Reduction of Quinones by Hydride Meisenheimer Adducts

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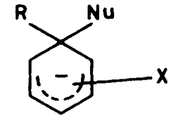
Hydride Meisenheimer adducts, prepared by the reaction of 1,3,5-trinitrobenzene or 2,4-dinitroaniline with tetrahydridoborate ions, can transfer hydride to a range of quinones in dimethyl sulphoxide solution. Rate constants are reported for the 1,3,5-trinitrobenzene adduct and tetrachloro-1,4-benzoquinone, tetrabromo-1,4-benzoquinone, and 2,6-dichloro-1,4-benzoquinone, and for the 2,4-dinitroaniline adduct with 1,4-benzoquinone. The rates increase with increasing reduction potential of the quinone. In all cases the hydroquinones formed are slowly oxidised back to quinones.

There are indications that the formation of the products of the hydride transfer is preceded by formation of a species having a low-intensity absorption maximum at >700 nm, which is tentatively ascribed to a charge-transfer complex.

4-Nitrobenzaldehyde reacts with the hydride adduct of 1,3,5-trinitrobenzene at a much lower rate.

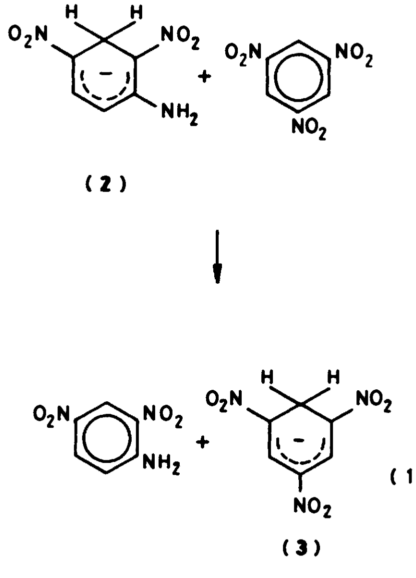
All the reactions observed are characterised by low energies of activation (in the range 36—51 kJ mol^{-1}) and large negative entropies of activation.

The formation of anionic Meisenheimer adducts (1) by attachment of a nucleophilic anion (Nu$^-$) to an aromatic polynitro compound (or other electron-depleted aromatic system) is



(1)

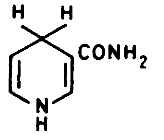
generally a reversible process. In the case of hydride adducts (for which Nu = R = H), the formation, by transfer of hydride from the tetrahydridoborate anion (BH_4^-) to the aromatic compound, is not directly reversible, since BH_3 is not a stable species in solution. Most of the adducts that have been examined undergo other reactions to form secondary products.[1] It has, however, been noted that, in the presence of a reactive hydride acceptor, a hydride Meisenheimer adduct may transfer hydride with re-formation of the parent aromatic compound. The reaction studied in this context was the hydride-transfer reaction (1).[2]



(1)

It seemed of interest to know whether other organic hydride acceptors similarly interact with these Meisenheimer adducts, perhaps with a view to their preparative use as mild reducing agents. The present paper examines the reaction between (3) and (to a smaller extent) (2) with some quinones, and that of (3) with 4-nitrobenzaldehyde. The rate of disappearance of the intensely coloured adduct ion is conveniently monitored by spectrophotometry, at very low concentrations.

Hydride transfers from hydride Meisenheimer adducts to quinones and other carbonyl compounds are reminiscent of the much discussed reductions by the structurally related dihydronicotinamide (4),[3] a model compound for enzymic reduction, and the reaction mechanisms may be comparable.



(4)

Experimental

The preparation of the Meisenheimer adducts (2) and (3) (as tetramethylammonium or potassium salts), methods for the purification of materials, and kinetic procedures were essentially those described earlier.[1,2] Rate measurements relate to reactions under conditions where first-order kinetics are observed [low concentrations of (3) with a large excess of the quinone]. The tabulated values (Tables 1 and 2) are second-order rate constants.

A specimen of 2,3,5,6-tetrachlorobenzene-1,4-diol was prepared by reduction of a suspension of chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) (0.5 g) in ethanol with tetramethylammonium tetrahydridoborate (0.1 g), stirred for 2 h at room temperature, followed by acidification with dilute hydrochloric acid and crystallisation of the precipitated product from acetic acid. It had m.p. 230 °C (lit.,[4] 232 °C) and i.r. and n.m.r. spectra in agreement with the expected structure. The same product (mixed m.p.) was obtained from the reaction of (3) (tetramethylammonium salt) (0.25 g) with chloranil (0.25 g) in dimethyl sulphoxide (5 ml) under nitrogen (30 min at 25 °C). The mixture was poured onto ice-cold dilute hydrochloric acid, and the precipitated product was again crystallised from acetic acid.

