acceptor solvents produce an increase in rates of S_NAr reactions in non-polar aprotic medium irrespective of whether the reaction is base-catalysed or not. This is unlike the case of hydrogen-bond donor co-solvent where conflicting effects were observed for base-catalysed and non-base catalysed reactions.⁸

2.1. Cause of rate increase

An in-depth study of the interaction of amine with added hydrogen-bond acceptor solvent, DMSO, was carried out by Angella and Scott.¹⁷ Using Bronsted-acid–base studies involving some amines with *p*-nitrophenol in benzene–

DMSO solvent system, these researchers established that DMSO, when present as a solvent, does increase the effective basicity of primary and secondary amines and that this is achieved through the formation of hydrogen-bond between amine hydrogens and DMSO thus:

$$RNH_2 + SO(CH_3)_2 \rightleftharpoons RHNH \cdots OS(CH_3)_2$$
(1)

Such aggregates should also be possible with other hydrogen-bond acceptor solvents, for example, acetonitrile used in the present study as show in Eq. 2,

$$RNH_2 + CH_3CN \stackrel{\wedge}{=} CH_3CN \cdots HNHR$$
(2)

where *K* is the association constant for aggregate formation.

The amine in the aggregate formed in Eq. 2 will be a better nucleophile than the free amine because of the increased nucleophilicity of the amine-acetonitrile aggregate. It is therefore proposed that the amine-acetonitrile aggregate of enhanced nucleophilicity attacks the substrate in the first step of the S_NAr reaction to produce the observed rate increase.

2.2. Catalysis by acetonitrile

Addition of small amounts of acetonitrile (0.019–0.153 M) to the benzene medium of the reaction of PTPE with cyclohexylamine caused a gradual increase in the second order rate constant, k_A (Table 2) with initial value being k_1 =12.84 mol⁻¹ s⁻¹, the rate constant for the non-base catalysed reaction in pure benzene. These observed increases in rate are due to the increased nucleophilicity of the amine in the amine-acetonitrile aggregate which attacks the substrate in the first step of the two-step S_NAr reaction, as well as the catalytic effect of acetonitrile on the reaction involving the remaining free amine with the substrate.

In earlier studies of S_NAr reactions carried out in benzene-DSMO mixtures by Bernasconi and Zollinger,¹⁵ and by Suhr,¹⁴ a considerable increase in reaction rate was observed in each case for small additions of hydrogenbond acceptor solvent (hba) to the reaction medium. The rate increase was considered to exceed that expected based on the probable increase in the dielectric constant of the aprotic medium. Bernasconi ruled out base catalysis because the pK_a of DMSO in water is zero. Suhr, on the other hand, attributed the increase to a sort of base catalysis. We also rule out base catalysis for the following reason: the reaction of PTPE with cyclohexylamine which was found not to be base-catalysed in our last paper⁸ has been found to be catalysed by the hba solvent, acetonitrile, in the present investigation. Since base catalysis occurs in the second step of S_NAr reactions, it means that the acetonitrile catalysis could only be taking place in the first step of the S_NAr reaction.

There is of course no doubt that the effect being observed is a form of catalysis because firstly, the interaction of the hba solvent with the amine results in increase in the rate of reaction and secondly, the increase in rate is proportional to the concentration of the added hba solvent. This is thus catalysis resulting from the enhanced nucleophilicity of the amine in the formed amine-solvent aggregate which will be reflected in the enhanced value of the first step rate constant k'_1 (compared to that of the free amine k_1) and the catalytic effect of the co-solvent, acetonitrile on the reaction of the substrate with the remaining free base, aniline, which will be reflected in the catalytic rate constant $k^{CH_3CN}_3$.

