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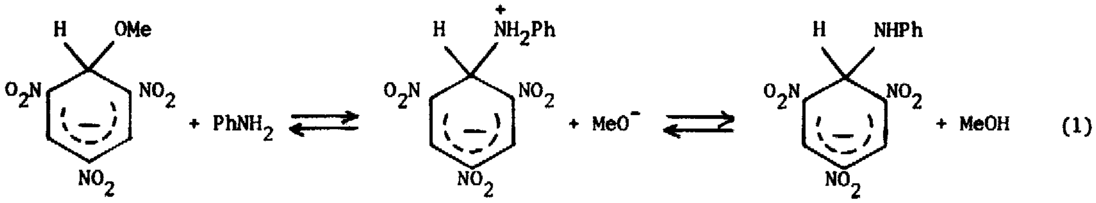
DISPLACEMENT VERSUS DISSOCIATIVE MECHANISMS IN REACTION OF ANILINE WITH THE 1,3,5-TRINITROBENZENE-METHOXIDE σ-COMPLEX.

E. Buncel and J. G. K. Webb

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

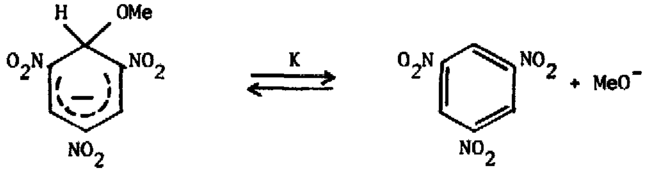
Whereas formation of σ-complexes form 1,3,5-trinitrobenzene (TNB) and primary or secondary aliphatic amines has been well established (1-5), the interaction of TNB with aromatic amines had been observed to give rise only to the weaker charge-transfer complexes (6,7). We reported, however, that the trinitrobenzene-anilide σ-complex, TNB.NHPh$^-$, can readily be obtained by reaction of aniline in dimethyl sulfoxide (DMSO) solution with the trinitrobenzene-methoxide σ-complex, TNB.OMe$^-$ (8). Subsequently, a number of TNB-aromatic amine complexes were obtained by this method (9). A possible displacement mechanism for this process (eq. 1),



(1)

as proposed by Butler (10), would be of considerable interest if such could be confirmed, since so far there has been no established precedent of a concerted SN2 reaction occurring at the sp^3 center of a Meisenheimer type σ-complex (11).

In accord with a displacement mechanism there is the observation that the TNB.OMe$^-$K$^+$ + PhNH$_2$ $\rightleftharpoons$ TNB.NHPh$^-$ + CH$_3$OH reaction occurs without formation of a spectrally detectable intermediate. This result, however, does not disprove the possible existence of reaction intermediates in concentrations less than detectable by our spectral technique. Hence this does not distinguish between the displacement mechanism discussed above and possible dissociative mechanisms to be considered below. However, one would expect a different rate law to be obeyed if reaction occurred in a concerted manner (eq. 1), or if it involved prior dissociation (eq. 2). The equilibrium in eq. 2 is known to be rapidly established and association



(2)

constants for the TNB + $MeO^- \rightleftharpoons$ TNB.OMe⁻ reaction (i.e. 1/K in eq. 2) have been found to vary from ~20 M^{-1} in methanol to ~10^5 M^{-1} in 70 mole per cent DMSO-methanol (12,13).

We have now performed a kinetic study of the $TNB.OMe^-K^+ + PhNH_2 \rightleftharpoons TNB.NHPh^-K^+ + MeOH$ reaction. The process proceeds smoothly in 90:10 mole per cent DMSO-methanol at 25° and pseudo first order rate constants (k_ψ) for the approach to equilibrium have been obtained from linear plots of $\log(A_e-A_t)$ vs. t, where A_e and A_t are the absorbances at equilibrium and at time t respectively. In Table 1 are presented the results of varying the aniline concentration. A plot of k_ψ against $[PhNH_2]$ is linear, of unit slope, and passing through the origin. Thus the reaction is first order in aniline concentration. In an attempt to define the rate law more completely, we have also varied the substrate concentration, and in Table 2 are presented the resulting k_ψ values. It is seen that the k_ψ values are not independent of $[TNB.OMe^-K^+]_o$, as would have been expected if reaction were simply first order in substrate concentration. This result excludes the displacement mechanism considered above as this would be subject to first order kinetics with respect to the σ-complex reactant.

TABLE 1. Effect of aniline concentration on the rate of formation of $TNB.NH^-K^+$ from $TNB.OMe^-K^+$ and aniline in 90:10 mole per cent DMSO-methanol at 25° in presence of 0.098 M Et_4NClO_4

$[PhNH_2]$ (M)	0.0496	0.0496	0.0980	0.0984	0.196	0.198
10^4 k_ψ (s^{-1})	3.47	3.30	6.75	6.90	12.7	12.9

TABLE 2. Effect of substrate concentration on k_ψ for formation of $TNB.NHPh^-K^+$ in the reaction of $TNB.OMe^-K^+$ with aniline (0.098 M) in 90:10 mole per cent DMSO-methanol at 25° in the presence of 0.098 M Et_4NClO_4.