Table 1. Rate constants for reaction of (3) with quinones

		k_2/dm^3 mol^{-1} s^{-1}		
t/°C	[Quinone]	Chloranil	Bromanil	2,6-Dichloro-1,4-benzoquinone
20	7×10^{-4}	6.9	4.9	0.48
25	7×10^{-4}	9.7	6.5	0.74
30	7×10^{-4}	12.2	7.9	1.13
35	7×10^{-4}	15.1	9.4	1.43
25	1.4×10^{-3}	10.3	6.3	0.72
25*	1.4×10^{-3}	11.1		
$E_a^{\ddagger}$/kJ mol^{-1}		36	37	51
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}		−114	−115	−86

* $(3)_{\text{initial}} = 1.75 \times 10^{-5}$M; in all other experiments $(3)_{\text{initial}} = 3.5 \times 10^{-5}$M.

Quinones and 4-nitrobenzaldehyde were recrystallised commercial materials.

The progress of the reactions was observed by use of a Pye-Unicam SP 8-100 spectrophotometer. At low concentrations (*ca.* 3.5×10^{-5}M) each) it is characterised by a decrease in the intense absorbance due to (3) (maxima at 585 and 478 nm) and of the band due to quinone [$\lambda_{\text{max.}}$ 285 nm, in the case of chloranil, 305 nm for bromanil (2,3,5,6-tetrabromo-1,4-benzoquinone) and 260 nm for 2,6-dichloro-1,4-benzoquinone]. The decreases were accompanied by an increase in absorbance attributable to the monoanion of the respective hydroquinone ($\lambda_{\text{max.}}$ 448 nm in the case of tetrachloro-1,4-diol), in agreement with earlier reports,[3,5] which is obscured by the absorbance due to (3) in the early stages of the reaction, and by an increase in absorbance due to the hydroquinone itself ($\lambda_{\text{max.}}$ 315 nm for the tetrachloro-, 338 nm for the tetrabromo-, and 305 nm for the 2,6-dichloro-compound). These concurrent changes were associated with the appearance of isosbestic points. In all cases the spectrum of the product slowly changed back to that of the parent quinone. This instability had previously been noted in oxidations effects with chloranil.[6] The reaction is presumably due to oxidation either by residual oxygen or by the solvent itself, but the observed rate constants k_2 for the reduction of chloranil were unaltered when the absorption cell was purged with nitrogen.

Solutions of 1,4-benzoquinone and (3) at the same low concentrations (*ca.* 3.5×10^{-5}M) showed no change in absorbance over 24 h. At higher concentrations (*ca.* 1.7×10^{-3}M each), decrease in the intense absorbance at 585 nm occurred, accompanied by appearance of a very weak broad absorption above 700 nm. Successive scans passed through an isosbestic point at 675 nm. Such weak long-wavelength absorption (and an isosbestic point at 670 nm) were also noticeable for solutions containing (3) and 2,6-dichloro-1,4-benzoquinone at corresponding concentrations, but the band both formed and disappeared again much more quickly. In the cases of chloranil and bromanil, a transient weak absorption above 700 nm was just discernible at these concentrations.

Reactions of the hydride adduct (2) with quinones were more rapid than that of (3). The rate was measurable by the method employed only for 1,4-benzoquinone. Under second-order conditions (both concentrations *ca.* 3.5×10^{-5}M), the observed second-order rate constant at 25 °C was 63 dm^3 mol^{-1} s^{-1}. For all the quinones studied with (2), the product spectrum was that of 2,4-dinitroaniline, which obscured the region of absorption for the quinones and hydroquinones.

The reaction of (3) with 4-nitrobenzaldehyde was slower than that with the quinones; the observed rate constants and derived parameters are given in Table 2.

