Evidence for General Base Catalysis in the Reaction between the Tris-*p*-methoxyphenylmethyl Cation and Water in Aqueous Solution at 25 °C

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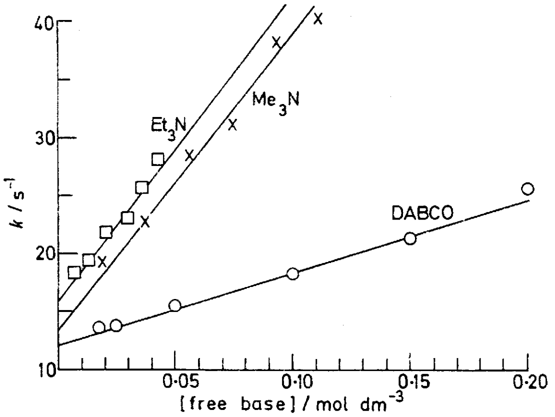
Stopped flow measurements on the rate of disappearance of the tris-*p*-methoxyphenylmethyl cation show that a small accelerating effect is produced by the bases 1,4-diazabicyclo[2.2.2]octane (DABCO), trimethylamine, and triethylamine, just as observed by Ritchie in the case of the Malachite Green cation. The alternative possibility that the bases might act as nucleophiles in forming quaternary ammonium ions as intermediates seems unlikely.

IN a survey [1] of the effects of additives upon the tris-*p*-methoxyphenylmethanol indicator system (the results of which were very similar to those published independently by Bunton and Huang [2]), Postle and Wyatt discounted the occurrence of general base catalysis on the grounds that primary and secondary amines (acting as nucleophiles) accelerated the rate of disappearance of the coloured cation while tertiary amines did not, except through their effect on the OH^- concentration. For the similar, but much slower, reaction of the Malachite Green (αα-bis-*p*-dimethylaminophenylbenzyl) cation, however, Ritchie [3] has since demonstrated that a small accelerating effect is attributable to general base catalysis by the tertiary bases 1,4-diazabicyclo[2.2.2]-octane (DABCO) and triethylamine. We therefore examined further the effects of these bases, and of trimethylamine, on the tris-*p*-methoxyphenylmethanol system, and now report similar results to those obtained by Ritchie.



Dependence of first-order constant for disappearance of cation on base concentration

Bunton and Huang,[4] in a further study of nucleophilic attack by a wide range of nitrogen-containing bases on the tris-*p*-methoxyphenylmethyl cation, have stressed the relative unimportance of general base catalysis compared with nucleophilic attack, but they also have found evidence for general base catalysis in the reaction with pyrrolidines.

As expected for such catalysis, our Figure shows the increase of the first-order rate constant of reaction (1)

$$(p\text{-MeO}\cdot C_6H_4)_3C^+ + H_2O \longrightarrow (p\text{-MeO}\cdot C_6H_4)_3C\cdot OH + H^+ \quad (1)$$

at 25 °C with increasing concentration of free base in buffered solutions of DABCO, trimethylamine, and triethylamine. Each point represents a mean of several rate determinations agreeing to within ±5%, the free base concentration being calculated from the total buffer concentration and the pH of the effluent from the mixing chamber of the stopped-flow apparatus (9·10 for DABCO, 9·65 for Me_3N, and 10·47 for Et_3N). In all cases the ionic strength was made up to 0·2 mol dm^{-3} and chloride was the only anion present (other than hydroxide). The stopped-flow rate measurements were made either with the apparatus described previously [1] or with a Canterbury stopped-flow instrument kindly loaned by Dr. A. R. Butler.

When the first-order constants for the disappearance of the cation are expressed as the sum $\{k_{H_2O} + k_{OH^-}[OH^-]\} + k_B[B]$, the values of the catalytic constants, k_B, are found to be 62 mol^{-1} dm^3 s^{-1} for DABCO, and *ca.* 260 mol^{-1} dm^3 s^{-1} for both trimethylamine and triethylamine. Our best value for k_{H_2O} agrees better with the 12 s^{-1} of Bunton and Huang [2] than with the 10·2 s^{-1} of Postle and Wyatt,[1] and the intercepts are roughly consistent with a k_{OH^-} near [3] 8200 mol^{-1} dm^3 s^{-1}. As with the Malachite Green system,[1] these figures for k_{H_2O}, k_B, and k_{OH^-} lie moderately well on a logarithmic plot against pK_a [8·82 (ref. 5) for protonated DABCO, 9·80 (ref. 6) for Me_3NH^+, and 10·87 (ref. 7) for Et_3NH^+], with a Brønsted coefficient of *ca.* 0·3 in this case; but the k_B value of the more basic triethylamine shows no increase over that of trimethylamine, possibly owing to a steric effect.

There still remains the possibility that the tertiary amines (though unable to release a proton) may act simply as nucleophiles, even if the resulting quaternary ammonium salt is subsequently converted into the alcohol. If that were the case however, the second-

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[6] D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.*, 1941, *A*, **177**, 499.

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order rate constants for nucleophilic attack by NH_3 and Et_2NH ($\log k/\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1} \simeq 3{\cdot}3$) would not be expected to be so much greater [1,4] than the values for the tertiary amines ($\log k/\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1} \simeq 2{\cdot}4$), especially since the unimportance of general base catalysis in the nucleophilic reactions [4] implies that the removal of the proton does not play a major role in determining their rates. General base catalysis of the nucleophilic attack by water therefore seems the more likely explanation of the effects of tertiary amines.

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