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REACTION MECHANISMS IN REDUCTIONS BY METAL-AMMONIA SOLUTIONS

A. J. Birch and D. Nasipuri
Department of Chemistry, University of Manchester

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Abstract—The mechanism is discussed of the reduction of monobenzenoid compounds by means of metals and acohols in liquid ammonia. Contrary to claims in the literature[1] *iso*quinoline and dibenzothiophene are both readily reducible by this method.

Recently[1] the mechanism of the metal-alcohol-liquid ammonia reductions of monobenzenoid compounds has been discussed in terms of the initial addition of a hydrogen atom, an hypothesis discussed by us in 1944[2] but shortly thereafter abandoned for what still appear sufficiently good reasons. We feel that a further critical consideration of the evidence is required in view of our belief that all of the phenomena can be correlated and explained on the basis of an initial stage of electron-addition.

Initial stage of reduction

The first observation of crucial importance in this field was that of Wooster[3] who showed that the presence of alcohol in liquid ammonia permitted the reduction of benzene to occur, giving 1:4-dihydrobenzene, whereas in its absence there was no reaction. Wooster also provided some evidence that alkyl- or methoxy-benzenes are similarly reducible, but he did not analyse or examine the products in detail and wrongly guessed their formulae to be 1-substituted-1:4-dihydrobenzenes. They were later shown to be 1-substituted-2:5-dihydrobenzenes.[2]

In the case of polycyclic compounds it was already known (e.g.[4]) that reduction could be experimentally carried out in two stages: an initial addition of metal electrons, to form an ionised salt, e.g. I → II, which by the action of a proton source (often in the working-up process) leads to a hydroderivative (e.g. III). We were impressed by the fact that if the processes are carried out under the correct experimental conditions the *same* product can be obtained from a two-stage process (when this is possible) and a one-stage process. We were reluctant, therefore, to postulate a new mechanism, such as hydrogen-atom addition, to account for the benzene reduction if a reasonable explanation could be found for the facts above. In lectures

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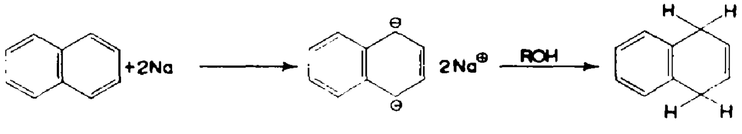
[1] W. Hückel, B. Graf and D. Munkner, *Liebigs Ann.* **614**, 47 (1958). cf. W. Hückel and I. Nabik, *Ber.* **89**, 2115 (1956); W. Hückel and G. Graner, *Ber.* **90**, 2017 (1957).
[2] A. J. Birch, *J. Chem. Soc.* 430 (1944).
[3] C. B. Wooster, *U.S. Patent* 2182242 (1938).
[4] W. Hückel and H. Bretschneider, *Liebigs Ann.* **540**, 157 (1937).

over a number of years (e.g.[5]) we have advanced an explanation based on the following equilibria and reactions:



I II III

$$\begin{tikzcd}
\mathrm{Ar}+\epsilon \arrow[r, shift left, "A"] & \mathrm{Ar}\ominus\bullet \arrow[l, shift left] \arrow[r, "\mathrm{ROH}"] \arrow[d, shift right, "\epsilon"'] & \mathrm{ArH}\bullet \arrow[r, dotted, "\epsilon"] & \mathrm{ArH}\ominus \arrow[r, "\mathrm{ROH}"] & \mathrm{ArH}_2 \\
& \mathrm{Ar}\ominus\ominus \arrow[u, shift right, "B"'] \arrow[r, "2\mathrm{ROH}"] & \mathrm{ArH}_2 & &
\end{tikzcd}$$

The important factors are the position of the equilibrium A, whether equilibrium B can be established at all and whether a sufficiently acid proton source (e.g. ROH) is present which can protonate the anion-radical. There is ample evidence for the reversibility of the electron-addition stage.[6] If the substance Ar contains only an isolated benzene ring, not carrying a carboxyl group, equilibrium A will be much further to the left than if Ar is polycyclic, when Ar⊗⊖ will be much more stable. Addition of a second electron (equilibrium B) seems also very unlikely in a monobenzenoid system, although it is possible (e.g.[4]) with polycyclic compounds in the presence of a solvent such as ammonia, which is polar enough to stabilise the resulting ions by solvation. This solvation in fact explains the favourable influence of ammonia on the reduction processes in general.

