

*Hydrogen Transfer. Part III.\* The Dehydrogenation of Hydroaromatic Hydrocarbons by Quinones. Quantitative Comparison of Donors.*

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The dehydrogenations of four hydroaromatic donors by 1:4-benzoquinone and 1:2-naphthaquinone have been studied kinetically. The reactivities decrease in the sequence 1:4-dihydrobenzene > 1:4-dihydronaphthalene > 9:10-dihydroanthracene > 1:2-dihydronaphthalene. This sequence is explained in terms of the mechanism postulated in Part II\* and is ascribed to the differences in the additional resonance stabilisation which accompanies the aromatisation of the donor.

In the preceding paper, the general features of the hydrogen transfer between 1:4-dihydronaphthalene and quinones, and the effects of structural variation in the acceptor, have been described. The present paper deals with a preliminary investigation of the effect of structural variation in the hydroaromatic donor.

The donors studied were 1:2- and 1:4-dihydrobenzene, 1:2- and 1:4-dihydronaphthalene, and 9:10-dihydroanthracene, mostly with 1:4-benzoquinone as acceptor. The reactions were followed by the experimental methods employed in Part II, and the results are summarised in the Table. Only an upper limit could be determined for the rate of dehydrogenation of 1:2-dihydrobenzene, as the main reaction which occurs is Diels-Alder addition of the quinone to the donor. The dehydrogenation of 9:10-dihydroanthracene was also complicated by a competitive Diels-Alder reaction, in this case between the quinone and the dehydrogenation product, anthracene; the second-order rate constants showed an upward or downward drift depending on whether the reaction was followed by disappearance of quinone or the appearance of quinol, and the values in the Table were obtained by extrapolating to zero time. No deviations from second-order kinetics were observed with 1:4-dihydrobenzene and 1:2-dihydronaphthalene.

*Rate constants for the dehydrogenation of various hydrocarbons by quinones.\**

Donor	Acceptor	Solvent	Temp.	10 <sup>4</sup> k (l. mole <sup>-1</sup> sec. <sup>-1</sup> )
1:4-Dihydrobenzene .....	Benzoquinone	Dioxan	80°	0.28
1:2-Dihydrobenzene .....	"	"	"	<0.02
1:4-Dihydronaphthalene ...	"	"	"	0.16
1:2-Dihydronaphthalene ...	"	"	"	0.0025
9:10-Dihydroanthracene ...	"	"	"	0.042
1:4-Dihydronaphthalene ...	Benzoquinone	Anisole	131	10.5
1:2-Dihydronaphthalene ...	"	"	"	0.066
9:10-Dihydroanthracene ...	"	"	"	3.8
1:4-Dihydronaphthalene ...	Chloranil	Phenetole	110	78
9:10-Dihydroanthracene ...	"	"	"	23
1:4-Dihydronaphthalene ...	Thymoquinone	Propionic acid	140	3.4
9:10-Dihydroanthracene ...	"	"	"	0.97
1:4-Dihydronaphthalene ...	1:2-Naphthaquinone	Anisole	131	35
1:2-Dihydronaphthalene ...	"	"	"	0.45

\* 0.1M-Solutions of both reactants, except for 1:4-dihydrobenzene and 1:4-dihydronaphthalene at 80° which were 0.2M.

The results in the Table show that the ease of dehydrogenation of the donors decreases in the sequence 1:4-dihydrobenzene > 1:4-dihydronaphthalene > 9:10-dihydroanthracene > 1:2-dihydronaphthalene. The relative rates at 80° are approximately in the ratios 100:50:10:1 and are similar for benzoquinone, chloranil, and thymoquinone.

Theoretically one of the main factors controlling the sequence of reactivities of the donors will be the gain in resonance energy ( $\Delta E_R$ ) accompanying aromatisation of the donor, which is bound to assist the reaction just as does the gain in resonance energy in the acceptor (Part II). The approximate values of  $\Delta E_R$  for 1:4-dihydrobenzene, 1:4-dihydronaphthalene, 1:2-dihydronaphthalene, and 9:10-dihydroanthracene are 36, 30, 25, and

\* Part II, preceding paper.

