Catalysis of Trinitrobenzene–Anilide σ-Complex Formation and Decomposition in Dimethyl Sulphoxide in the Presence of Tetraethylammonium Chloride and Perchlorate

By **Erwin Buncel** * and **Walter Eggimann**, Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

The effect of tetraethylammonium chloride and perchlorate on the reaction TNB + $PhNH_2$ + DABCO $\rightleftharpoons$ TNB,$NHPh^-$ + DABCO,H^+, in dimethyl sulphoxide at 25°, has been investigated. The equilibrium constant for σ-complex formation increases by 340-fold on increasing [Et_4NCl] from 0 to 1.2M. This increase in K results from a 2.5-fold increase in the forward rate constant and a 140-fold decrease in the reverse rate constant. The corresponding changes in these parameters obtained with Et_4NClO_4 are modest though in the same direction. The effect observed with Et_4NCl is larger than in past studies of electrolyte effects on σ-complex formation and decomposition, or in S_NAr processes. The catalytic effect of Et_4NCl in the present system is ascribed to association of Cl^- with the conjugate acid of DABCO to yield the DABCO,$H^+ \cdots Cl^-$ heteroconjugate complex with consequent decrease in the rate of the reverse reaction.

THE evaluation of structural and environmental changes on Meisenheimer complex formation has led to increased understanding of the factors required for stabilization of these anionic σ-complexes.[1] In addition, since such species have been postulated as metastable intermediates in aromatic nucleophilic substitution (S_NAr) reactions,[2] the stable σ-complexes provide an indirect method of

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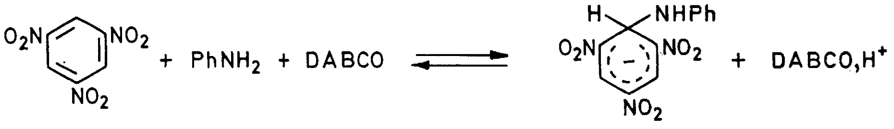
[1] (*a*) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, 1966, **16**, 16; (*b*) E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev.*, 1968, **22**, 123; (*c*) M. R. Crampton, *Adv. Phys. Org. Chem.*, 1969, **7**, 211; (*d*) M. J. Strauss, *Chem. Rev.*, 1970, **70**, 667.

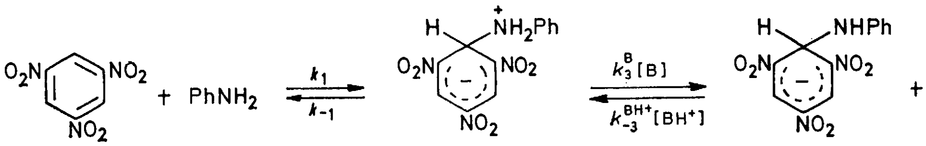
[2] (*a*) J. F. Bunnett, *Quart. Rev.*, 1958, **12**, 1; (*b*) J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, Amsterdam, 1968; (*c*) F. Pietra, *Quart. Rev.*, 1969, **23**, 504; (*d*) S. D. Ross, in 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, vol. 13; (*e*) C. F. Bernasconi, *M.T.P. Int. Rev. Sci. Org. Chem. Ser.* 1, 1973, **3**, 33; (*f*) D. M. Brewis, N. B. Chapman, J. S. Paine, J. Shorter, and D. J. Wright, *J.C.S. Perkin II*, 1974, 1787.

evaluating the factors which influence reactivity in S_NAr processes. In this regard it is of interest that whereas in S_NAr processes both aliphatic and aromatic amines are effective nucleophiles,[2] the situation with respect to σ-complex formation appears to be different. Whereas trinitrobenzene (TNB) reacts readily with primary (or secondary) aliphatic amines to yield the TNB,NHR⁻ σ-complexes,[3] the interaction between TNB and aniline was believed to give rise only to the weaker charge-transfer type complexes.[4] We showed [5] however that in dimethyl sulphoxide (DMSO) solution, in the presence of the tertiary amine 1,4-diazabicyclo[2.2.2]-octane (DABCO), or triethylamine, reaction (1) occurs readily. An indirect method of formation of (1) and other arylamine analogues has been found to be the reaction of the TNB,OMe⁻ σ-complex with $ArNH_2$ in DMSO solution.[6]



