Hydrogen Exchange in 2,4,6-Trinitrotoluene

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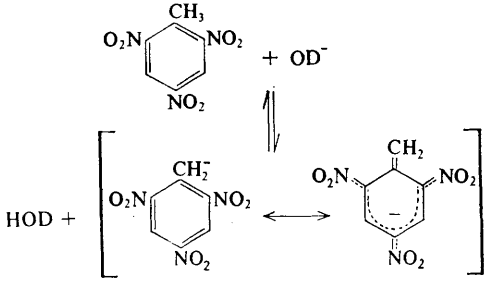
SINCE the 2,4,6-trinitrobenzyl anion is isoelectronic with the picrate anion one might expect an unusually high acidity for the methyl hydrogens in 2,4,6-trinitrotoluene. Formation of the 2,4,6-trinitrobenzyl anion has in fact been postulated in a number of processes involving the interaction of 2,4,6-trinitrotoluene in basic media.[1] Direct evidence for this carbanion is, however, not so well substantiated. The observation of a spectral absorption in solutions of 2,4,6-trinitrotoluene in ethanolic sodium ethoxide[1a] is not definitive evidence for the 2,4,6-trinitrobenzyl anion since other coloured species are also known to be formed in basic solutions of 2,4,6-trinitrotoluene: charge-transfer complexes,[2] radical anions,[3] and σ-complex adducts[4] (*cf.* ref. 5). The proton transfer process was tested[1b] by means of a hydrogen–deuterium exchange experiment: only 23 atom per cent deuterium was incorporated into 2,4,6-trinitrotoluene after exposure to pyridine–D_2O for 2—3 weeks.[1b] Recently the interpretation of the previous studies[1a,b] in terms of the 2,4,6-trinitrobenzyl anion has been questioned[5c] and the view expressed[5c] that the acidity of the methyl hydrogens should not be large enough to allow ionization by ethoxide ion. It is also noted that in a related study[6] in which formation of a nitrobenzyl type anion was indicated on the basis of other evidence, the incorporation into the substrate of deuterium from the reaction medium could not be demonstrated.[6]

We report the observation of a ready exchange of the methyl protons of 2,4,6-trinitrotoluene in a basic medium. 2,4,6-Trinitrotoluene (0·5M) in 90% dimethylformamide–10% D_2O containing NaOD (0·1M) gave a purple coloured solution. The introduction of hydrogen into the medium was followed by observing the appearance of the 3450 cm.$^{-1}$ absorption due to HOD.[7] After 5 min. the HOD absorption corresponded to 50% of the theoretical value and in 30 min. the equilibrium HOD absorption was reached for exchange of the methyl hydrogens. In an attempt to observe nuclear hydrogen exchange (*cf.* ref. 8) the temperature was raised to 100°. A slow liberation of HOD was observed but the solution rapidly discoloured and attempts at recovery of unreacted substrate were unsuccessful. Apparently extensive decomposition had occurred. The trinitrotoluene from the room temperature treatment with NaOD–D_2O–dimethylformamide could readily be recovered in good yield on acidification. The n.m.r. spectrum of the recrystallized material (m.p. 80·5—81·5°) showed that the methyl hydrogens were 86% exchanged, while deuterium analysis† showed 89% exchange (theoretical equilibrium deuteriation for the D:H ratio in this system is 88%).

The results reported here provide direct evidence for the ionization of 2,4,6-trinitrotoluene according to the equation



The possible involvement of other species in this system is under active consideration.

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† Analysis by J. Nemeth, Urbana, Ill., by the combustion–falling drop method.

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