10^4 x $[TNB.OMe^-K^+]$ (M)	2.05	3.84	4.18	8.32	24.6	25.4
10^4 k_ψ (s^{-1})	9.97	6.92	6.90	4.90	2.88	2.75

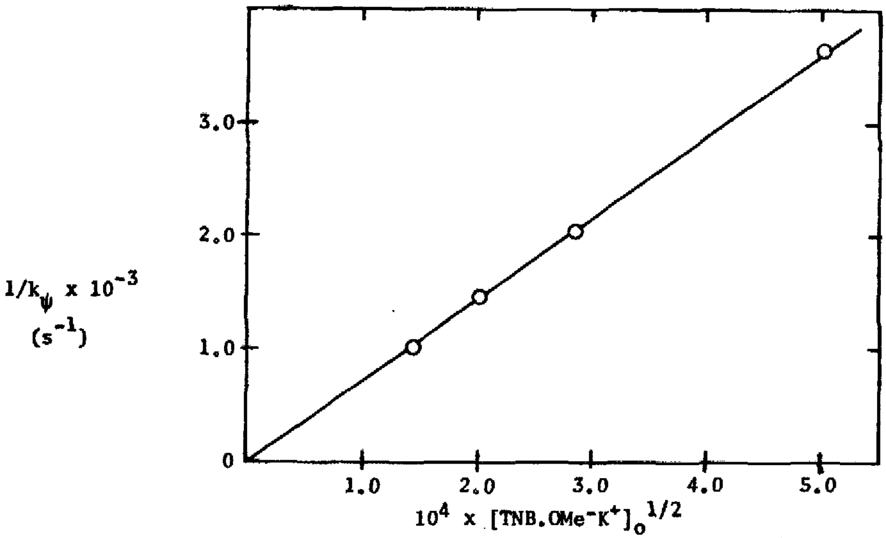
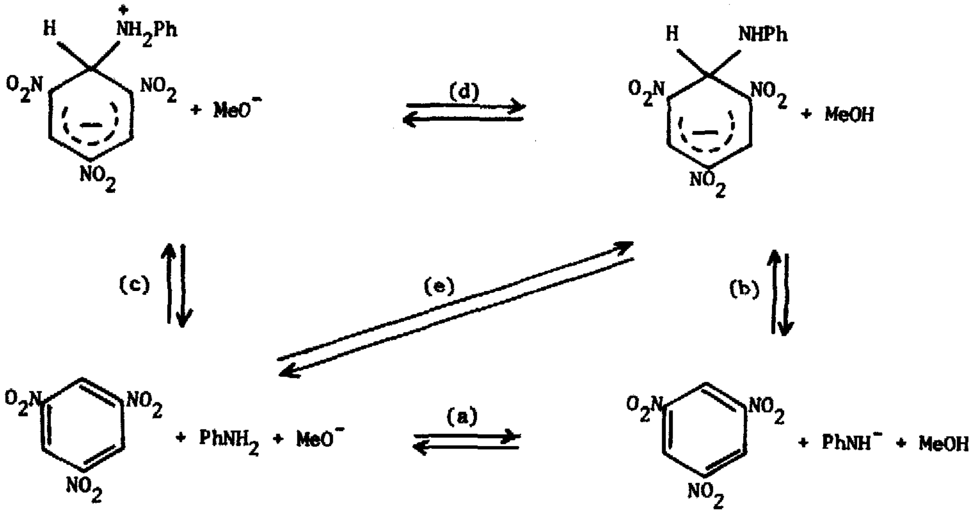


Fig. 1. Plot showing the inverse dependence of k_ψ on $[TNB.OMe^-K^+]_o^{1/2}$ in the reaction of $TNB.OMe^-K^+$ with aniline (0.10 M) in 90:10 mole per cent DMSO-methanol at 25°

Reactions involving the dissociation of reactant into two or more components are characterized by rate laws involving fractional order terms (14). We have, accordingly, explored various data treatments and have found that a plot of k_ψ versus $1/[TNB.OMe^-K^+]_o^{1/2}$ is linear, passing through the origin (Fig. 1).

The observation of non-first-order kinetic behaviour with respect to $TNB.OMe^-K^+$ is to be expected if reaction involves initial dissociation of substrate according to eq. 2. The free TNB so formed could then react by one of several pathways, shown in Scheme 1 (16). The



SCHEME 1

Scheme envisages the possibility of reaction proceeding via anilide ion (paths a,b), via a zwitterionic intermediate (paths c,d), or by a concerted route (path e). Further work is in progress in order to differentiate between the possibilities of Scheme 1, and to establish the nature of the rate-determining step. It may be noted, however, that Scheme 1 accounts for the absence of reaction between TNB and aniline alone and shows the requirement of a stronger base in σ-complex formation between nitroaromatic compounds and aromatic amines in general.

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