(1)

(1)



(2)

$$\ln \frac{[\text{TNB,NHPh}^-]_t([\text{TNB}]_0 - [\text{TNB,NHPh}^-]_e) + [\text{TNB}]_0[\text{TNB,NHPh}^-]_e}{[\text{TNB}]_0([\text{TNB,NHPh}^-]_e - [\text{TNB,NHPh}^-]_t)} = \frac{2[\text{TNB}]_0 - [\text{TNB,NHPh}^-]_e}{[\text{TNB,NHPh}^-]_e} k_f^1 t \qquad (3)$$

$$K = \frac{[\text{TNB,NHPh}^-]_e[\text{DABCO,H}^+]_e}{[\text{TNB}]_e[\text{PhNH}_2]_e[\text{DABCO}]_e} = \frac{(A_e/\varepsilon l)^2}{([\text{TNB}]_0 - A_e/\varepsilon l)([\text{PhNH}_2]_0 - A_e/\varepsilon l)([\text{DABCO}]_0 - A_e/\varepsilon l)} \qquad (4)$$

A kinetic study [7a] of reaction (1) has provided a clue to the different behaviour of the aromatic and aliphatic systems. Correspondingly, a deuterium isotope effect study with $PhND_2$[7b] has shed light on some outstanding problems with respect to the observation of base catalysis and isotope effects in S_NAr systems.[8] Our interpretations were based on a detailed analysis of the rate and equilibrium constants of σ-complex formation as given in the two-stage mechanism (2).

Our previous study [7a] was concerned primarily with the effect of variation of the concentration of DABCO, in order to characterize the form of base catalysis and hence to obtain information concerning the rate-determining step. It was found that use of a constant concentration of tetraethylammonium chloride as added electrolyte was required in order to obtain constancy of K values. As a result of this indication that salt effects could be important in this system, a more extended study of this effect was undertaken. The results have shown that the degree of conversion to product in equation (1) can be profoundly influenced by added Et_4NCl, and that the effect arises from a very large electrolyte dependence of the rate constant for decomposition of TNB,NHPh⁻. The observed effects are larger than previously observed in studies of electrolyte effects on σ-complex formation [9,10] or in S_NAr processes.[11]

RESULTS

Reaction (1) was studied in DMSO solution at 25° under pseudo-first-order conditions, with $PhNH_2$ and DABCO in large excess over TNB. The system can thus be described by TNB $\underset{k_r^2}{\overset{k_f^1}{\rightleftharpoons}}$ TNB,NHPh⁻ + DABCO,H⁺, *i.e.* a first-order forward and second-order reverse reaction. One can evaluate k_f^1, the pseudo-first-order rate constant for the

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[3] (*a*) R. Foster and C. A. Fyfe, *Tetrahedron*, 1966, **22**, 1831; (*b*) M. R. Crampton and V. Gold, *J. Chem. Soc.* (*B*), 1967, 23; (*c*) C. F. Bernasconi, *J. Amer. Chem. Soc.*, 1970, **92**, 129; (*d*) M. J. Strauss, S. P. B. Taylor, and A. Reznick, *J. Org. Chem.*, 1972, **37**, 3076.

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[5] E. Buncel and H. W. Leung, *J.C.S. Chem. Comm.*, 1975, 19.

[6] (*a*) E. Buncel and J. G. K. Webb, *Canad. J. Chem.*, 1974, **52**, 630; (*b*) E. Buncel, H. Jarrell, H. W. Leung, and J. G. K. Webb, *J. Org. Chem.*, 1974, **39**, 272; (*c*) E. Buncel and J. G. K. Webb, *Tetrahedron Letters*, 1976, **4417**; (*d*) E. Buncel, J. G. K. Webb, and J. F. Wiltshire, *J. Amer. Chem. Soc.*, 1977, **99**, 4429.

[7] (*a*) E. Buncel and W. Eggimann, *J. Amer. Chem. Soc.*, 1977, **99**, 5958; (*b*) E. Buncel, H. W. Leung, and W. Eggimann, *J.C.S. Chem. Comm.*, 1977, 55.

