Hydrogen Transfer. Part I. Introductory Survey.

By E. A. Braude and R. P. Linstead.

[Reprint Order No. 5152.]

Reactions involving the transfer of hydrogen in organic systems are classified. The interrelations between such reactions are briefly discussed, and the general background and scope of the work to be described in subsequent parts of this series are indicated.*

Reactions in which covalently bonded hydrogen changes its site of attachment, either inter- or intra-molecularly,† are formally amongst the simplest of organic chemical processes. At the same time, they are amongst the most important from both the synthetical and the biochemical point of view. Although many such reactions have been extensively investigated, hydrogen transfer presents many unexplored features of practical as well as theoretical interest. Comparatively little has been done, for example, towards bringing

---

* For a preliminary summary, see Linstead, Braude, Mitchell, Wooldridge, and Jackman, *Nature*, 1952, **169**, 100.

† Such reactions may be designated by the general term " hydrogen transfer."

the different types of hydrogen transfer into relation with one another and towards establishing a generalised system of hydrogen-donors and hydrogen-acceptors. The existence of a scale of covalent hydrogenation levels, related in certain respects to the scales of ionic hydrogenation levels, *i.e.*, oxidation–reduction potentials in double proton transfer and acid–base strengths in single proton transfer, is implicit in the vast amount of available factual material, but little systematic work has been done on this aspect.

With these and connected objects in view, a broad study of hydrogen-transfer reactions is being undertaken in these laboratories. The purpose of the present introductory paper is to establish briefly the general background, to classify the principal types of hydrogen transfer, and to indicate the plan of our investigations.

Hydrogen transfer, in the sense in which the term is used here, can be classified as follows: (A) hydrogen migration (transfer within one molecule, though not necessarily intramolecular); (B) hydrogen disproportionation (transfer between identical donors and acceptors); (C) transfer-hydrogenation (transfer between unlike donors and acceptors). Each type of reaction could conceivably be brought about by (i) thermal, (ii) homogeneous catalytic, (iii) heterogeneous catalytic, and (iv) photochemical means. Examples of many of the possible categories are known but the state of knowledge over the whole field varies greatly and there are a number of significant gaps, consideration of which suggests several promising new lines of enquiry. As the following summary will show, catalysed hydrogen transfer in homogeneous systems has been very much more fully studied than either thermal, heterogeneously catalysed, or photochemical transfer, and our present investigations are mainly concerned with the last three categories.

Of the three types of thermal hydrogen transfer, migration is normally limited to high temperature ranges since the energy of activation will usually be of the same order as the dissociation energy of a least one of the X–H bonds concerned. A similar limitation exists in thermal disproportionation since the absence of any overall change in bond types in such reactions normally precludes any large free-energy change and any appreciable stabilisation of a bimolecular transition state. Thus *cyclo*hexene is reported not to disproportionate at temperatures as high as 600° in the absence of catalysts (Zelinski, *Ber.*, 1925, **58**, 185) whereas disproportionation is quite rapid even at room temperature in the presence of suitable catalysts (cf. below and Part VI). A few cases of apparently thermal disproportionation of hydroaromatic compounds near 200° have been observed (cf. Cook, Johnston, and Loudon, *J.*, 1950, 537) but it seems probable that even these are in reality heterogeneously catalysed reactions. By contrast, thermal transfer can be envisaged between unlike donors and acceptors such that *both* products are stabilised with respect to the reagents and that the stabilisation becomes effective in the transition state. An excellent example is the reaction between a hydroaromatic or hydroheterocyclic compound and a quinone to give the dehydro-compound and the quinol. This has been employed quite frequently for dehydrogenation at elevated temperatures (Clar and John, *Ber.*, 1930, **63**, 2967; Criegee, *Ber.*, 1936, **69**, 2578; Prokopetz and Pavlenko, *J. Gen. Chem. U.S.S.R.*, 1939, **9**, 1468; Arnold *et al.*, *J. Amer. Chem. Soc.*, 1939, **61**, 1407; 1940, **62**, 983; Campbell *et al.*, *J.*, 1945, 530; 1949, 1555; 1951, 2511; Crawford and Nelson, *J. Amer. Chem. Soc.*, 1946, **68**, 134; Braude, Jones, Sondheimer, and Toogood, *J.*, 1949, 607; Barnes, Pausacker, and Schubert, *ibid.*, p. 1381; Tucker, *ibid.*, p. 2182; Buu-Hoï *et al.*, *J. Org. Chem.*, 1949, **14**, 492, 802; Horner and Merz, *Annalen*, 1950, **570**, 89; Buchta and Kallert, *Annalen*, 1951, **573**, 220; Dost and van Nes, *Rec. Trav. chim.*, 1951, **70**, 403; Holzer, Ziegler, Zinke, Wiesenberger, and Sobotka, *Monatsh.*, 1953, **83**, 180) but has otherwise been little investigated. We have found that such transfers take place under quite moderate conditions and lend themselves to quantitative study; a survey of the reactions of a wide range of quinones with different types of hydrocarbon donors is described in Parts II, III, and IV and further kinetic as well as thermochemical data will be reported later. A second, related example of thermal hydrogen transfer involves nitro-compounds as acceptor and has been observed with Diels–Alder adducts (Clar, *Ber.*, 1936, **69**, 1686; Bergmann *et al.*, *J. Amer. Chem. Soc.*, 1938, **60**, 1331; 1942, **64**, 176; *J. Org. Chem.*, 1942, **7**, 303; Swain and Todd, *J.*, 1942, 626; Braude and Fawcett, *J.*, 1951, 3117) and with hydroheterocyclic compounds (Ziegler and Zeiser, *Annalen*, 1931, **485**, 174) as donors. Whereas we believe both these examples to involve heterolytic fission of the X–H bonds, contrary to current views (*e.g.*, Waters, " The Chemistry of Free Radicals," Oxford Univ. Press, 1948, p. 257; Dost and Van Nes, *loc. cit.*), thermal transfers involving homolytic fission are well known. Most of these concern unstable free radicals as acceptors, but such reactions can also be realised with " stable " free radicals, and thermal hydrogen transfer between hydroaromatic compounds and one such radical, diphenylpicrylhydrazyl, is described in Part V.