2.3. Mechanism of the base-catalysed reaction

As in the previously studied reaction involving methanol addition,⁸ S_NAr reactions in non-polar aprotic solvents on addition of a small amount of acetonitrile can be assumed to involve the attack of the amine-acetonitrile aggregate, as well as the free amine, on the substrate to produce the zwitterionic intermediate. Since amine-acetonitrile aggregate formation via hydrogen bonding is likely to be a very rapid equilibrium process, two possible roots for conversion of the zwitterionic intermediate into products are proposed. The reaction of phenyl 2,4,6-trinitrophenyl ether with aniline in benzene-acetonitrile mixtures (at low acetonitrile concentrations) can be represented by Scheme 1, where S stands for the substrate, B for the base, $B \cdots NCCH_3$ for the amine-acetonitrile aggregate, [SB] for the zwitterionic intermediate and k'_1 , the enhanced first-step rate constant involving the attack of the amine-acetonitrile aggregate on the substrate, $k_3^{CH_3CN}$, the rate constant for the acetonitrilecatalysed reaction of the substrate with the remaining free amine and $k_3^{\rm B}$, the amine catalytic rate constant for the conversion of the zwitterionic intermediate into products.





Since the amine may exist in free or hydrogen-bonded forms as given by Eq. 2, the stoichiometric measured concentration, B_{Stoich} will be related to the free base [B]_{Free} by Eq. 3.

$$[B \cdots NCCH_3] + [B]_{Free} = [B]_{Stoich}$$
(3)

From Eqs. 2 and 3, the unmeasurable quantities $[B \cdots NCCH_3]$ and $[B]_{Free}$ are derived in terms of the measurable quantity $[B]_{Stoich}$.

Application of the steady-state hypothesis to Scheme 1 in terms of the stoichiometric base concentration leads to Eq. 4 for the observed overall rate-constant k_A ,

$$k_{\rm A} = \frac{\frac{k_1' K[{\rm CH}_3{\rm CN}]}{1+K[{\rm CH}_3{\rm CN}]} + \frac{k_1}{1+K[{\rm CH}_3{\rm CN}]} + \frac{k_{{\rm CH}_3{\rm CN}]}({\rm CH}_3{\rm CN}]}{1+K[{\rm CH}_3{\rm CN}]} \left(k_2 + \frac{k_3[{\rm B}]^2}{(1+K[{\rm CH}_3{\rm CN}])^2}\right)}{k_{-1}'[{\rm CH}_3{\rm CN}] + k_{-1} + k_2 + \frac{k_3^3[{\rm B}]^2}{1+K[{\rm CH}_3{\rm CN}]^2}}$$
(4)

where [B] is the total (stoichiometric) base concentration and *K* is the association constant for amine-acetonitrile aggregate formation. At low base concentration,

$$(1 + K[CH_3CN])^2 \approx (1 + K[CH_3CN])$$

in Eq. 4.

For the base-catalysed reaction, when the second step is rate-determining, Eq. 5 holds

$$k'_{-1}[CH_3CN] + k_{-1} \gg k_2 + \frac{k_3^B[B]^2}{1 + K[CH_3CN]^2}$$
 (5)

and Eq. 4 becomes Eq. 6.

$$k_{\rm A} = \frac{\frac{k_1' K[{\rm CH}_3{\rm CN}]}{1+K[{\rm CH}_3{\rm CN}]} + \frac{k_1}{1+K[{\rm CH}_3{\rm CN}]} + \frac{k_{{\rm CH}_3{\rm CN}}[{\rm CH}_3{\rm CN}]}{1+K[{\rm CH}_3{\rm CN}]} \left(k_2 + \frac{k_3[{\rm B}]^2}{1+K[{\rm CH}_3{\rm CN}]}\right)}{k_{-1}'[{\rm CH}_3{\rm CN}] + k_{-1}}$$
(6)

If we assume that acetonitrile increases the nucleophilicity of the amine considerably, $k'_1 \gg k_1$ and correspondingly, it can also be assumed that $k'_{-1} \gg k_{-1}$

$$\therefore k_{\rm A} = \frac{\frac{k_1' K[{\rm CH}_3{\rm CN}]}{1+K[{\rm CH}_3{\rm CN}]} + \frac{k_1}{1+K[{\rm CH}_3{\rm CN}]} + \frac{k_{{\rm CH}_3{\rm CN}}[{\rm CH}_3{\rm CN}]}{1+K[{\rm CH}_3{\rm CN}]} \left(k_2 + \frac{k_3[{\rm B}]^2}{1+K[{\rm CH}_3{\rm CN}]}\right)}{k_{-1}'[{\rm CH}_3{\rm CN}]}$$
(7)