[8] (*a*) H. Zollinger, *Adv. Phys. Org. Chem.*, 1964, **2**, 163; (*b*) F. Pietra, D. Vitali, and S. Ferdiani, *J. Chem. Soc.* (*B*), 1968, 1595; (*c*) I. Giardi, G. Illuminati, and G. Sleiter, *Tetrahedron Letters*, 1968, 5505.

[9] (*a*) J. H. Fendler, E. J. Fendler, and M. V. Merritt, *J. Org. Chem.*, 1971, **36**, 2172; (*b*) C. F. Bernasconi, *J. Amer. Chem. Soc.*, 1968, **90**, 4982; (*c*) P. Bemporad, G. Illuminati, and F. Stegel, *ibid.*, 1969, **91**, 6742; (*d*) F. Terrier, *Ann. Chim.* (*France*), 1969, **4**, 153.

[10] M. R. Crampton and H. A. Khan, *J.C.S. Perkin II*, 1972 (*a*) 1173; (*b*) 2286; (*c*) 1973, 1103; (*d*) M. R. Crampton, *ibid.*, 1975, 825.

[11] (*a*) J. D. Reinheimer, W. F. Kieffer, S. W. Frey, J. C. Cochran, and E. W. Barr, *J. Amer. Chem. Soc.*, 1958, **80**, 164; (*b*) J. D. Reinheimer, J. T. Gerig, and J. C. Cochran, *ibid.*, 1961, **83**, 2873; (*c*) C. A. Bunton and L. Robinson, *ibid.*, 1968, **90**, 5965; (*d*) S. D. Ross, *Tetrahedron*, 1969, **25**, 4427; (*e*) D. Ayediran, T. O. Bamkole, and J. Hirst, *J.C.S. Perkin II*, 1974, 1013.

TABLE 1

Effect of added tetraethylammonium chloride on rate and equilibrium parameters for reaction (1); [TNB] 9.8×10^{-5}M, [$PhNH_2$] 4.9×10^{-3}M, [DABCO] 1.96×10^{-3}M, in dimethyl sulphoxide at 25°

[Et_4NCl]/M	Conversion [a] (%)	K/l mol^{-1}	$10^4k_f^1$/s^{-1}	$10^2k_f^2$/l mol^{-1} s^{-1}	k_f^3/l^2 mol^{-2} s^{-1}	k_r^2/l mol^{-1} s^{-1}
0	9.6	0.111	2.26	4.61	23.5	212
0.010	16.4	0.349	2.48	5.06	25.8	73.9
0.020	19.4	0.518	2.52	5.15	26.3	50.8
0.050	27.0	1.13	2.72	5.56	28.4	25.7
0.100	34.1	1.80	2.80	5.71	29.1	16.2
0.200	43.7	3.81	3.20	6.53	33.3	8.74
0.300	49.2	5.48	3.46	7.07	36.1	6.58
0.500	58.2	9.32	3.89	7.94	40.5	4.35
1.00	75.7	29.0	4.90	10.0	51.1	1.76
1.16	79.6	38.0	5.35	10.9	55.6	1.46

[a] Average values derived from three separate runs, with mean deviation of 3% in the conversion.

TABLE 2

Effect of added tetraethylammonium perchlorate on rate and equilibrium parameters for reaction (1); [TNB] 9.8×10^{-5}M, [$PhNH_2$] 4.9×10^{-3}M, [DABCO] 1.96×10^{-3}M, in dimethyl sulphoxide at 25°

[Et_4NClO_4]/M	Conversion [a] (%)	K/l mol^{-1}	$10^4k_f^1$/s^{-1}	$10^2k_f^2$/l mol^{-1} s^{-1}	k_f^3/l^2 mol^{-2} s^{-1}	k_r^2/l mol^{-1} s^{-1}
0.010	12.1	0.179	2.18	4.45	22.7	127
0.050	14.2	0.255	2.28	4.65	23.7	93.0
0.100	15.3	0.297	2.20	4.49	22.9	77.1
0.200	15.3	0.298	2.18	4.45	22.7	76.2

[a] As in Table 1.