If the equilibrium A is produced at all with monobenzenoid substances then protonation of the anion-radical will permit reduction to proceed irreversibly. Ammonia apparently cannot provide the necessary proton because of its low acidity (pK about 34) but alcohols (pK about 16–18) can do so. This can be rationalised on the expected low basicity of the anion-radical, by analogy with ketyl radicals,[6] and is supported by the fact that even anions of type ArH⊖ have a basicity of the same order as $NH_2\ominus$. With more highly acidic proton sources (the limit has not been defined) evolution of hydrogen gas occurs as a rapid competing reaction. The evolution of hydrogen gas from sodium and alcohols in ammonia is very slow.[7]

The first stages of the process are formally, but only formally, equivalent to the addition of a hydrogen atom. The distinction is important because on our mechanism it is possible to arrive at conclusions concerning relative rates and possible products by considering the nature and reactivity of the anion radical on the basis of the known electronic effects of substituents and of the ring system. For example, increasing difficulty of reduction can be correlated with increasing substitution by electron-repelling groups.[6]

We must briefly consider the evidence put forward by Hückel *et al.*[1] to support the hydrogen atom mechanism. The effect of finely divided transition metals in preventing reduction,[1] first observed with iron,[2] we have attributed to an acceleration of the slow reaction of alkali metal and alcohol in ammonia to give hydrogen gas; i.e. adsorbed hydrogen atoms are catalytically formed on the metal surface and combine to hydrogen molecules, thus rapidly removing the reducing agent. A possible

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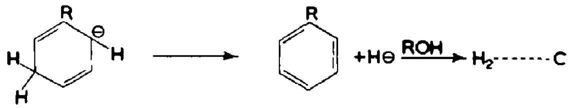
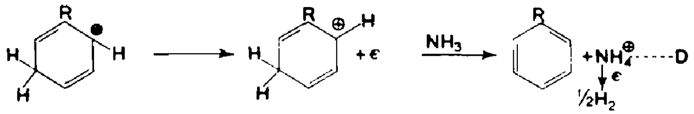
[5] A. J. Birch, *J. Roy. Inst. Chem.* 100 (1957).

[6] A. J. Birch, *Quart. Rev.* 69 (1950).

[7] A. J. Birch, *J. Chem. Soc.* 811 (1945).

practical explanation of the similar catalytic effects of aromatic compounds on hydrogen evolution may be the decomposition C below. In fact, potassium hydride is rapidly eliminated from the dihydroalkylbenzenes by the action of potassium amide in ammonia.[8] An alternative explanation is that in the ionising environment the protonated anion-radical may lose an electron to give the protonated hydrocarbon, a derivative of a strong acid which would immediately produce an ammonium cation (D). For experimental reasons not at present readily explicable, ammonium cations rapidly produce hydrogen gas with sodium in ammonia, and could well react with a very mobile electron before being neutralised by an anion.





Hückel *et al.*[1] also note differences in the behaviour on reduction at −50° of mixtures of alkylbenzenes compared with mixtures of naphthalene and alkylbenzenes. This they attribute to the naphthalene being reduced by initial electron addition while the monocyclic compounds are reduced by hydrogen atoms. Since these hydrocarbons at least partially crystallise and have a very low solubility in ammonia especially in the presence of ions, we feel that these results cannot be simply interpreted in mechanistic terms, depending as they must on complex phase relations and details of experimental procedure.

A more important discrepancy is the claim[1] that *iso*quinoline and dibenzothiophene are reducible in a two-stage process of metal addition followed by proton addition, but not by the one-stage process, in which they are said merely to catalyse the evolution of hydrogen gas. It must be noted that differing *products* by the two process are explicable (e.g.[6]) but since on our view the presence of alcohol assists the initial stage then reduction of some kind should occur in one stage if it occurs in two stages.

