Base Catalysis of Aromatic Nucleophilic Substitution Reactions in Aprotic and Dipolar Aprotic Solvents

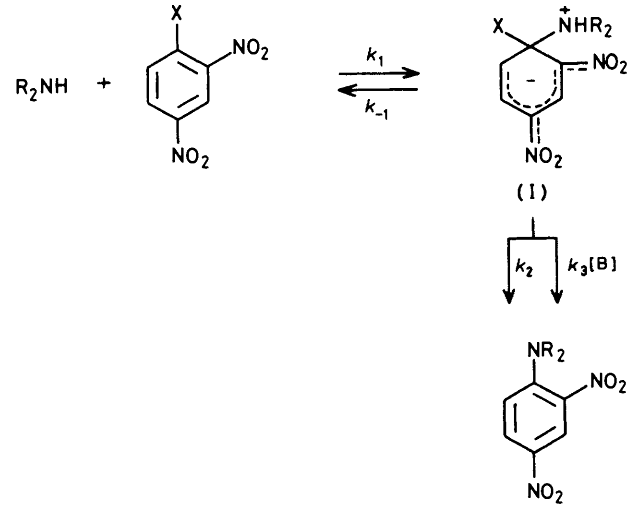
By **Titus O. Bamkole, Jack Hirst,*** and **Ikenna Onyido**, Department of Chemistry, University of Ibadan, Ibadan, Nigeria

For base-catalysed aromatic nucleophilic substitution reactions in benzene, catalysis by added base is observed irrespective of whether the catalyst is a stronger or a weaker base than the nucleophile. In acetonitrile, catalysis is only observed if the catalyst has either approximately the same strength or is a stronger base than the nucleophile. These observations are shown to indicate a difference in the mechanism of catalysis in the two solvents.

THE accepted mechanism for aromatic bimolecular nucleophilic substitution reactions when either primary or secondary amines are the nucleophiles is given in Scheme 1. Application of the steady state hypothesis gives equation (1) where k_A is the observed second-order

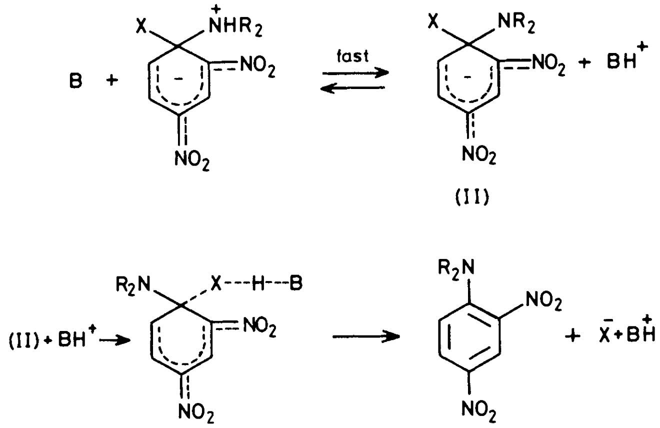
$$k_A = \frac{k_1(k_2 + k_3[B])}{(k_{-1} + k_2 + k_3[B])} \tag{1}$$

rate constant. In principle, either the formation of (I) or its decomposition to products can be rate determining and the two can be distinguished by observing whether the reaction is base catalysed or not. If $k_{-1} \ll k_2 + k_3[B]$, then $k_A = k_1$ and the reaction is not base catalysed. If this condition does not hold, the decomposition of the intermediate to products is rate limiting and the reaction is base catalysed. The catalyst, B, can be either the nucleophile or an added base, and in the latter case when the reaction is carried out in nonaqueous solvents, the two most commonly used are pyridine and 1,4-diazabicyclo[2.2.2]octane (DABCO). A measure of the catalytic power of various bases in a given reaction is given by the magnitude of the k_3/k_2 ratio.