On expanding and re-arranging, Eq. 7 becomes Eq. 8.

$$k_{\rm A} = \frac{k_1' k_2 K}{k_{-1}'} + \frac{k_1 k_2 K}{k_{-1}'} + \frac{k_2 k_3^{\rm CH_3 CN}}{k_{-1}'} + \left(\frac{k_1' k_2 K^2}{k_{-1}'} + \frac{k_2 k_3^{\rm CH_3 CN} K}{k_{-1}'}\right) [\rm CH_3 CN] + \left(\frac{k_1' k_3^{\rm B} K}{k_{-1}'} + \frac{k_3^{\rm B} k_3^{\rm CH_3 CN}}{k_{-1}'}\right) [\rm B]^2$$
(8)

At constant acetonitrile concentration, this equation reduces to Eq. 9.

$$k_{\rm A} = k' + k'' [{\rm B}]^2 \tag{9}$$

where k' and k'' are defined by Eqs. 10 and 11, respectively.

$$k' = \frac{k_1' k_2 K}{k_{-1}'} + \frac{k_1 k_2 K}{k_{-1}'} + \frac{k_2 k_3^{\text{CH}_3 \text{CN}}}{k_{-1}'} + \left(\frac{k_1' k_2 K^2}{k_{-1}'} + k_2 k_3^{\text{CH}_3 \text{CN}} K\right) [\text{CH}_3 \text{CN}]$$
(10)

$$k'' = \frac{k_1' k_3^B K}{k_{-1}'} + \frac{k_3^B k_3^{\text{CH}_3\text{CN}}}{k_{-1}'}$$
(11)

The plots of k_A against [aniline]² gave straight lines giving credence to Eq. 8. The values of intercepts and slopes are listed in Table 3.

When the amine concentration is kept constant, while the acetonitrile concentration is varied, Eq. 12, becomes applicable.

$$k_{\rm A} = k' + k'' [\rm CH_3 \rm CN] \tag{12}$$

Table 3. Values of intercepts and slopes of the plots of k_A against [aniline]² at constant acetonitrile concentrations for the reaction of phenyl 2,4,6-trinitrophenyl ether with aniline in benzene–acetonitrile mixtures

% Acetonitrile	$10^4 k' / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^2 k'' \mathrm{dm^6/mol^{-2} s^{-1}}$		
0.1	1.09	2.24		
0.2	1.32	2.46		
0.3	1.59	2.69		
0.4	1.85	2.94		
0.6	2.75	3.29		

where k'	and k''	are	given	by	Eqs.	13	and	14,	respe	ctivel	y.
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$$k' = \frac{k_1' k_2 K}{k_{-1}'} + \frac{k_1 k_2 K}{k_{-1}'} + \frac{k_2 k_3^{\text{CH}_3 \text{CN}}}{k_{-1}'} + \left(\frac{k_1 k_3^{\text{B}} K}{k_{-1}'} + \frac{k_3^{\text{B}} k_3^{\text{CH}_3 \text{CN}}}{k_{-1}'}\right) [\text{B}]^2$$
(13)

$$k'' = \frac{k_1' k_2 K^2}{k_{-1}'} + \frac{k_2 k_3^{\text{CH}_3\text{CN}} K}{k_{-1}'}$$
(14)

The plots of k_A against [acetonitrile] gave straight lines in accordance with Eq. 12. The values of the intercepts and slopes with the correlation coefficients are listed in Table 4.