forward reaction, *via* equation (3),[12] from the slope of the graph obtained on plotting the left-hand term against time, substituting [TNB,$NHPh^-$]$_e$ = $A_e/\varepsilon l$ and [TNB,$NHPh^-$]$_t$ = $A_t/\varepsilon l$. A_e and A_t are the absorbances at $\lambda_{max.}$ (446 nm) due to the σ-complex at equilibrium and at time t respectively, ε is the molar extinction coefficient of the complex (30 400 l mol^{-1} cm^{-1}), and l is the cell pathlength used in the measurements (1 cm). The second- and third-order forward rate constants are given by $k_f^2 = k_f^1/[PhNH_2]$ and $k_f^3 = k_f^1/[PhNH_2][DABCO]$, respectively. The second-order rate constant for the reverse process, k_r^2, is obtained from $k_r^2 = k_r^3/K$. The equilibrium constant K for the reaction is evaluated using equation (4).

Under the chosen reaction conditions the approach to equilibrium could be followed by means of conventional time scale spectrophotometry. In the case of added Et_4NCl, extensive measurements relating to k_f^1 and K could be made, while limited results were obtained using Et_4NClO_4 as added salt. In the latter case the occurrence of an unknown side reaction was noted at >0.2M by the advent of a new spectral absorption at 480 nm. However with Et_4NCl the entire concentration range could be covered, until saturation, with no evidence of any process other than formation of the TNB,$NHPh^-$ complex.

In Table 1 are shown the rate and equilibrium data pertaining to the effect of Et_4NCl on reaction (1), while Table 2 shows the corresponding data obtained with Et_4NClO_4. The results are represented graphically in Figure 1. It is seen that Et_4NCl has a profound effect on the extent of conversion to TNB,$NHPh^-$. Thus at constant concentration of $PhNH_2$ and DABCO, the extent of conversion increases from *ca.* 10% at [Et_4NCl] 0 to *ca.* 80% at [Et_4NCl] 1.2M. Correspondingly, K increases from 0.11 to 38, that is by 340-fold. The effect of Et_4NClO_4 is seen to be much smaller.

The rate data in Table 1 show that k_f^1 (or k_f^2, k_f^3 equivalently) increases by 2.5-fold over the range of Et_4NCl concentrations. However, k_r^2 decreases by 140-fold over this range and is mainly responsible for the very large electrolyte effect on K and on the extent of conversion.

DISCUSSION

The literature contains a number of reports [9,10] relating to electrolyte effects on σ-complex formation and decomposition processes and it is pertinent to consider these results in light of the present work. The past studies have focused in the main on the reaction type in equation (5), in which at least two of the substituents X—Z are electron withdrawing, generally nitro groups. Fendler *et al.*[9a] investigated the effect of inert salts on the

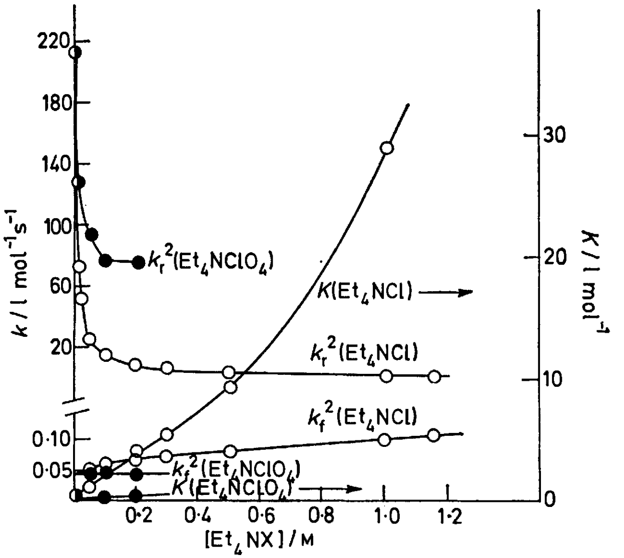

FIGURE 1 Dependence of rate and equilibrium parameters for reaction (1) on electrolyte concentration. Right hand scale refers to K(Et_4NCl) and K(Et_4NClO_4) only. Lower portion of left hand scale refers to k_f^2(Et_4NCl) and k_f^2(Et_4NClO_4). Upper portion of left hand scale refers to k_r^2(Et_4NCl) and k_r^2(Et_4NClO_4). Open circles signify Et_4NCl, closed circles Et_4NClO_4