SCHEME 1

The mechanism of the base-catalysed path in dipolar aprotic solvents is believed to be that proposed by Bunnett and Davies [1] and shown in Scheme 2. In this mechanism, the first formed intermediate is rapidly and reversibly converted into its conjugate base from which the slow electrophilically catalysed expulsion of the leaving group takes place. Experimental evidence in support of this mechanism has been given by Orvik and Bunnett [2] and by Ayediran *et al.*[3]



SCHEME 2

In solvents of low dielectric constant such as hydrocarbons it is generally believed that this step takes place by a different mechanism. Capon and Rees [4] proposed the cyclic transition state given in Figure 1 for reactions in benzene and more recently [5] we have suggested a modification of the Bunnett mechanism to take into account the strength and range of electrostatic forces in this type of solvent. To the best of our knowledge there exists no experimental evidence for this belief, the original postulate appears to be based on the assumed need for electrophilic catalysis to assist the departure of poor leaving groups and at the same time, because of the inability of these solvents to stabilise ionic species, avoid

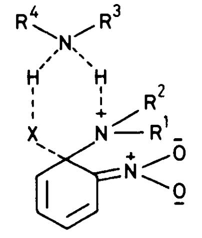


FIGURE 1

the charged entities demanded by the Bunnett mechanism. We now present evidence for a difference in behaviour of catalysts in benzene and acetonitrile which demands either a different mechanism, or at least a modification of the mechanism which operates in dipolar aprotic solvents.

When the solvent is benzene the following results have been reported. Bernasconi and Zollinger have investigated the reactions of 1-fluoro-2,4-dinitrobenzene with a series of nucleophiles. When the nucleophile was piperidine[6] they observed strong catalysis by piperidine, moderate catalysis by DABCO, and weak catalysis by pyridine. The piperidine and DABCO catalysis was interpreted as true base catalysis while that of pyridine was believed to be predominantly a medium effect. Stronger catalysis by pyridine was observed with other nucleophiles, the values of k_3/k_2 for these and other bases for these reactions are given in Table 1. Pietra[7] has shown that the rate of the third-order reaction between 2,4-dinitrophenyl phenyl ether and piperidine (first order in substrate, second order in amine) is increased by the addition of pyridine. The pK_a values of some amines are assembled in Table 2, and it is clear that in benzene, base catalysis occurs irrespective of whether the base strength in water of the catalyst is greater or less than that of the nucleophile. Additionally, in order to extend the number of direct comparisons of reactions in benzene and acetonitrile, we have studied the addition of DABCO and pyridine to the reaction of 2,4-dinitrophenyl phenyl ether with morpholine in benzene. The results are given in Table 3 and illustrated graphically in Figure 2. Again catalysis is observed irrespective of the relative basicities in water of the catalyst and nucleophile. Bernasconi and Zollinger[8]

TABLE 1

Values of k_3/k_2[a] for the reactions of 1-fluoro-2,4-dinitrobenzene with various nucleophiles in benzene at 25 °C

	Catalyst		
Nucleophile	Nucleophile	DABCO	Pyridine
p-Anisidine[b]	>22	>5 500	>975
Benzylamine[c]	320	24.4	93
N-Methylbenzylamine[c]	595	630	16
Morpholine[d]	982	444	58
n-Butylamine[e]	210		183

[a] Values calculated by C. F. Bernasconi, ' MTP International Reviews of Science,' Butterworths, London, 1973, Series 1, vol. 3. [b] Ref. 8. [c] C. F. Bernasconi and Hch. Zollinger, *Helv. Chim. Acta*, 1967, **50**, 3. Part of the catalysis by pyridine is believed to be due to a medium effect. [d] G. Becker, C. F. Bernasconi, and Hch. Zollinger, *Helv. Chim. Acta*, 1967, **50**, 10. [e] F. Pietra and D. Vitali, *J. Chem. Soc. B*, 1968, 1200.

TABLE 2

The pK_a of some amines in water and acetonitrile

Amine	pK_a[a] (H_2O)	pK_a[b] (MeCN)
Aniline	4.60	10.56
p-Anisidine	5.3	
Benzylamine	9.37	16.76
N-Methylbenzylamine	9.58	
Morpholine	8.31	16.6
Piperidine	11.22	18.92
n-Butylamine	10.59	18.26
Pyridine	5.18	12.3
DABCO	8.60	18.3
4-Methylpyridine	6.08	13.65

[a] Data taken from D. D. Perrin, ' Dissociation Constants of Organic Bases in Aqueous Solution,' IUPAC–Butterworths, London, 1965. [b] Data taken from J. F. Coetzee, *Prog. Phys. Org. Chem.*, 1967, **4**, 45.