Hydrogen transfer under conditions of homogeneous catalysis is well known and the mechanisms by which various catalysts facilitate the fission of X–H bonds in solution are fairly well understood. Migration is represented by acid- and base-catalysed prototropy (cf. Baker, "Tautomerism," Routledge, London, 1934; " Hyperconjugation," Oxford Univ. Press, 1952; and references there cited). The first case of acid-catalysed hydrogen disproportionation appears to have been noted by Knoevenagel and Fuchs (*Ber.*, 1902, **35**, 1788) in the case of diethyl dihydrolutidinedicarboxylate, while base-catalysed disproportionation occurs in the Cannizzaro reaction (cf. Alexander, *J. Amer. Chem. Soc.*, 1947, **69**, 289; 1948, **70**, 2592; Burr, *ibid.*, 1951, **73**, 5170; Pfeil, *Chem. Ber.*, 1951, **84**, 229) and has also been observed in dihydroquinoline and dihydro*iso*quinoline derivatives (Huntress and Shaw, *J. Org. Chem.*, 1948, **13**, 679; Brodrick and Short, *J.*, 1949, 2587; Johnson and Buell, *J. Amer. Chem. Soc.*, 1952, **74**, 4513). Homogeneously catalysed transfer hydrogenation is represented by the Meerwein–Ponndorf and Oppenauer interconversions of alcohols and aldehydes and ketones in the presence of metal alkoxides (cf. Bersin in " Newer Methods of Preparative Organic Chemistry," Interscience Publ. Corp., New York, 1948; Djerassi in " Organic Reactions," Vol. VI, New York, 1951; Jackman and Macbeth, *J.*, 1952, 3252; Doering and Ashner, *J. Amer. Chem. Soc.*, 1953, **75**, 393) and by the acid-catalysed reduction of olefins by aromatic hydrocarbon donors (Ipatieff, Pines, *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 2123, 3859; 1949, **71**, 3534; 1950, **72**, 1563, 5521). This part of the subject is strikingly more advanced than the remainder and requires no further comment here.

