Concerted and Non-concerted Hydrogen Transfer: the Thermal Disproportionation of 1,2- and 1,4-Dihydronaphthalenes

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Summary A concerted mechanism is proposed for the thermal disproportionation of 1,2-dihydronaphthalene at *ca.* 300 °C in solution in which naphthalene and tetralin are formed in 1 : 1 ratio; under similar conditions 1,4-dihydronaphthalene underwent isomerisation (to 1,2-dihydronaphthalene) and disproportionation in concurrent reactions, both of which are catalysed by the glass surface of the reaction vessel.

Among the various categories of pericyclic reactions,[1] concerted group transfers (*i.e.* processes in which n σ-bonds $+$ m π-bonds $\rightleftharpoons$ n σ-bonds $+$ m π-bonds)[2] have not been well characterised. The *cis*-hydrogenations of olefinic C=C by hydrogen transfer from di-imine[3] provide the majority of examples, and these reactions are of some synthetic importance.[4] Mackenzie[5] has reported on the stereospecific intramolecular hydrogen transfers of certain members in the isodrin series. These reactions are unambiguous examples of group transfers. A concerted bimolecular mechanism has been invoked[1,5,6] to explain the formation of *cis*-1,2-dimethylcyclohexane (6·6%) from the reduction of 1,2-dimethylcyclohexene by *cis*-9,10-dihydronaphthalene.[6] However, dehydrogenation of cyclohexa-1,4-diene by phencyclone, and of cyclohexa-1,3-diene by quinones is non-stereospecific.[7] The lack of quantitative data, and the relatively few examples of group transfers leads to difficulty in making sensible predictions on how best to promote reactions in this category.

The pyrolysis of 1,2-dihydronaphthalene in various solvents at 301 °C† followed second-order kinetics and produced cleanly naphthalene and tetralin in strict 1 : 1 ratio. Solvent (dielectric constant ϵ at 25 °C) 10^5k l mol^{-1} s^{-1}: n-dodecane (2·01) 3·40, 1-chloronaphthalene (5·04) 4·80, n-hexanenitrile (17·26) 4·57, and dimethylformamide§ (36·71) 4·68. Dependence of k on temperature over the range 290—317 °C in 1-chloronaphthalene as solvent gave $E_a = 37{\cdot}0 \pm 1{\cdot}2$ kcal mol^{-1}, $\Delta H^{\ddagger} = 35{\cdot}9 \pm 1{\cdot}2$ kcal mol^{-1} and $\Delta S^{\ddagger}$ (578 K) $= -17{\cdot}1 \pm 2{\cdot}0$ cal K^{-1} mol^{-1}.¶

Although the decomposition of 1,2-dihydronaphthalene was accelerated by the addition of t-butyl hydroperoxide

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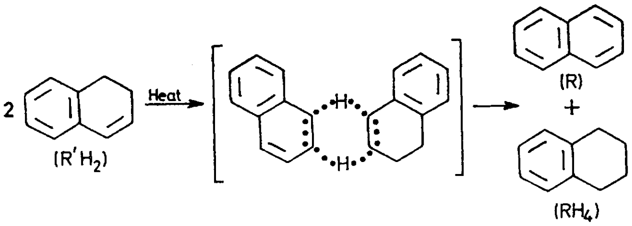
† Reactions were conducted in sealed ampoules under an inert atmosphere. Starting materials were purified and dried by standard procedures, particular care being taken to exclude peroxides and acidic or basic impurities. Analyses were by g.l.c. using phenylcyclohexane as internal standard. Most results were obtained in chloronaphthalene for which the standard deviation in 10^5k was 0·14.

§ Appreciable decomposition of DMF occurs at this temperature.

¶ Error limits are derived from the standard deviations for slope and intercept of the least squares Arrhenius plot.

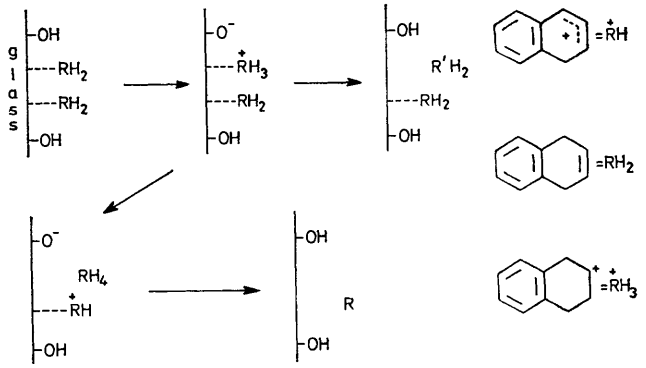
and di-t-butyl peroxide, no rate depression was observed in separate runs conducted in the presence of radical inhibitors (*e.g.* 4-methyl-2,6-di-t-butylphenol, hydroquinone, or *p*-nitrotoluene). In fact with hydroquinone a small *rate enhancement* was obtained ($10^5k = 5\cdot50$ l mol^{-1} s^{-1} at 301°C in $C_{10}H_7Cl$), and the enhancement was much more pronounced with the more acidic inhibitor benzenethiol ($10^5k = 12\cdot25$ l mol^{-1} s^{-1}, same conditions).[8] Many other inhibitors are disqualified because of their dehydrogenating properties. For example, the stable radical galvinoxyl oxidised 1,2-dihydronaphthalene to naphthalene under the reaction conditions. Hence, although both free radical and carbonium ion mechanisms can be caused to operate, in the absence of additives there is no evidence requiring such homogeneous multistep pathways. Heterogeneous catalysis by the surface of the glass vessel was also ruled out, which contrasts with the behaviour of 1,4-dihydronaphthalene.



