Hydride Transfer from Cyclohexadienyl Anions: The Reaction between the Hydride Meisenheimer Adduct of 2,4-Dinitroaniline and 1,3,5-Trinitrobenzene

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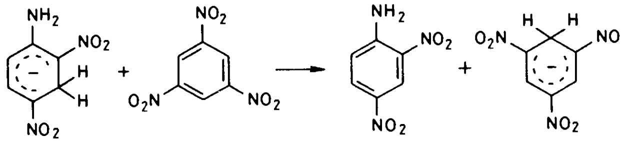
The hydride Meisenheimer adduct of 2,4-dinitroaniline transfers hydride to 1,3,5-trinitrobenzene to form its corresponding hydride Meisenheimer adduct. The reaction is practically irreversible. In dilute solution in dimethyl sulphoxide it exhibits second-order kinetics and the observation of several sharp isosbestic points shows that it occurs without formation of any detectable intermediate species.

The reaction of borohydride salts with 1,3,5-trinitrobenzene (TNB)[1] and some derivatives of 1,3-dinitrobenzene[2] leads to substituted cyclohexadienyl anions that can be looked upon as hydride Meisenheimer adducts of the parent aromatic compounds. The dimethyl sulphoxide (DMSO) solutions of some of these adducts are relatively stable, and the question arises whether the adducts could themselves function as hydride donors and serve as mild reducing agents. To examine the ease of the hydride transfer from carbon–hydrogen bonds of this type we have prepared the tetramethylammonium salts of (I) and of (II), and have observed the reaction (1) of (I) with 1,3,5-trinitrobenzene by monitoring the u.v.–visible absorption spectrum.

The reaction proceeds essentially to completion, and there is no indication of the occurrence of a reaction in the reverse direction when solutions of (II) and of 2,4-dinitroaniline are mixed. It occurs at a conveniently measurable rate when the low concentrations appropriate to optical absorption spectra are employed. At higher concentrations (*ca.* 0.2M), convenient for the observation of proton n.m.r., the reaction appears to be almost instantaneous, and the proton resonances observed after mixing solutions of trinitrobenzene and of (I), both in fully deuteriated DMSO, correspond to the known spectra of 2,4-dinitroaniline and (II).

The observed pseudo-first-order rate constants (Table) are proportional to the concentration of the reagent (TNB) in large excess, indicating the overall second-order and bimolecular character of the reaction (1). Using the second-order rate constants one can calculate the heat of activation of the reaction to be quite low (8—9 kcal mol^{-1}; *ca.* 35 kJ mol^{-1}). The corresponding entropy of activation is negative, as expected for a bimolecular process. Its numerical value ($\Delta S^{\ddagger}$ *ca.* -25 cal K^{-1} mol^{-1}; *ca.* -105 J K^{-1} mol^{-1}) is large, but falls within the range reported for reactions of this type.

When hydride Meisenheimer adducts are kept in DMSO solution on their own, several reactions are found to occur,[2] depending on the substrate from which the Meisenheimer adduct is formed. The present work indicates that hydride transfer to another chemical species must be included amongst these possibilities. The observations point to the existence of a class of hydride transfer reactions that could be more fully explored with a view to (*a*) establishing relative thermodynamic stabilities of cyclohexadienyl anion systems and (*b*) exploitation of the adducts as mild reducing agents. The examples chosen in the present exploratory study establish relative stabilities in the sense that the equilibrium of reaction (1) lies essentially on the right-hand side. It should also be noted that both compounds were selected because of their relatively high stability and that for preparative applications as reducing agents the use of the less stable hydride Meisenheimer adducts ought also to be considered.



(I)

(II)

(1)

Table. Rate constants for reaction (1)

10^5-$[(I)]_{initial}$/M	[TNB]/$[(I)]_{initial}$	T/°C	$10^2k_1/s^{-1}$	k_2/ l mol^{-1} s^{-1}
3.5	20	20	0.27	3.9
3.5	40	20	0.70	4.9
3.5	80	20	1.20	4.4
3.5	80	25	1.90	6.7
3.5	80	30	2.30	8.3
3.5	80	35	2.90	10.2

Experimental

DMSO was distilled from calcium hydride under reduced pressure and then stored over molecular sieve (4A). Acetonitrile was distilled and also stored over molecular sieve (4A).

Tetramethylammonium salts of (I) and of (II) were prepared by adding a solution of the respective aromatic parent compound (14 mmol) in acetonitrile (60 cm^3) to a stirred suspension of tetramethylammonium borohydride (10 mmol) in an equal volume of acetonitrile. The reaction vessel was flushed with nitrogen and protected from light. The mixture was stirred for 90 min, filtered, and then slowly added to an excess volume of cold diethyl ether. The required salts precipitated from the solutions on standing for 1 h at 0 °C. They were recrystallised from a mixture of acetonitrile and diethyl ether. The salt of (I) (yield 77%) is a hygroscopic dark violet solid, m.p. 110 °C. It is very soluble in DMSO, soluble in acetonitrile, acetone, water, and methanol, and insoluble in carbon tetrachloride and diethyl ether. It is decomposed by most polar solvents and only freshly prepared solutions in DMSO were used for kinetic experiments. The solid decomposed slowly even when kept at 0 °C in a sealed tube under nitrogen with exclusion of light. It remained usable for *ca.* 1 month. The salt of (II) formed violet-brown crystals (yield 90%, m.p. 131—132 °C, lit.,[1] 131—132 °C), which were stable for at least 6 months when stored in the same manner. Its solubility in different solvents is qualitatively similar to that of the salt of (I).

The absorption maxima of solutions of the tetramethylammonium salt of (I) in DMSO occur at 274 (ε 7 900), 347 (16 000), and 567 nm (18 000) and those of the corresponding salt of (II) at 478 (ε 24 000) and 585 nm (11 000). The progress of the reaction (I) can therefore be monitored most easily by measuring the increase in absorbance at 478 nm. Rate measurements were performed under pseudo-first-order conditions, using a large excess of trinitrobenzene, with the results given in the Table. Periodic scans of the absorption spectrum, between 300 and 700 nm, of dilute equimolar solutions of (I) and trinitrobenzene showed, besides the large increase in absorption at about 478 nm, decreases in absorption around 567 and 347 nm and an increase (shoulder) in the absorption near 630 nm. The spectra also exhibited four sharp isosbestic points (at 603, 510, 354, and 323 nm), clearly indicating the absence both of significant concentrations of intermediates in reaction (1) and of reactions destroying the products at a significant rate.

Acknowledgements

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