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Hydrogen Exchange in 1,3,5-Trinitrobenzene:[1] Effect of Base

By E. BUNCEL* and E. A. SYMONS

(*Department of Chemistry, Queen's University, Kingston, Ontario, Canada*)

THE recently reported[2,3] conclusive evidence for the occurrence of hydrogen exchange in 1,3,5-trinitrobenzene has removed some of the ambiguity of earlier reports[4] on the topic. However these observations of hydrogen exchange were confined to two media, tritiated methanolic sodium methoxide[2] and sodium deuteroxide in dimethylformamide–D_2O,[3] and hence can give no information on the feasibility of the proton transfer process between trinitrobenzene and amines, concerning which a number of conflicting views have been expressed in the literature.[4a,4d,5] The question may also be raised whether the proton transfer reaction from 1,3,5-trinitrobenzene may be effected by other Brønsted bases, apart from alkoxide and amines.

Previously we had shown[3] that the exchange process between deuteroxide and trinitrobenzene in $HCONMe_2$–D_2O medium is slow at room temperature but occurs readily at 100°; this contrasts with the much more ready hydrogen exchange observed with *m*-dinitrobenzene[1,6] under corresponding conditions. The reaction conditions used in the present work were hence as follows: concentrations, trinitrobenzene 0·5 M; base 0·1 M; medium, 90% $HCONMe_2$–10% D_2O; temperature, 100°; time, 3 hr. (except as noted). The anionic bases were present as the sodium salts. The extent of deuteration was determined by infrared spectroscopy on recovered samples of trinitrobenzene. The maximum exchange for the deuterium:hydrogen ratio in the system is 87%. Our results of extent of exchange with various bases are as follows: deuteroxide, 87%; sulphite, 76%; acetate, 85%; benzoate, 87%; piperidine, 74%; n-hexylamine, 78%; triethylamine, 37%; diazabicyclo[2,2,2]octane, 81%; pyridine (6 days), 27%.

The results show that exchange does indeed occur, both with anionic and with neutral bases, and that the deuteroxide-induced exchange does not vastly exceed that with the other bases (excepting pyridine). The reactivity of the anionic bases exceeds that of the amines, in accord with considerations of medium effects.[7] The relative reactivity of the amines is informative. The order n-hexylamine ~ piperidine > pyridine follows approximately a decreasing order of base strengths of these amines† (neither piperidine[5b] nor pyridine[5a] were believed to be able to take part in

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† The base strengths of the amines and of the other bases concerned are not known for the medium under study. They will differ from the values in aqueous medium, but the relative order of base strengths will usually remain unaffected for bases of a given charge type, except for amines where solvation can result in anomalous orders within a given series (primary, secondary, tertiary) of amines (ref. 8).

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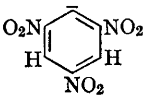
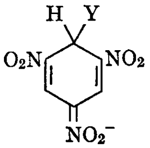
proton transfer, though under different reaction conditions). Of the two tertiary amines, the bicyclic amine with the nitrogens at the bridgeheads is considerably more reactive than triethylamine, despite the greater (by two units) pK† of the latter. This observation, which finds explanation in steric hindrance to proton transfer,[9] indicates that proton abstraction is caused by the amines and not by deuteroxide ion formed in a hydrolytic equilibrium. The data with the amines thus suggest general base catalysis of hydrogen abstraction in 1,3,5-trinitrobenzene. Brønsted-base catalysis of aromatic hydrogen abstraction has not been tested previously (*cf.*, ref. 1 for data on *m*-dinitrobenzene).



(I)



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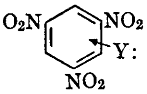

(III)

The mechanism of the exchange process is indicated[2,3] to be abstraction of a proton by base (Y:) with formation, in low concentration, of the trinitrophenyl anion (I), followed by its neutralization by D_2O of the medium. It is well established, however, that the interaction of an aromatic polynitro-compound with base can also lead to the formation of Meisenheimer adducts (II)[10] and of charge-transfer complexes (III).[11] It is also considered[5d] that whereas primary and secondary amines take part in Meisenheimer complex formation, tertiary amines do not. It is noteworthy that in the present study all the reaction solutions, except for the case of pyridine, were intensely coloured, indicating that complex formation of some type occurred in these systems. The nature of these complexes and their effect on hydrogen exchange is under study.

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