TABLE 3

Rate constants (l $mol^{-1} s^{-1}$) for the reactions of 2,4-dinitrophenyl phenyl ether with morpholine and piperidine, 1-fluoro-2,4-dinitrobenzene with morpholine and aniline in acetonitrile, and of 2,4-dinitrophenyl phenyl ether with morpholine in benzene in the presence of added bases at 30.0 °C

1 Reaction of 2,4-dinitrophenyl phenyl ether[a] with morpholine (Morph)

A No added base k_3/k_2 = 189.9

$10^2\{\text{Morph}\}/\text{M}$	4.08	8.00	12.03	16.01
10^4k_A	3.35	6.63	9.45	12.6
$10^2\{\text{Morph}\}/\text{M}$	20.90	24.94		
10^4k_A	15.4	19.5		

B In the presence of pyridine (Py)

$10^2\{\text{Morph}\}/\text{M}$	12.03	12.03	12.07	12.08
$10^2\{\text{Py}\}/\text{M}$		5.63	11.36	20.34
10^4k_A	9.45	9.76	9.51	9.92
$10^2\{\text{Morph}\}/\text{M}$	12.22			
$10^2\{\text{Py}\}/\text{M}$	40.72			
10^4k_A	9.61			

C In the presence of 4-methylpyridine (4-Pic)

$10^2\{\text{Morph}\}/\text{M}$	12.03	12.01	12.07	12.05
$10^2\{\text{4-Pic}\}/\text{M}$		5.73	10.18	21.59
10^4k_A	9.45	9.88	10.5	9.66
$10^2\{\text{Morph}\}/\text{M}$	12.02			
$10^2\{\text{4-Pic}\}/\text{M}$	40.75			
10^4k_A	10.9			

D In the presence of DABCO

$10^2\{\text{Morph}\}/\text{M}$	12.03	12.13	12.15	12.12
$10^2\{\text{DABCO}\}/\text{M}$		2.57	5.23	10.44
10^4k_A	9.45	9.92	11.0	12.2
$10^2\{\text{Morph}\}/\text{M}$	12.14	12.12	12.22	12.03
$10^2\{\text{DABCO}\}/\text{M}$	15.13	20.35	24.03	30.41
10^4k_A	13.1	15.1	15.6	16.0

[a] Initial {Ether} 3.013—3.897 × 10^{-4}M.

2 Reaction of 2,4-dinitrophenyl phenyl ether[a] with piperidine (PIP)

A In the presence of pyridine (Py) at [PIP] 2.11 × 10^{-2}M

$10^2\{\text{Py}\}/\text{M}$		5.31	10.89	24.34
10^2k_A	1.56	1.57	1.54	1.57
$10^2\{\text{Py}\}/\text{M}$	40.54			
10^2k_A	1.61			

B In the presence of pyridine (Py) at [PIP] 8.62 × 10^{-3}M

$10^2\{\text{Py}\}/\text{M}$		5.36	11.3	20.5
10^3k_A	6.90	7.01	6.93	6.71
$10^2\{\text{Py}\}/\text{M}$	42.5			
10^3k_A	6.84			

C In the presence of DABCO at [PIP] 2.11 × 10^{-2}M

$10^2\{\text{DABCO}\}/\text{M}$		2.02	9.53	15.42
10^2k_A	1.56	1.55	1.55	1.50

D In the presence of DABCO at [PIP] 8.61 × 10^{-3}M

$10^2\{\text{DABCO}\}/\text{M}$		2.46	5.34	10.53
10^3k_A	7.01	19.0	22.3	30.8
$10^2\{\text{DABCO}\}/\text{M}$	15.26	20.08	24.86	
10^3k_A	34.2	36.0	36.6	

[a] [Ether] 3.013—3.23 × 10^{-4}M.

TABLE 3 (*continued*)

3 Reaction of 1-fluoro-2,4-dinitrobenzene [a] (Fluoro) with aniline

A In the presence of pyridine (Py) at $[\text{Aniline}]_0$ 0.10M

$10^2\{\text{Py}\}/\text{M}$		7.42	10.40	22.93
10^4k_A	2.01	5.26	7.14	14.6
$10^2\{\text{Py}\}/\text{M}$	35.86	46.78	67.33	87.65
10^4k_A	20.1	25.5	35.1	44.7
$10^2\{\text{Py}\}/\text{M}$	109.0			
10^4k_A	53.4			

B In the presence of DABCO at $[\text{Aniline}]_0$ 0.10M

$10^2\{\text{DABCO}\}/\text{M}$		6.02	11.42	15.54
10^4k_A	2.01	13.8	24.5	31.0
$10^2\{\text{DABCO}\}/\text{M}$	20.85	24.63	30.82	
10^4k_A	38.1	47.1	49.9	

[a] Initial [Fluoro] 3.26×10^{-4}M.