Table 4. Values of intercepts and slopes of the plots of k_A against [acetonitrile] at constant aniline concentrations for the reaction of phenyl 2,4,6-trinitrophenyl ether with aniline in benzene–acetonitrile mixtures at 25 °C

[Aniline]/mol ⁻¹	$10^2 k' / \text{mol}^{-1} \text{ s}^{-1}$	$10^2 k'' \mathrm{dm^6/mol^{-2} s^{-1}}$	r	
0.15	0.538	4.30	0.999	
0.20	0.8581	6.25	0.998	
0.25	1.347	8.76	0.9998	
0.30	1.933	11.25	0.9988	

2.4. Mechanism of the reaction that is not base-catalysed

For the reaction of PTPE with cyclohexylamine which is not base-catalysed, but is catalysed by acetonitrile, Scheme 2 applies.



Application of steady-state hypothesis to Scheme 2, working in terms of the stoichiometric base concentration gives the observed overall second order rate constant k_A as

$$k_{\rm A} = \frac{k_2 \left(\frac{k_1' K[{\rm CH}_3 {\rm CN}]}{1+K[{\rm CH}_3 {\rm CN}]}\right) + \frac{k_1}{1+K[{\rm CH}_3 {\rm CN}]} + \frac{k_3^{{\rm CH}_3 {\rm CN}}[{\rm CH}_3 {\rm CN}]}{1+K[{\rm CH}_3 {\rm CN}]}}{k_{-1}' [{\rm CH}_3 {\rm CN}] + k_{-1} + k_2}$$
(15)

Since the reaction is not base-catalysed, the first step is

rate-determining and the inequality in Eq. 16 holds.

$$k_2 \gg k'_{-1}[CH_3CN] + k_{-1}$$
 (16)

$$k_{\rm A} = \frac{k_1' K[{\rm CH}_3 {\rm CN}] + k_1 + k_3^{\rm CH}_3 {\rm CN}[{\rm CH}_3 {\rm CN}]}{1 + K[{\rm CH}_3 {\rm CN}]}$$

At low acetonitrile concentration, $1 + K[CH_3CN] \approx 1$

$$\therefore k_{\rm A} = k_1 + (k_1' K + k_3^{\rm CH_3CN}) [\rm CH_3CN]$$
(17)

The reaction of PTPE with cyclohexylamine in benzene is not base-catalysed but is catalysed by acetonitrile and so conforms with Scheme 2 and Eq. 17 derived from it.

A plot of the second-order rate constant k_A against [acetonitrile] thus gives a straight line with the intercept k_1 being 12.84×10^{-3} dm³ mol⁻¹ s⁻¹ and slope given by $k'_1K + k_3^{CH_3CN}$, showing that the reaction is catalysed by acetonitrile.

When no acetonitrile is present in the reaction medium Eq. 17 reduces to Eq. 18.

$$k_{\rm A} = k_1 \tag{18}$$

The observed rate constant then becomes equal to the rate constant for the formation of the zwitterionic intermediate complex in the first step of the reaction in pure benzene, as is usually the case with non base-catalysed reactions.

2.5. Other hydrogen-bond acceptors

Other hydrogen-bond acceptors such as triethylamine or pyridine, being stronger bases with high pK_a values, 11.01 and 5.58, respectively, can easily act as hydrogen-bond acceptors by forming aggregates with weaker amines like aniline (pK_a , 4.61). These aggregates will be similar to that proposed for acetonitrile and aniline (Eq. 2). The formed amine–amine aggregate [$R_3N\cdots$ HNHR] can further use the second proton on the aniline to engage in similar hydrogenbond formation with a second tertiary amine molecule thus:

$$2R_3N + RNH_2 \stackrel{\wedge}{\rightleftharpoons} R_3N \cdots HNRH \cdots NR_3$$
(19)

where K is the association constant for the aggregate formation.

The aggregate formed in Eq. 19 will be a better nucleophile than that of the free amine molecule. It is this new aggregate with much enhanced nucleophilicity that now attacks the substrate in the first step of the S_NAr reaction to give the intermediate complex shown in Scheme 3, where S stands for the substrate, B for the base, and SB for the zwitterionic intermediate.

Scheme 3 is similar to Scheme 1 except that two molecules of hydrogen-bond acceptor (non-nucleophilic amine) are involved in aggregate formation with the nucleophilic amine.