Under our usual experimental conditions (which are not those attributed to us by Hückel *et al.*[1] see below) we find that both of these substances are readily reducible.

In the case of quinoline the major product is 1:2:3:4-tetrahydroquinoline containing a trace of dihydroquinoline, as shown by the isolation of a very small proportion of the crystalline trimer, m.p. 187°, of the latter. Using two equivalents of sodium about half of the starting-material is unchanged. The production of the tetrahydro-derivative is not surprising. Either of the possible dihydro-derivatives reduced in the heterocyclic ring (IV) or (V) should more readily be reducible than the starting-material; the former is a styrene derivative, the latter contains $>C{=}N-$. Reduction in the heterocyclic ring is to be expected because of the higher electron-affinity of

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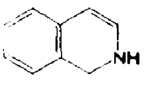
[8] A. J. Birch, *J. Chem. Soc.* 1642 (1947).

nitrogen compared with carbon. The production of dihydro*iso*quinoline in absence of ethanol[1] is to be expected not because the initial step is different but because the anion (VI) should survive until the reaction is worked up since its negative charge will prevent further electron addition as noted in cases.[6,9]



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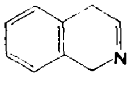
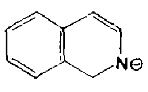
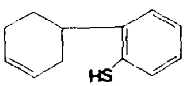


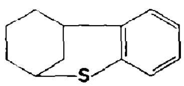
V



VI



VII



VIII

Hückel *et al.* probably failed to observe the reduction above since they were expecting a dihydro-derivative rather than the tetrahydro-derivative actually formed.

Dibenzothiophene is readily reducible, but requires six equivalents of sodium. The use of two equivalents[1] would therefore leave unchanged two-thirds of the starting-material; Hückel *et al.*[1] apparently missed the alkali-soluble product (VII). The position of the double bond in (VII) has not been definitely determined, except that it cannot be conjugated with the benzene ring. The initial thiol, convertible to a crystalline derivative by the action of sodium chloroacetate, cyclises on distillation to what must be a bridged-ring product such as (VIII). This can be oxidised to a crystalline sulphone, and cannot be dehydrogenated by sulphur to dibenzothiophene under conditions where the latter is fairly stable.

In connexion with experimental conditions it may be noted that the process attributed by Hückel *et al.*[1] to Wibaut and Haak[10] is in fact closely similar to our usual experimental procedure. We have not since 1944 used the process of addition of the substance in alcohol to the metal dissolved in ammonia. We dissolve the substance, with at least 10 per cent of ethanol (or methanol) in the ammonia with a co-solvent such as ether or tetrahydrofuran if necessary, and add the metal slowly The reason for this was clearly pointed out in 1946[11] and lies in the ability of the excess metal (or metal amide produced) to catalyse conjugation of double bonds which leads to further reduction. The very useful procedure of Wilds and Nelson[12] using initially excess lithium metal must partially owe its success to the lesser tendency of this metal or its derivative to produce such secondary reactions.

Structures of the products

The structures of the dihydrobenzenes will be determined by two factors which should be definable on the above mechanism. (i) The position of addition of the proton to the anion-radical $Ar\otimes\ominus$ and (ii) the position of addition of the second proton to the mesomeric anion $ArH\ominus$. The expectation would be that addition to the anion-radical should occur in the position of greatest *free* charge density, i.e. *meta*

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[9] A. J. Birch, *J. Proc. Roy. Soc. N.S.W.* 83, 245 (1950); A. J. Birch and H. Smith, *Quart. Rev.* 17 (1958).

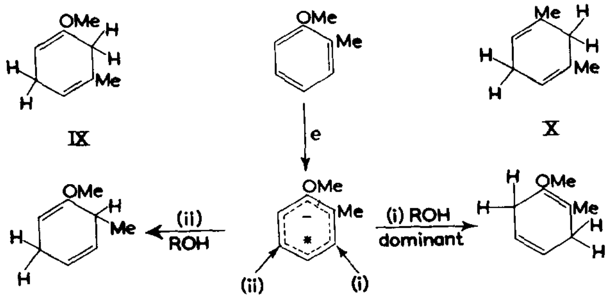
[10] J. P. Wibaut and F. A. Haak, *Rec. Trav. Chem. Pays-Bas* 67, 85 (1948).