4 Reaction of 1-fluoro-2,4-dinitrobenzene [a] with morpholine in acetonitrile

A Reaction in the presence of pyridine (Py) at [Morph] 5.33×10^{-4}M

$10^4\{\text{Py}\}/\text{M}$		5.76	20.6	41.2
$10k_A$	6.85	6.65	6.96	6.66
$10^4\{\text{Py}\}/\text{M}$	82.3			
$10k_A$	6.80			

B Reaction in the presence of DABCO at [Morph] 5.33×10^{-4}M

$10^4\{\text{DABCO}\}/\text{M}$		5.62	11.6	22.5
$10k_A$	6.85	7.90	8.38	8.95
$10^4\{\text{DABCO}\}/\text{M}$	39.3	55.3	100	
$10k_A$	9.61	9.89	10.8	

[a] $[\text{Fluoro}]_0$ 4.80×10^{-5}M in all runs.

5 Reaction of 2,4-dinitrophenyl phenyl ether [a] with morpholine in benzene

A With morpholine alone

$10\{\text{Morph}\}/\text{M}$	1.03	2.01	3.14	3.99
10^5k_A	2.32	4.63	8.29	10.2
$10\{\text{Morph}\}/\text{M}$	5.03	6.03		
10^5k_A	14.0	19.3		

B In the presence of pyridine (Py) at [Morph] 9.14×10^{-2}M

$10\{\text{Py}\}/\text{M}$		1.23	2.89	4.17
10^5k_A	1.92	2.42	2.91	3.35
$10\{\text{Py}\}/\text{M}$	6.49			
10^5k_A	4.49			

C In the presence of DABCO at [Morph] 9.14×10^{-2}M

$10^2\{\text{DABCO}\}/\text{M}$		9.74	11.2	15.4
10^5k_A	1.92	2.58	3.29	3.83
$10^2\{\text{DABCO}\}/\text{M}$	23.4	34.7		
10^5k_A	4.74	5.18		

[a] $[\text{Ether}]_0$ 2.96×10^{-4}M in all cases.

obtained a similar upward curving dependence of the rate constant on the nucleophile concentration, but linear dependence on DABCO and pyridine concentrations for the reaction of 1-fluoro-2,4-dinitrobenzene with *p*-anisidine. They explained the upward curvature as due to a medium effect superposed on base catalysis by the nucleophile.*

We have investigated the effect of the addition of pyridine and DABCO on a series of reactions in acetonitrile which are known [5,9-11] to be base catalysed in this solvent and the results are assembled in Table 3. To enable comparison with previous work, the reaction of 2,4-dinitrophenyl phenyl ether with morpholine was studied as a function of morpholine concentration and the value of 190 obtained for k_3/k_2 is in good agreement with the literature value [5] of 185.

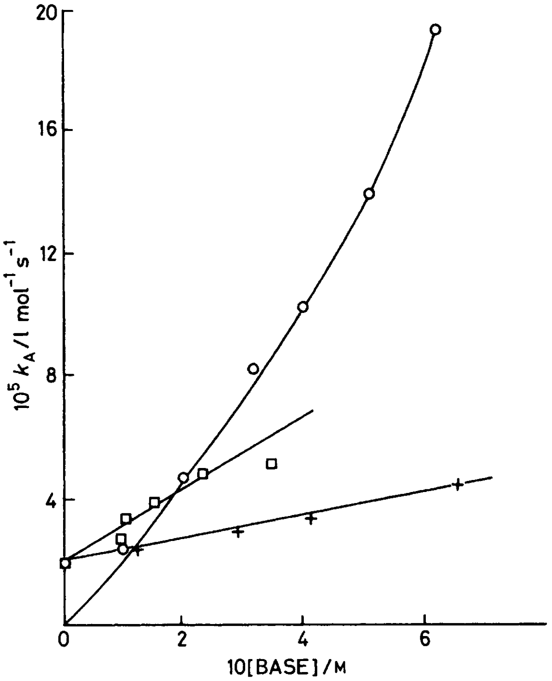


FIGURE 2 Plots of 10^5k_A against 10[base] for the reaction of 2,4-dinitrophenyl phenyl ether with morpholine in benzene at 30.0 °C: ○, morpholine; □, DABCO; ×, pyridine