Application of the steady-state hypothesis to Scheme 3 with the necessary assumptions gives the observable second-order rate constant k_A as shown in Eq. 20.



Scheme 3.

$$k_{\rm A} = \frac{k_1' k_2 K}{k_{-1}'} + \frac{k_1 k_2 K}{k_{-1}'} + \frac{k_2 k_3^{\rm R_3 N}}{k_{-1}'} + \left(\frac{k_1' k_2 K^2}{k_{-1}'} + \frac{k_2 k_3^{\rm R_3 N} K}{k_{-1}'}\right) [\rm R_3 N]^2 + \left(\frac{k_1' k_3^{\rm B} K}{k_{-1}'} + \frac{k_3^{\rm B} k_3^{\rm R_3 N}}{k_{-1}'}\right) [\rm B]^2$$
(20)

A plot of k_A against $[R_3N]^2$ should therefore give a straight line thus giving credence to the fact that two molecules of the non-nucleophilic amine as well as two molecules of the nucleophilic amine (aniline) are involved in the catalysis of the reaction.

This thus explains the kinetic behaviour observed by Nudelman and Montsserat in their reaction of 2,4dinitrofluorobenzene with aniline in toluene when a nonnucleophilic amine such as pyridine was added as catalyst.¹³ It is thus obvious that these authors' assertions¹² that such kinetic behaviour could not be explained by the mechanism of Banjoko et al. but by only the 'dimer nucelophile' mechanism is clearly erroneous as already established in our previous paper.⁸

3. Conclusion

Addition of hydrogen-bond acceptor solvent to S_NAr reactions involving a substrate and an amine in non-polar aprotic solvent results in the formation of amine-solvent aggregates of increased nucleophilicity thus causing an increase in the rate of reaction in addition to its catalytic effect. The role of the hydrogen-bond acceptor co-solvent could, however, be played by the addition of a more basic non-nucleophilic amine, that is, one having a higher pK_a than the nucleophilic amine. The resulting amine–amine aggregate will be a better nucleophile than the nucleophilic amine.

4. Experimental

Phenyl 2,4,6-trinitrophenyl ether (PTPE) was prepared by the reaction of potassium phenolate with picril chloride in aqueous ethanol. The product was precipitated with water and recrystallised from ethanol.¹⁸ Aniline was dried over potassium hydroxide for 3 days and twice distilled over Zn powder (bp 182–183°C, lit.¹⁹ 184°C). Cyclohexylamine was heated under reflux for 6 h and then distilled. The process was repeated twice and the middle fraction distilling at 132 °C was collected (lit. 132–133 °C).¹⁹ Analar acetonitrile (500 cm³) was poured over phosphorous pentoxide in a 1-dm³ round bottomed flask, refluxed for 3 h and then distilled. The process was repeated twice and the fraction that distilled at 81 °C was collected and stored in a dessicator (lit.¹⁹ bp 81 °C). Reaction products were prepared by the reaction of the substrate with twice its molar concentration of the appropriate amine in benzene. The volume of each reaction was reduced to about a third to allow the precipitation of the product.

N-(2,4,6-Trinitrophenyl)aniline was crystallised from glacial acetic acid and then toluene, mp 181 °C (lit.²⁰ 181–182 °C), λ_{max} (C₆H₆) 370 nm.

N-(2,4,6-Trinitrophenyl)cyclohexylamine was crystallised from toluene, mp 90–91 °C (lit.²⁰ 181–182 °C), λ_{max} (C₆H₆) 370 nm.