[11] A. J. Birch, *J. Chem. Soc.* 595 (1946).

[12] A. L. Wilds and H. A. Nelson, *J. Amer. Chem. Soc.* 57, 5360 (1953).

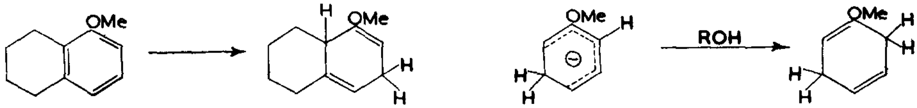
to an *o*, *p*-directing substituent, since accumulation of charge in the *ortho* and *para* positions will be opposed by the substituent. Similarly, addition might be expected *para* to a *m*-directing group, but in practice carboxyl is the only group of this type which is not itself reduced before the ring. In this case in fact the 1:4-dihydrobenzoic acid finally results.[13]

With two or more substituents, on the same grounds, we would expect addition: (i) *meta* to the most strongly *o*- *p*-directing group; and (ii) for preference not in a position occupied by an *o*-*p*-directing group. With *meta*- or *para*- dialkyl- or methoxy-alkyl- etc. benzenes the results agree quite simply with expectations,[6] the products being 2:5-dihydro-derivatives, e.g. *m*-tolyl methyl ether → (IX);[2] *m*-xylene → (X)[2]. Benzenes with *ortho* substituents involve a further complication. Experimentally, addition occurs *ortho* rather than *para* to a substituent, for example 1-methoxy-2-methyl benzene gives a mixture of the 2:5- and 3:6-dihydroderivatives, in which the latter predominates.[2] 5-Methoxy-1:2:3:4-tetrahydronaphthalene appears to give only one product (XI)[2] in accord with the rule.



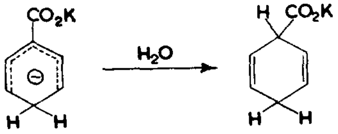
IX

X



XI

XII



XIII

This rule can presumably be correlated with the usual greater effect of an alkyl group in the *para* rather than the *ortho* position; it is also observed in cases of ether fissions with metal–ammonia solutions.[6]

The position of addition of the second proton has already been considered in detail[13] and it has shown experimentally that anions of types (XII) or (XIII) do lead on irreversible protonation to unconjugated dihydrobenzenes identical with those produced by direct reduction of the corresponding aromatic compounds. Such mesomeric anions are therefore likely intermediates in the reduction, as already

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[13] A. J. Birch, *J. Chem. Soc.* 1551 (1950).

postulated. Hückel *et al.*[1] apparently do not disagree with our views on these later stages.

We feel that the problem of the initial stage is not yet settled, but that our approach can at present explain all the known facts, and that it provides a more logical basis for correlations and a better aid to finding appropriate experimental conditions.

EXPERIMENTAL

Reduction of iso*quinoline*

(a). To a solution of *iso*quinoline (12·5 g) in liquid ammonia (300 cc) and ethanol (45 cc) was added sodium (5 g, 2·25 atoms) in small pieces over 5 mins. After evaporation of the ammonia, water was added and the product worked up as usual to give a yellow oil (11·8 g) b.p.121–122°/10 min; n_D^{22} 1·1578. The ultra-violet absorption curve was nearly identical with that of a mixture of equal parts of *iso*quinoline and 1:2:3:4-tetrahydro*iso*quinoline. The components were separated by passing moist carbon dioxide into an ethereal solution to precipitate the carbonate of the tetrahydro-compound. The weight of carbonate produced also supports the equal ratio of products. Tetrahydro*iso*quinoline was characterised as the picrate m.p.199–200° and hydrochloride m.p.198°, and *iso*quinoline as the picrate m.p. 223°. Several cc of the product kept after addition of a few drops of methanol deposited a few mg of crystals m.p.187° which may be one of the trimers of dihydro*iso*quinoline (cf.[1]); the original material therefore probably contains a very small proportion of dihydro-derivative.