From Table 3, the reaction of 1-fluoro-2,4-dinitrobenzene with aniline in acetonitrile is catalysed by both DABCO and pyridine. When the nucleophile is changed to morpholine, although catalysis by DABCO is still observed, there is no catalysis by pyridine. The reaction of 2,4-dinitrophenyl phenyl ether with morpholine is catalysed by morpholine and DABCO, but not by pyridine or 4-methylpyridine, but when the nucleophile is changed to piperidine the results are a little more complicated. At low (8.61×10^{-3}M) concentrations of piperidine, no catalysis is observed by pyridine and there is a curvilinear dependence on DABCO concentration as shown in Figure 3. At higher (2.11×10^{-2}M) piperidine concentrations no catalysis by either pyridine or DABCO is observed. This reaction is known [9] to be very strongly catalysed by piperidine and at high nucleophile concentrations the presence of DABCO probably leads to the condition $k_{-1} \ll k_2 + \sum k_3[\text{B}_i]$ and catalysis is not observable.

The results in Table 3 show that in acetonitrile catalysis only occurs if the added base has a basicity either approximately the same as, or greater than, that of the nucleophile. The only apparent exception to this

---

* An alternative explanation could be that if extensive homoconjugation occurs between the nucleophile N and its conjugate acid $\overset{+}{\text{N}}\text{H}$, $\text{N} + \overset{+}{\text{N}}\text{H} \rightleftharpoons \text{N}\overset{+}{\text{H}}\text{N}$, then at least part of the electrophilic catalysis in Scheme 2 could be due to the homoconjugate. In a system for which $k_{-1} \gg k_2 + k_3[\text{B}]$ and $k_{-1} \gg k_2 + k^1{}_3[\text{B}]^2$, where $k^1{}_3$ is the rate constant for electrophilic catalysis by the homoconjugate, this would give curvature as in Figure 2. In a system for which $k_{-1} \sim k_2 + k_3[\text{B}]$, superposition of this effect could give rise to curvatures ranging from that of Figure 2, through a straight line to that depicted in Figure 3.

is the catalysis by DABCO of the reaction between 2,4-dinitrophenyl phenyl ether and piperidine which occurs at low piperidine concentration. From Table 2, however, although piperidine is over 400 times a stronger base than DABCO in water, the two amines have approximately the same basicity in acetonitrile.

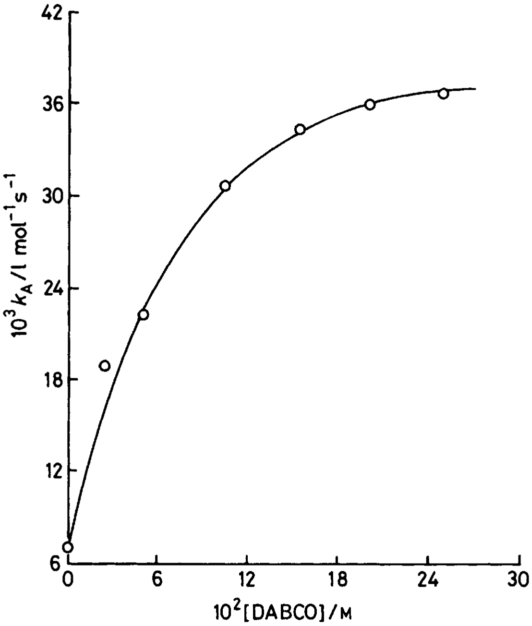


FIGURE 3 Plots of 10^3k_A against 10^2[DABCO] for the reaction of 2,4-dinitrophenyl phenyl ether with piperidine in acetonitrile at 30 °C

The results in acetonitrile are readily explicable in terms of the mechanism of the base-catalysed path given in Scheme 2. Bernasconi [12] has shown that the Meisenheimer complexes formed from 1,3,5-trinitrobenzene and primary and secondary amines are 100—400 times less basic than the nucleophiles from which they are derived and differences of at least this order of magnitude would be expected between (II) and the nucleophile. Hence abstraction of a proton from (I) by the nucleophile will always be thermodynamically favourable, but this is not necessarily true for the added catalyst when it is a considerably weaker base than the nucleophile. Furthermore the concentrations of the nucleophile (N) and the catalyst (C) usually employed ensures that when the equilibrium constant for the reaction $\overset{+}{C}H + N \rightleftharpoons \overset{+}{N}H + C$ is large, the only effective electrophilic catalyst present for the slow stage of the reaction is the conjugate acid of the nucleophile. Hence, on this mechanism, catalysis by the nucleophile and added bases whose basicity is approximately the same as or greater than that of the nucleophile will be observed but there will be no catalysis by bases whose base strength is much less than that of the nucleophile.

