Catalysis by Tertiary Amines of σ-Complex Formation Between 1,3,5-Trinitrobenzene and Aniline

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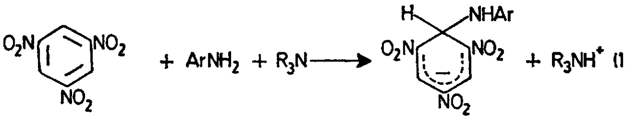
Summary The trinitrobenzene–anilide σ-complex is readily formed directly from trinitrobenzene and aniline in the presence of diazabicyclo-octane or triethylamine in dimethyl sulphoxide.

The observation that 1,3,5-trinitrobenzene (TNB) does not react with aniline to yield a Meisenheimer type σ-complex is puzzling since σ-complex formation between TNB and primary (or secondary) aliphatic amines is well documented.[1] We have recently shown that the TNB-anilide complex can be obtained, indirectly, however, from reaction of the TNB-methoxide σ-complex with aniline in dimethyl sulphoxide (DMSO) solution.[2] This reaction can be extended to substituted anilines.[3]

In view of the unreactivity of TNB with aniline, the nature of the TNB·OMe$^-$-aniline reaction poses a number of questions, and direct displacement[4] and dissociative mechanisms have been advanced.[5] We have now observed that the TNB–anilide σ-complex can be formed directly from TNB and aniline, in the presence of triethylamine or 1,4-diazabicyclo[2,2,2]octane (DABCO), in DMSO solution.

The u.v.-visible spectrum obtained in the interaction of

TNB with aniline in the presence of DABCO is typical of σ-complexes of TNB;[6] in the present case there are characteristic twin absorption peaks at 446 and 524 nm (broad), with a ratio of 1·7:1 in the extinction coefficients. For example, addition of 50μl of a solution of TNB (2·5 × 10^{-2}M) in DMSO to 2·5 ml of a solution containing aniline and DABCO (0·1 M each) in DMSO gives a red solution. Comparison with the previously observed[3] spectral characteristics of the TNB-anilide complex (ϵ_{446} 30,400, ϵ_{523} 17,700) shows that *ca.* 85% conversion has occurred. The degree of conversion into the σ-complex increases as the concentration of DABCO is increased, at a given concentration of TNB and aniline. The reaction occurs readily at 25 °C; with [TNB] = 1·54 × 10^{-3}M, [DABCO] = 0·01 M, [$PhNH_2$] = 0·135 M, the pseudo-first-order rate constant for formation of the anilide complex is 0·153 s^{-1}. N.m.r. spectroscopy (*cf.* refs. 2 and 3) confirmed σ-complex formation in the TNB–$PhNH_2$–DABCO–DMSO system; use of triethylamine in place of DABCO likewise afforded the σ-complex.



(1)

Reaction (1) thus affords ready access to trinitrobenzene-arylamine σ-complexes.

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