SCHEME 1

We interpret the results in favour of a concerted mechanism for the hydrogen transfer (Scheme 1); the geometrically realizable $[{}_{\sigma}2_s + {}_{\sigma}2_s + {}_{\pi}2_s]$ interaction of orbitals is allowed by the general Woodward-Hoffmann rule.[1,2] The main feature which distinguished bimolecular group transfers from other *two-component* pericyclic reactions is the severe limitation imposed on *k* by *both* $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ terms.

Validation of Scheme 1 awaits stereochemical information. The preparation of suitably labelled 1,2-dihydronaphthalenes provides a surprisingly difficult synthetic challenge; we have, for example, been unable to repeat the reported[9] synthesis of *cis*-1,2-dihydro-1,2-dimethylnaphthalene. For 1,4-dihydronaphthalene the geometrically 'possible' $[{}_{\sigma}2_s + {}_{\sigma}2_s + {}_{\pi}2_s + {}_{\pi}2_s]$ transfer is unfavourable according to the Woodward–Hoffmann theory. Indeed, at 301 °C in 1-chloronaphthalene, 1,4-dihydronaphthalene is decomposed in two concurrent reactions: (i) isomerisation to 1,2-dihydronaphthalene and (ii) disproportionation to naphthalene and tetralin. The rate of formation of the disproportionation products was greater than was found in the 1,2-dihydronaphthalene thermolyses, and it is clear that 1,2-dihydronaphthalene is not, by and large, the precursor of these products in this case. Homogeneous stepwise processes appear to be ruled out by various observations, including the absence of inhibitor effects and the finding that toluene-*p*-sulphonic acid greatly promoted isomerisation but not disproportionation. Both reactions, however, were strongly catalysed by the addition of glass powder (largely 40—200 mesh, obtained by grinding ampoule tubing) with very little dependence on the cleaning and pretreating procedures used. This would appear to indicate that the catalytic action is due to surface hydroxy-groups on the glass rather than to leachable ions; Scheme 2 is a tentative explanation.



SCHEME 2

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[1] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 181.

[2] G. B. Gill and M. R. Willis, 'Pericyclic Reactions,' Chapman and Hall, London, 1974.

[3] S. Hünig, H. R. Müller, and W. Thier, *Angew. Chem. Internat. Edn.*, 1965, **4**, 271.

[4] For example see: A. F. Thomas, 'Deuterium Labelling in Organic Chemistry,' Appleton-Century-Crofts, New York, 1971; H. O. House, 'Modern Synthetic Reactions,' 2nd edn., Benjamin, New York, 1972.

[5] K. Mackenzie, *J. Chem. Soc.*, 1965, 4646; *J. Chem. Soc.* (*C*), 1969, 1784.

[6] W. von E. Doering and J. W. Rosenthal, *J. Amer. Chem. Soc.*, 1967, **89**, 4534.

[7] I. Fleming and E. Wildsmith, *Chem. Comm.*, 1970, 223; see also B. A. Arbuzov, L. A. Shapshinskya, and G. A. Prytkova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1962, 2084.

[8] The disproportionation of dihydronaphthalenes under *aqueous acidic* conditions is well documented, see for example: H. Tournier, R. Longeray, and J. Dreux, *Tetrahedron Letters*, 1970, 21; J. P. Quillet, A. Duperrier, and J. Dreux, *Bull. Soc. chim. France*, 1967, 255.

[9] L. M. Jackman and J. W. Lown, *J. Chem. Soc.*, 1962, 3776.

[10] Heterogeneous hydrogen transfer at the surface of noble metals is well documented, see for example: E. A. Braude, R. P. Linstead, and P. W. D. Mitchell, *J. Chem. Soc.*, 1954, 3578. Vapour phase isomerisation by zeolites or alumina: G. Arich, S. Volpe, and P. Alessi, *Chem. Ind.* (*Milan*), 1970, **52**, 223.