From the results of catalysis in benzene, this mechanism cannot apply in this solvent if the entities concerned behave as separate kinetic units, unless there is a very drastic increase in the basicity of pyridine relative to morpholine when the solvent is changed from water or acetonitrile to benzene and an even more dramatic one relative to the basicities of piperidine and n-butylamine. In order to obtain an estimate of the relative basicities in benzene and acetonitrile the method of Bernasconi *et al.*[13] of measuring the equilibrium constants * for ion-pair formation between picric acid and amines was employed initially. With morpholine in benzene, however, ion-pair formation went to completion so the less acidic 2,4-dinitrophenol was substituted for picric acid. The ratio of the equilibrium constants for ion-pair formation in benzene between this substrate and the amines are (*cf.* Experimental section) $5 \times 10^3 : 5 \times 10^2 : 4.5 \times 10^2 : 1$ for piperidine, n-butylamine, morpholine, and pyridine, respectively. In acetonitrile the reactions of 2,4-dinitrophenol with piperidine and n-butylamine both went to completion, and with morpholine and pyridine there is some doubt as to whether the reaction results in the formation of free ions or ion pairs. There is however little difference between the relative values of the equilibrium constants calculated on the assumption of free ions (8.5×10^3) or ion-pair formation (6.8×10^3). The results indicate that although there is a considerable decrease in the relative ' basicities ' in benzene compared to acetonitrile the relative values of the equilibrium constants ensure that under the conditions used in these kinetic investigations, any equilibrium between pyridinium and morpholinium ions will be almost entirely in favour of the morpholinium ions. Furthermore it can now be seen that when in benzene the ratio of the basicity of the nucleophile (piperidine) to that of pyridine is 5×10^3 then catalysis by pyridine is observed but in acetonitrile when the ratio of the basicity of the nucleophile (morpholine) to pyridine is of the same order of magnitude there is no catalysis by pyridine. We conclude that the mechanism of base catalysis given in Scheme 2 does not operate in benzene.

Although the present results exclude Scheme 2 as the mechanism of catalysis in benzene, they do not indicate what the mechanism is in this solvent. Catalysis could take place by the cyclic mechanism proposed by Capon and Rees,[4] or by the modification of the Bunnett mechanism which we [5] proposed, whereby because of the strength of electrostatic forces in solvents of low dielectric constant, reaction takes place within aggregates. In the latter mechanism catalysis by pyridine would be observed if heteroconjugation occurred between the conjugate acid of the nucleophile and pyridine, and the heteroconjugate participated in electrophilic catalysis of the departure of the leaving group.

---

* The method gives results which are easily reproducible, and our value of the basicity of pyridine relative to that of dimethyl sulphoxide (k_{py}/k_{DMSO}) in benzene of 3.0×10^3 is in good agreement with that of 2.9×10^3 obtained by Bernasconi *et al.* We agree with these authors however in not placing any special value on the figures as an exact estimate of the individual equilibrium constants, our interest is in the order of magnitude of the relative basicities.

EXPERIMENTAL

Details of the purification of the substrates, nucleophiles, and acetonitrile and the procedure for the spectrophotometric determination of the rates of formation of the products of the reactions have already been given.[9,10] DABCO was a commercial product recrystallised twice from benzene. Benzene was stored, with occasional shaking, over sulphuric acid for several days, then distilled from phosphorus pentaoxide and finally fractionated. Pyridine and 4-methylpyridine were stored over potassium hydroxide pellets and then distilled. 2,4-Dinitrophenol was prepared by the method of Vogel[14] and recrystallised twice from ethanol–water, m.p. 114—115° (lit.,[14] 115—116°).