Earlier work on hydrogen transfer under conditions of heterogeneous catalysis has been concerned mostly with reactions at gas–solid interphases, whereas in the present context our interest lies primarily in surface catalysis in liquid systems and it is to such systems that the following remarks mainly refer. Numerous cases of hydrogen migration catalysed by hydrogenation catalysts have been described, particularly for olefinic acids (cf. Moore, *J. Soc. Chem. Ind.*, 1919, **38**, 320; Hilditch and Vidaharti, *Proc. Roy. Soc.*, 1929, *A*, **122**, 552), steroids (cf. Reindel, Walter, and Rauch, *Annalen*, 1927, **452**, 34; Windaus *et al.*, *ibid.*, 1934, **508**, 105; 1938, **534**, 22; **536**, 204; Wieland *et al.*, *ibid.*, 1941, **543**, 34; 1943, **554**, 1; Eck and Hollingsworth, *J. Amer. Chem. Soc.*, 1941, **63**, 2986; Staveley and Bollenback, *ibid.*, 1943, **65**, 1285, 1290, 1600; Henbest, Jones, and their co-workers, *J.*, 1952, 4883; Budziarek, Johnson, and Spring, *J.*, 1953, 534), and terpenes (cf. Wallach, *Annalen*, 1911, **381**, 64; 1914, **403**, 87; 1918, **414**, 349; Richter and Wolff, *Ber.*, 1926, **59**, 1733, Treibs and Schmidt, *Ber.*, 1927, **60**, 2335; Linstead, Michaelis, and Thomas, *J.*, 1940, 1139), as well as a variety of other systems (cf. Levina *et al.*, *J. Gen. Chem. U.S.S.R.*, 1934, **4**, 1250; 1936, **6**, 1092; 1937, **7**, 747; 1938, **8**, 1776; 1939, **9**, 2287; Delépine and Horeau, *Compt. rend.*, 1938, **206**, 27; Badoche, *ibid.*, 1942, **215**, 142; Wiemann and Laude, *ibid.*, 1948, **226**, 345; Small, Turnbull, and Fitch, *J. Org. Chem.*, 1938, **3**, 204; Horning, *ibid.*, 1945, **10**, 263; Weiss and Weiner, *ibid.*, 1949, **14**, 194; Grob and Hofer, *Helv. Chim. Acta*, 1952, **35**, 2095; Leonard and Berry, *J. Amer. Chem. Soc.*, 1953, **75**, 4989). We have found that such migrations can be effected in many systems which also undergo base-catalysed prototropy, but that the two types of migration exhibit quite different structural specificities, as would be expected. Hydroaromatic derivatives are amongst those particularly prone to metal-catalysed hydrogen migration, and such systems also undergo disproportionation on transition metals, often with remarkable ease, as has long been known (cf. Knoevenagel and Bergdolt, *Ber.*, 1903, **36**, 2857; Wieland, *Ber.*, 1912, **45**, 484; Boeseken and Groot, *Rec. Trav. chim.*, 1918, **37**, 255; Zelinski *et al.*, *Ber.*, 1911, **44**, 2305; 1923, **56**, 1249, 1723 *et seq.*; Levina *et al.*, *J. Gen. Chem. U.S.S.R.*, 1936, **6**, 764 *et seq.*; Linstead *et al.*, *J.*, 1937, 1146; 1940, 1134; Serini and Logemann, *Ber.*, 1938, **71**, 186). The ready occurrence of migration and disproportionation in suitable structures suggests that metal-catalysed transfer-hydrogenation could similarly be effected, provided certain conditions such as co-adsorption of donor and acceptor on the catalyst are fulfilled. Somewhat surprisingly, only a few incidental observations of metal-catalysed transfer-hydrogenation are to be found in the literature, but a systematic study has now shown that such processes can be realised for a wide range of hydrogen-acceptors. The transfer-hydrogenation of ethylenic compounds, nitro-compounds, and certain other types of acceptors, with *cyclo*hexene and other hydroaromatic donors, is described in Parts VI, VII, and VIII. Kinetic and thermochemical studies on metal-catalysed disproportionation and transfer will be reported subsequently.

We turn lastly to photochemical hydrogen transfer. The electronic spectra associated with X–H bonds lie in the far ultra-violet (cf. Price, *Ann. Reports.*, 1939, **36**, 47; Platt and Klevens, *Rev. Mod. Physics*, 1944, **16**, 182), and photochemical hydrogen transfer brought about by near ultra-violet or visible light usually depends on light absorption in the relevant region by the acceptor. Very few cases of photochemical hydrogen migration or disproportionation are known, but an instructive example of migration occurs in the rearrangement of 1 : 4 : 9 : 10-tetrahydronaphtha-5 : 8-quinones to 1 : 4-dihydronaphtha-5 : 8-quinols (Braude, Jones, and Stern, *J.*, 1947, 1087); here the energy intake (~80 kcal./mole) is through the 3650 Å band of the diacetylethylene system and this reaction is closely analogous to the previously mentioned thermal transfer-dehydrogenation of hydroaromatic compounds by quinones. Photochemical hydrogen transfer between alcohols and quinones, and many similar donor–acceptor combinations, was extensively studied by Ciamician and Silber (*Ber.*, 1901, **34**, 1531 *et seq.*). These transformations are the photochemical analogues to the Meerwein–Ponndorf and Oppenauer reactions (see above), but have found little synthetical use except in the preparation of pinacols (cf. Cohen, *Rec. Trav. chim.*, 1920, **39**, 242; Bachmann, *Org. Synth.*, 1934, **14**, 8; Weizmann, E. Bergmann, and Hirshberg, *J. Amer. Chem. Soc.*, 1938, **60**, 1530; F. Bergmann and Hirshberg, *ibid.*, 1943, **65**, 1429; Moustafa, *Nature*, 1948, **162**, 856). The original investigators reported hardly any details and we are now studying such reactions under controlled conditions. The energy change accompanying the reaction between benzoquinone and methanol to give quinol and formaldehyde can be estimated from bond and resonance energies to be quite small (ΔH *ca.* -5 kcal.), but the corresponding reaction with water to give molecular oxygen is calculated to be endothermic by *ca.* 55 kcal. This increment could theoretically still be supplied through direct light absorption by the quinone, but such reactions, which are closely related to the least well understood step in natural photosynthesis, have so far only been realised in the presence of intact plant cells or chloroplasts (cf. Warburg and Lüttgens, *Naturwiss.*, 1944, **32**, 161; Aronoff, *Plant Physiology*, 1946, **21**, 393; Arnon and Whatley, *Arch. Biochem.*, 1949, **23**, 141; Clendenning *et al.*, *ibid.*, 1950, **29**, 387; *Canad. J. Res.*, 1950, **28**, *C*, 78, 102, 114; Punnett and Fabiyi, *Nature*, 1953, **172**, 947). The systematic investigation of model systems may contribute to the elucidation of this important problem.

DEPARTMENT OF ORGANIC CHEMISTRY,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, LONDON, S.W.7.

[*Received, February 24th*, 1954.]