Kinetic procedure. The reactions were studied spectrophotometrically under conditions of excess nucleophile over substrate by measuring the increase in absorbance of the product of the reaction of each amine at the respective absorption maximum. The reaction of aniline with the substrate was carried out using pipette procedure. Solutions of PTPE (25 cm^3 , $1.0 \times 10^{-3} \text{ mol dm}^{-3}$) and aniline (50 cm^3 , 1.5×10^{-1} to 3.0×10^{-1} mol dm⁻³) were allowed separately to attain 29 °C in a thermostated bath. The aniline solution (25 cm³) was quickly transferred into the substrate solution and thoroughly mixed. A 2 cm³ aliquots of the reaction mixture was immediately pipetted and added to 20 cm^3 of quenching mixture (1 mol dm⁻³ H₂SO₄/methanol solution) in a small container. The instant of addition of the aliquot to the quenching mixture was noted as the initial time (zero time) for the reaction. Ten of such aliquots were afterwards pipetted at regular time intervals, t, and each added to 20 cm³ of the quenching mixture. The absorbance of each quenched reaction mixture was determined. The reaction of cyclohexylamine with the substrate (which was much faster) was monitored directly in the spectrophotometer. For reactions in mixed solvents, the acetonitrile content (v/v) refers to its final volume in the reaction mixture. In all cases the absorption spectrum of the reaction mixture at 'infinity time' corresponded within 2% of the 'mock' infinity prepared by using the respective N-(2,4,6trinitrophenyl)amine obtained as a product of the reaction. The observed pseudo-first-order rate constants were obtained by the least squares method as the slope of the correlation $\log(A_{\infty} - A_t)$ against t, where A_{∞} is the optical density of the reaction solution measured at 'infinity' time (more than 10 half lives). In all cases, the reaction followed pseudo-first-order kinetics well to at least 70% reaction. The second-order rate constants k_A were obtained by dividing the pseudo-first-order rate constants by the amine concentrations. All rates were accurate to within $\pm 2\%$.

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References and notes

- Bernasconi, C. F.; Zollinger, H. Helv. Chim. Acta 1966, 49, 2570–2581.
- 2. Bernasconi, C. F.; de Rossi, R. H. J. Org. Chem. 1976, 41, 44-49.
- Bamkole, T. O.; Hirst, J.; Onyido, I. J. Chem. Soc., Perkin Trans. 2 1982, 889–893.
- 4. Banjoko, O.; Ezeani, C. J. Chem. Soc., Perkin Trans. 2 1982, 1357–1360.
- 5. Nudelman, N. S.; Palleros, D. J. Org. Chem. 1983, 48, 1607–1612.
- 6. Nudelman, N. S.; Palleros, D. J. Org. Chem. 1983, 48, 1613–1618.
- 7. Banjoko, O.; Ezeani, C. J. Chem. Soc., Perkin Trans. 2 1986, 531–536.
- 8. Banjoko, O.; Babatunde, I. A. *Tetrahedron* **2004**, *60*, 4645–4654. In Figure 2 of this paper PhO should have been

F and NO₂ in position 6 of the phenyl rings deleted. [B] in Eq. (12) should have been deleted.

- Banjoko, O.; Bayeroju, I. A. J. Chem. Soc., Perkin Trans. 2 1988, 1853–1857.
- Nudelman, N. S.; Palleros, D. J. J. Chem. Soc., Perkin Trans. 2 1984, 1277–1280.
- 11. Nudelman, N. S.; Marder, M.; Gurevich, A. J. Chem. Soc., Perkin Trans. 2 1997, 229–233.
- 12. Nudelman, N. S.; Montserrat, J. M. J. Chem. Soc., Perkin Trans. 2 1990, 1073–1076.
- Nudelman, N. S.; Alvaro, C. E. S.; Yankelevich, Jeanette S. J. Chem. Soc., Perkin Trans. 2 1997, 2125–2130.
- 14. Suhr, H. Chem. Ber. 1963, 67, 893-896.
- 15. Bernasconi, C. F.; Zollinger, H. Helv. Chim. Acta 1966, 49, 103-111.
- Nudelman, N. S.; Palleros, D. J. Chem. Soc., Perkin Trans. 2 1985, 479–484.
- 17. Angella, R.; Scott, R. M. J. Phys. Chem. 1980, 84, 3600-3604.
- Banjoko, O.; Otiono, P. J. Chem. Soc., Perkin Trans. 2 1981, 399–402.
- CRC Handbook of Chemistry and Physics, 53rd ed.; 1972– 1973, p C-106, C-81.
- 20. Wedekind, E. Ber. 1900, 33, vol. I, 432.