Determination of the Equilibrium Constants for the Reactions of 2,4-*Dinitrophenol with Amines*.—(1) *Benzene solutions*. A solution of 2,4-dinitrophenol (1.576×10^{-4}M) has an absorbance, A_{HA}, of 0.322 at 360 nm in a 1 cm cuvette. In the presence of concentrations of piperidine $>5 \times 10^{-2}$M the phenol is completely converted into the ion pair, whose absorbance A_{IP} under exactly the same conditions is 2.170. The same concentration of the phenol in the presence of 1.18×10^{-4}M-piperidine, 1.23×10^{4}M-n-butylamine, 9.14×10^{-4}M-morpholine, and 6.90×10^{-1}M-pyridine yielded absorbances, A, of 0.685, 0.382, 0.657, and 0.835. Since in the equilibrium HA + B $\rightleftharpoons$ IP, where IP represents the formation of an ion pair, $[IP] = [HA]_0(A - A_{HA})/(A_{IP} - A_{HA})$ where $[HA]_0$ represents the stoicheiometric concentration of the phenol, and $[HA]_0 - [IP] = [HA]_e$ and $[B]_0 - [IP] = [B]_e$ where $[HA]_e$ and $[B]_e$ are the equilibrium concentrations of the phenol and base and $[B]_0$ the stoicheiometric concentration of the base, the equilibrium constant $K = [IP]/[HA]_e[B]_e$ can be calculated. The values of K obtained are 2.81×10^3, 2.85×10^2, 2.50×10^2, and 5.57×10^{-1} for piperidine, n-butylamine, morpholine, and pyridine, giving the ratios of their basicities toward 2,4-dinitrophenol in benzene as $5 \times 10^3 : 5 \times 10^2 : 4.5 \times 10^2 : 1$.

(2) *Acetonitrile solutions*. A 1.185×10^{-4}M solution of the phenol in a 1 cm cuvette has an absorbance of 0.255 at 370 nm. In the presence of either 1.346×10^{-4}M-piperidine or 1.194×10^{-4}M-n-butylamine complete dissociation occurs and the solution has an absorbance of 1.580. The same concentration of the phenol in the presence of 1.136×10^{-4}M-morpholine and 0.155M-pyridine gave solutions with absorbances of 1.085 and 0.910. The assumption of ion-pair formation gives values of K of 4.26×10^4 for morpholine and 6.31 for pyridine, ratio $6.75 \times 10^3 : 1$. If the reaction results in the formation of free ions according to the equation $HA + B \rightleftharpoons \overset{+}{B}H + A^-$ the values of K_f defined by $[\overset{+}{B}H]_e[A]_e/[HA]_e[B]_e$ are 3.16 and 3.70×10^{-4}, ratio $8.54 \times 10^3 : 1$.

[1/1226 *Received*, 4*th August*, 1981]

REFERENCES

[1] J. F. Bunnett and G. T. Davies, *J. Am. Chem. Soc.*, 1960, **82**, 665.

[2] J. A. Orvik and J. F. Bunnett, *J. Am. Chem. Soc.*, 1970, **92**, 2417.

[3] D. Ayediran, T. O. Bamkole, and J. Hirst, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1013.

[4] B. Capon and C. W. Rees, *Ann. Rep.*, 1963, **60**, 279.

[5] D. Ayediran, T. O. Bamkole, J. Hirst, and I. Onyido, *J. Chem. Soc., Perkin Trans. 2*, 1977, 597.

[6] C. F. Bernasconi and Hch. Zollinger, *Helv. Chim. Acta*, 1966, **49**, 103.

[7] F. Pietra, *Tetrahedron Lett.*, 1965, 2405.

[8] C. F. Bernasconi and Hch. Zollinger, *Helv. Chim. Acta*, 1966, **49**, 2570.

[9] D. Ayediran, T. O. Bamkole, J. Hirst, and I. Onyido, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1580.

[10] T. O. Bamkole, J. Hirst, and I. Onyido, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1317.

[11] D. Ayediran, T. O. Bamkole, and J. Hirst, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1396.

[12] C. F. Bernasconi, M. C. Muller, and P. Schmid, *J. Org. Chem.*, 1979, **44**, 3189.

[13] C. F. Bernasconi, M. Kaufmann, and Hch. Zollinger, *Helv. Chim. Acta*, 1966, **49**, 2563.

[14] A. I. Vogel, ' A Textbook of Practical Organic Chemistry,' Longman, London, 1956, 3rd edn., p. 678.