Table 2. Rate constants for reaction of (3) with 4-nitrobenzaldehyde

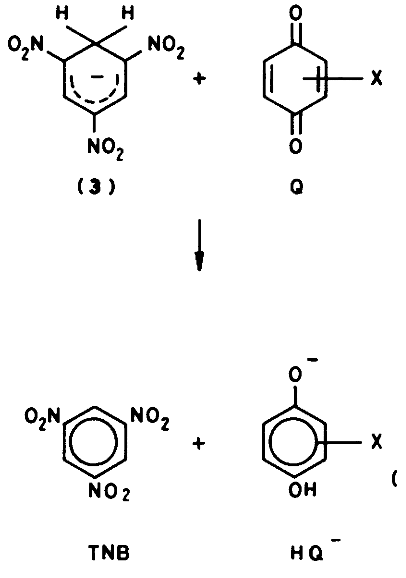
[4-Nitrobenzaldehyde] = 0.21M; $(3)_{\text{initial}} = 3.5 \times 10^{-5}$M

t/°C	20	25	30	35
10^4k_2	3.3	4.2	6.8	9.0

E_a 46 kJ mol^{-1}
$\Delta S^{\ddagger}$ −163 J K^{-1} mol^{-1}

Disucussion

Dilute solutions containing the Meisenheimer adduct reagent (3) and one of the quionones show a gradual decrease of the absorbance due to these reagents, and at the same time an increase in absorbance attributable to the hydroquinone and its anion. The overall reaction taking place is represented in equation (2). Second-order rate constants corresponding to this process are given in Table 1.



(3) Q

TNB HQ$^-$

(2)

The hydroquinone anion formed according to equation (2) is in part converted into the hydroquinone itself. This reaction, a proton transfer, most probably involves water, present even in dried dimethyl sulphoxide unless stringent precautions are taken. Less probably, the proton donor may be dimethyl sulphoxide itself. Hydroquinone anions are more susceptible to oxidation than hydroquinones themselves, and their presence in the solution may account for the observation that the reduced reaction product slowly reverts to quinone.

The representation of the main reaction by the equation (2) is probably an oversimplification, since there were indications in some cases of the formation of an intermediate species with a very weak absorbance at long wavelengths (>700 nm). An absorption band in the same region has recently been reported by Fukuzumi and Tanaka[5] for the reduction of chloranil by 1-benzyl-1,4-dihydronicotinamide. This reduction is also formally represented as a hydride transfer from the reducing agent to chloranil. On the basis of their observation the authors suggested that the long-wavelength absorption was due to a charge-transfer complex between the reagents, as a proposed definitive conclusion of a long-standing controversy on the mechanism of the important dihydronicotinamide reductions. They were able to support this interpretation by isolation (immediately upon mixing of the reagents) of a solid product in which the carbonyl-stretching band of chloranil was still present. Proceedings by analogy, it is tempting to assign the absorbance above 700 nm observed in our work also to a charge-transfer complex (CT), between (3) and the quinone (Q). On this tentative assumption, reaction (2) should be written as (3).

$$(3) + Q \underset{-1}{\overset{1}{\rightleftharpoons}} CT \xrightarrow{2} TNB + HQ^- \qquad (3)$$

Since the absorption spectra of the solutions exhibited isosbestic points (for the disappearance of reactants and appearance of TNB and HQ^-) any intermediate CT can be present in only low concentration. In these circumstances it is not possible to deduce from the observed reaction order [first-order in (3) and in Q] whether step 1 is rate-limiting or whether there is a pre-equilibrium followed by rate-limiting hydrogen transfer in the low-concentration intermediate CT. With benzoquinone, the reaction does not proceed beyond CT and, in that case, step 1 must be rate-limiting. For solutions of 2,6-dichloro-1,4-benzoquinone at high concentration, it was still possible to see an initial increase in the absorbance ascribed to CT. Accordingly, it seems to follow that at the very much lower concentrations at which the main kinetic runs (Table 1) were performed, the formation of the intermediate would be a slow process. It would therefore be rate-limiting, which is an unexpected conclusion. On this interpretation the rate constants (Table 1) and activation parameters (Table 2) refer to the formation of a charge-transfer complex. These tentative inferences require fuller investigation, especially in relation to corresponding reductions by dihydronicotinamides.

Of course, the experimental observations do not rule out that the observed species is an intermediate of a different and as yet unspecified type. The low activation energies and large negative entropies of activation observed in all the hydride-transfer reactions here under consideration suggest that a common mechanism applies in all cases.

Some exploratory comparative experiments (Table 1) with 4-nitrobenzaldehyde suggest that the reduction of activated aldehydes by hydride Meisenheimer adducts is a closely similar reaction.

Acknowledgements

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