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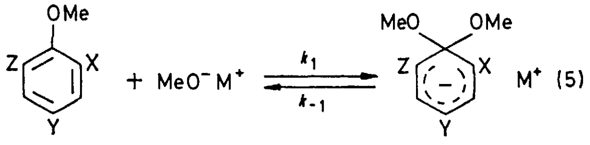
[12] K. Schwetlick, 'Kinetische Methoden zur Untersuchung von Reaction Mechanisme,' VEB Verlag, Berlin, 1971, p. 67.

decomposition of (2; X = Y = Z = NO_2) in water at 25° and found that, except for LiCl and $LiClO_4$ which



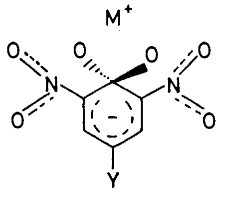
(2)

enhanced k_{-1} (*ca.* 20%), the other salts examined ($NaNO_3$, NaCl, NaBr, Me_4NCl, $NaClO_4$, KCl, *p*-$MeC_6H_4SO_3Na$) caused a decrease in k_{-1} (to about half the original value, maximum one quarter with 2M-*p*-$MeC_6H_4SO_3Na$).

Another type of observation relating to this problem consisted of the finding from several laboratories [9,10] that the calculated equilibrium constants K_c for (5) in methanol increase with the stoicheiometric base concentration even in the range of low [NaOMe] values. For example for (2; X = Y = NO_2, Z = CO_2Me) K_c increases from 13.2 to 40.5 l mol^{-1} as [NaOMe] is increased from 0.004 to 0.04M.[10a] In intensive studies of this effect Crampton found that the increase in K_c is caused by a small increase in k_1 and a larger decrease in the k_{-1} value. With $Bu^n{}_4NOMe$ as the base the increase in K_c was less pronounced than with KOMe or NaOMe while with LiOMe the effect was reversed, a slight decrease in K_c being obtained with increasing alkoxide concentration.[10b] Significantly, addition of crown ether resulted in only small variation in K_c, k_1, and k_{-1} as [NaOMe] was increased.[10d] To explain these observations, Crampton proposed the ion association scheme in equation (6).

$$\begin{tikzcd} \text{P} + \text{MeO}^- + \text{M}^+ \arrow[r, shift left, "K_1"] \arrow[d, shift left] & \text{POMe}^- + \text{M}^+ \arrow[l, shift left] \arrow[d, shift left] \\ \text{MeO}^-,\text{M}^+ \arrow[u, shift left, "K_3"] & \text{POMe}^-,\text{M}^+ \arrow[u, shift left, "K_2"] \end{tikzcd} \qquad (6)$$

For $M^+ = K^+$, Na^+, or Bu_4N^+ the adduct $POMe^-$ would be stabilized by ion pair formation to a greater extent than methoxide ion ($K_2 > K_3$), while the reverse would hold for $M^+ = Li^+$. It was suggested that a specific



(3)

interaction occurs between the cation and the geminal methoxy groups in the 1,1-complex, as indicated in (3). This proposal is also in accord with the finding that the methoxide ion complex of TNB shows no evidence of association with cations in methanol.[13]

However, it is clear from the results of the present work that σ-complex formation and decomposition for TNB as the nitroaromatic compound can be subject to profound salt effects. In fact the 340-fold increase in the equilibrium constant in the present system is considerably larger than observed in the studies of electrolyte effects on reaction (5).* It is interesting also that though the reactants in (1) are uncharged while in (5) an anionic species adds to the nitroaromatic compound, the direction of the electrolyte effect is qualitatively similar in the two systems. Thus whereas in reaction (5) classical theories of electrolyte effects [14] on rates and equilibria could not explain the direction of the effect, in the present system [equation (1)] such theories can explain the direction though not the magnitude of the effect.