(b). A solution of *iso*quinoline (12·5 g) in liquid ammonia (450 cc) and ethanol (70 cc) was reduced with sodium (10 g, 4·5 atoms). Worked up as before, the product was 1:2:3:4-tetrahydro-*iso*quinoline as an almost colourless oil (11·5 g) b.p.118–120°/10 min. The picrate had m.p. 199–200° (Found: C, 50·1; H, 3·7; N, 15·25; Calc, for $C_9H_{11}N, C_6H_3O_7N_3$: C, 49·7; H, 3·9; N, 15·5%). The hydrochloride had m.p. 198° (Found: C, 63·25; H, 7·5; N, 8·15; Calc, for $C_9H_{11}N$, HCl: C, 63·7; H, 7·1; N, 8·3%). The ultra-violet spectrum of the base in ethanol had λ_{max} 266 mμ, ε 410; λ_{max} 273 mμ, ε 410, and λ_{min} 240 mμ.

Reduction of dibenzothiophene

(a). Dibenzothiophene (6 g) in dry ether (120 cc) was added to liquid ammonia (350 cc) and ethanol (35 cc). Sodium (2·2 g, 3 atoms) was then introduced and the product worked up as usual but in an atmosphere of nitrogen. The ethereal extract gave unchanged dibenzothiophene (3·1 g) m.p. 96–97° in an almost pure state. The alkaline solution was acidified and extracted with ether. The resulting oil did not crystallise, but after warming with sodium chloroacetate in alkaline solution under nitrogen gave rise to 2 (cyclo*hex-2'-enyl) phenylthiol carboxymethyl ether* from light petroleum (b.p. 40–60°) m.p. 96–98° (Found: C, 68·00 H, 6·45; S, 12·3; Equiv. 248 $C_{14}H_{16}O_2S$ requires C, 67·7; H, 6·45; S, 12·9%, Equiv. 248). Distillation of the reduction product gave an oil (2·8 g) b.p. 100°/0·2 min n_D^{22} 1·6050 (Found: C, 75·9; H, 7·3; S, 17·2 $C_{12}H_{14}S$ requires C, 75·8; H, 7·4; S, 16·8%), possibly 3:4-*benz-2-thia*(1:3:3)*bi*cyclo*nonene* (VIII). It no longer dissolved in alkali and gave no nitroprusside test. The ultra-violet absorption had λ_{max} 250 mμ, ε 8900 and λ_{max} 288 mμ, ε 1500. It gave no picrate, and an attempt to dehydrogenate it with sulphur at 200° failed to yield dibenzothiophene. Oxidation of the substance (0·5 g) was carried out in acetic acid (5 cc) with hydrogen peroxide (5 cc 30%) at reflux for 30–40 mins. The product, was diluted with water, extracted with ether and the viscous oil crystallised from ethyl acetate-light petroleum (b.p. 40–60°). The *sulphone* crystallised in plates m.p. 75–76·5° (Found: C, 64·4; H, 6·2; S, 13·1; $C_{12}H_{14}O_2S$ requires C, 64·9; H, 6·3; S, 14·4%).

It was found that by increasing the proportion of sodium in the original reduction to 6·5 atoms the yield of alkali-soluble product was 85%. The substance so obtained was warmed in alkaline solution with excess methyl sulphate. The resulting alkali-insoluble oil, b.p. 110°/0·2 min is presumably 2(cyclo*hex-2'-enyl)phenylthiol methylether*. Found: C, 76·1; H, 7·95; S, 15·4. $C_{13}H_{16}S$ requires C, 76·45; H, 7·9; S, 15·65; λ_{max} 253 mμ, ε 7720. (cf. the absorption of *cyclo*hexylphenyl sulphide[14] λ_{max} 258·5 mμ, ε, 7000).

Acknowledgement—We are indebted to the Colombo Plan for a Fellowship (D. N.).

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[14] H. P. Koch, *J. Chem. Soc.* 391 (1949).