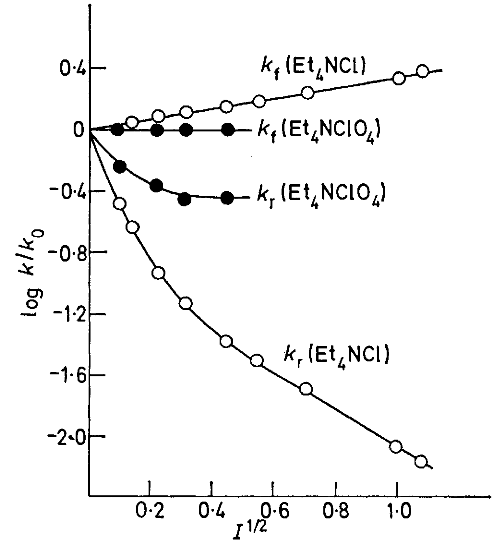


FIGURE 2 Dependence of rate constants in reaction (1) on square root of ionic strength for the Et_4NCl and Et_4NClO_4 electrolytes

Addition of an electrolyte is expected to result in a moderate increase in k_f for the reaction between neutral species yielding ionic products. Similarly a decrease in $k_r{}^2$ values with electrolyte concentration is expected in the reverse process since in forming the transition state charge will be dissipated. It is noted that the S_NAr reaction between 1-chloro-2,4-dinitrobenzene and aniline, which is believed to proceed *via* a zwitterionic intermediate analogous to that shown in equation (2), shows an increase in rate with added ionic halides (NaCl > LiBr > Me_4NCl) but a decrease in rate with added perchlorates ($LiClO_4$ > $NaClO_4$).[11b] However the main problem in explanation of the present results is the magnitude of the Et_4NCl effect on $k_r{}^2$ which appears to be unprecedented. Figure 2 gives plots of log k/k_0 against $\sqrt{I^{\frac{1}{2}}}$ where I is the calculated ionic strength. The $k_f{}^2$ data show a linear correlation while the $k_r{}^2$ data give the appearance of two linear portions on this

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* The equilibrium constant K_c for reaction (5; X = Y = NO_2, Z = CO_2Me, $M^+ = Na^+$) was found to increase by *ca.* 50—100 on addition of barium chloride or barium perchlorate,[10c] which was ascribed to association of Ba^{2+} with the σ-complex. Significantly the effects of $BaCl_2$ and $Ba(ClO_4)_2$ were found to be similar, which contrasts with the present work.

[13] V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1964, 1692.

[14] (*a*) C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell University Press, Ithaca, 1969, 2nd edn., ch. 7; (*b*) L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, 1970, 2nd edn., ch. 7.

graph. The theoretical significance of these correlations is not fully apparent.[14]

In attempting to explain our results one might suggest that the anionic σ-complex has a dominant effect, though obviously not in the specific sense of ion association as depicted in (**3**).* Stabilization of the large polarizable anionic σ-complex TNB,NHPh$^-$ by the tetra-alkylammonium cation could be expected on theoretical grounds.[16] However if this were the factor mainly responsible for the observed effect then one would have expected Et_4NClO_4 to have an effect comparable with that of Et_4NCl whereas this is not the case. This suggests that chloride ion has some catalytic role which is responsible for the observed effect.

We propose that the probable mode of action of electrolytes in this system is by association of type (7),

$$BH^+ + X^- \rightleftharpoons BH^+ \cdots X^- \qquad (7)$$

which has been termed heteroconjugation by Kolthoff.[17] Evidence for anion heteroconjugation has been obtained in various aprotic solvents, by conductance and absorption spectroscopy. These methods also provide a quantitative estimate of the effectiveness of various anions in formation of heteroconjugates. For example i.r. measurements have shown that the comparative shifts in ν(O–H) of *p*-cresol (0.1M) in $CHCl_3$ produced by various anions (R_4N^+ salts; 0.03M) are in the order $Cl^- > Picrate^- > Br^- > NO_3^- > I^- > ClO_4^-$.[18] It is clearly significant in relation to the present study that Cl^- and ClO_4^- are at the extremes in this comparison. Heteroconjugation by these anions in DMSO has not been studied, but one could reasonably expect the same order as above, though quantitatively the effect could be smaller than in $CHCl_3$ because of readier hydrogen bonding between the BH^+ species and DMSO.[19] In fact the larger solvation of ClO_4^- than Cl^- in DMSO (by polarizability interaction)[20] should result in an even larger differentiation between Cl^- and ClO_4^- in their capacity for heteroconjugation. Thus we propose that the decreased acidity, and hence the decreased catalytic effect, of the heteroconjugate ion DABCO,$H^+ \cdots Cl^-$ towards the anionic TNB,NHPh$^-$ σ-complex is the factor mainly responsible for the decrease in k_r^2 with increasing [Et_4NCl]. Furthermore the levelling off in k_r^2 at the higher Et_4NCl concentrations could then be explained on the basis of self association of the electrolyte into ion pairs and higher aggregates, which would diminish the ability of Cl^- to partake in heteroconjugation [equation (7)].

The above interpretation of electrolyte effects is a qualified one in the absence of information concerning the effect of electrolyte concentrations on the reactant activities. A separation of initial state and transition state contributions in the reaction of 1-chloro-2,4-dinitrobenzene with aniline showed that both terms are important.[11c] In the present system a complete evaluation of initial state effects does not appear feasible at present since the TNB,NHPh$^-$ σ-complex has not yet been isolated as a pure material, so as to allow the necessary activity coefficient measurements to be made. Variation of the activity coefficients of the neutral species in this system (TNB, $PhNH_2$, and DABCO) is not expected to be of sufficient magnitude to account for the observed rate effects.

It is interesting to note, in relation to S_NAr processes, that a recent study of the reaction of trimethylamine with 4-fluoronitrobenzene in dimethyl sulphoxide[11e] has revealed the operation of specific salt effects which could be interpreted on the basis of the two-stage intermediate complex mechanism. There has been no study to date of salt effects on σ-complex formation between nitroaromatic compounds and aliphatic amines in dimethyl sulphoxide, parallel to the present study.

EXPERIMENTAL

The purification of TNB, $PhNH_2$, DABCO, Et_4NCl, and DMSO has been given previously.[7a] Tetraethylammonium perchlorate (Eastman) was recrystallized twice from benzene and dried *in vacuo*. Solutions were prepared in the dry box under nitrogen.

The rate of formation of complex (1) was followed spectrophotometrically by monitoring the increase in absorption at 446 nm [$\lambda_{max.}$ for (1)] using a Beckman Acta IV instrument fitted with a thermostatted cell holder as described previously.[7a] At the completion of the reactions the spectra were taken in full. For the runs with added Et_4NCl the spectrum characteristic of (1) was obtained over the entire range of salt concentrations, which also held for [Et_4NClO_4] < 0.2M. However, when the Et_4NClO_4 concentration exceeded 0.2M, a change in the spectrum near 480 nm indicated the advent of some side reaction, which was accompanied also by irreproducible kinetic results. The other runs showed good reproducibility and the results given are the mean values of three runs. The rate and equilibrium constants were obtained by computer programming of equations (3) and (4) which generated also a least, square error analysis and linear plots for the left-hand side of equation (3) against time. These plots showed good linearity for *ca.* 90% conversion with respect to the equilibrium position (standard deviation of slope 0.5—1%). An error of ±3% in the overall extent of conversion leads to an error of ±5% in k_f *via* equation (3). The corresponding error in *K via* equation (4) is ±10% when the extent of conversion is 60%, and ±25% when the extent of conversion is 80%.

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* In a study of σ-complex formation between 2,4,6-trinitrotoluene and isopropoxide and t-butoxide ions (competitive with proton abstraction), the dependence of the rate and equilibrium parameters on [Pr^iONa], [Bu^tONa], and [Bu^tOK] was explained by ascribing a specific role to the RO^-, M^+ ion pair.[15]

[15] (*a*) E. Buncel, A. R. Norris, K. E. Russell, P. Sheridan, and H. Wilson, *Canad. J. Chem.*, 1974, **52**, 1750; (*b*) E. Buncel, A. R. Norris, K. E. Russell, and H. Wilson, *ibid.*, p. 2306.

[16] E. S. Halberstadt and J. E. Prue, *J. Chem. Soc.*, 1952, 2234.

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[19] I. M. Kolthoff, M. K. Chantooni, jun., and S. Bhowmik, *J. Amer. Chem. Soc.*, 1968, **90**, 23.

[20] (*a*) B. G. Cox, *Ann. Rep. Chem. Soc. A*, 1973, 249; (*b*) E. Buncel and H. Wilson, *Adv. Phys. Org. Chem.*, 1977, **14**, 133.