20 kcal., based on the following experimental resonance energies : 1 : 4-dihydrobenzene, 0(assumed) \* ; benzene, 36 (Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Amer. Chem. Soc.*, 1936, **58**, 147; cf. Klages, *Ber.*, 1949, **82**, 358) ; 1 : 4-dihydronaphthalene, 37 (Williams, *J. Amer. Chem. Soc.*, 1942, **64**, 1395) ; 1 : 2-dihydronaphthalene, 42; naphthalene, 67 (Klages, *loc. cit.*); 9 : 10-dihydroanthracene, 77; anthracene 97 (Magnus and Becker, *Erdöl and Kohle*, 1951, **4**, 115). Thus, for the three 1 : 4-dihydro-derivatives at least, the sequence of resonance-energy gains is the same as the sequence of reactivities and a roughly linear relation exists between  $\log k$  and  $\Delta E_R$ . 1 : 2-Dihydronaphthalene is somewhat less reactive than expected on this basis, an anomaly probably related, at least in part, to the non-equivalence of the 1- and the 2-hydrogen atoms.

If the entropies of activation are assumed to be approximately constant, the relative rates of the four hydrocarbons correspond to increases in the heats and free energies of activation of about 0.4, 1.2, and 2 kcal. relative to 1 : 4-dihydrobenzene. These differences are much smaller than those in  $\Delta E_R$  and although the present measurements are insufficient to yield an accurate relation, it is instructive to express them in the form of relation (1)† which connects  $\Delta G^\ddagger$  for a single acceptor (benzoquinone) with the resonance-energy gains of different donors :

$$\Delta G^\ddagger = 29.6 - 0.1\Delta E_R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This may be compared with the relation (2) previously deduced (Part II) between  $\Delta G^\ddagger$  for a single donor (1 : 4-dihydronaphthalene) and the free-energy gains of different acceptors :

$$\Delta G^\ddagger = 38.0 - 0.071\Delta G^\circ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Both relations are of the same form and indicate that the energy of activation is made up of two parts of opposite sign. One part, the intercept of the plots on the  $\Delta G^\ddagger$  axis, represents the energy required to stretch the C-H bond in the donor from its normal distance to that in the transition state and is approximately constant. [The numerical values of the intercepts in relations (1) and (2) are not comparable, because  $\Delta G^\circ$  includes the bond energy changes whereas  $\Delta E_R$  does not.] The other part, which is variable, and controls the slope of the plots, represents the driving force provided by the resonance energy gains in the products. It is almost certainly no coincidence that the slopes of the straight lines represented by relations (1) and (2) have nearly identical values; they indicate that, in the transition state, aromatic character and additional resonance stabilisation are developed to a small and roughly equal extent (*ca.* 10%) in both donor and acceptor.

The results are in accord with a two-step mechanism (2) of the type proposed in Part II and may be regarded as additional evidence against the one-step mechanism (1) involving a pseudocyclic transition state, which was previously considered and rejected for other reasons; in such a transition state, aromatic character should be highly developed and resonance stabilisation should amount more nearly to 50% than to 10% of that in the final products. The same objection applies, though less forcibly, to a one-step mechanism involving a linear transition state and differing from (2) in that the transfer of one hydrogen atom (in the form of a proton) to a solvent molecule would be synchronised with the transfer of the other hydrogen atom (in the form of a hydride ion) to the quinone acceptor. The problem of distinguishing between such one-step and two-step mechanisms is rather analogous to the question whether or not the ejection of a proton is kinetically significant in electrophilic aromatic substitution (cf. Braude, *Ann. Reports*, 1949, **46**, 131 and references there cited); like the latter it could be conclusively resolved by studying the effects of isotopic substitution, although the interpretation of the results would be more complicated owing to the circumstance that a hydrogen atom is involved in both the presumed steps in the transfer reaction instead of in only one in the substitution reaction. Fortunately, such experiments seem hardly necessary, for, apart from the present evidence, the synchronised removal of the proton by the solvent is rendered extremely unlikely by the fact (Part II) that dehydrogenation proceeds with comparable facility in phenetole and decalin although

\* 1 : 4-Dihydrobenzene will have a small resonance energy arising from hyperconjugation, but this is unlikely to exceed 3 kcal. and does not affect the present argument.

† Relation (1) is not a strict thermodynamic equation since the so-called resonance energies are really enthalpies and not free energies, but this does not significantly affect the present argument.

the latter solvent must be practically devoid of proton-acceptor properties. Presumably, in such a solvent, the proton is removed directly by a quinol anion, when the transfer of the hydride ion is complete.

If the conclusion that the transfers of the two hydrogen atoms are kinetically independent is accepted, the existence of a semiquantitative correlation between the reactivity and resonance-energy gain of donors permits elaboration of the two-step mechanism. This mechanism postulates the formation, in the rate-determining step, of the conjugate acid of the aromatic hydrocarbon ( $R\cdot H^+$ ), but the precise nature of this intermediate has so far been purposely left undefined. Two possibilities can be envisaged. In the first, one of the two reactive carbon-hydrogen bonds in the donor remains substantially unchanged during the rate-determining step, and the intermediate is a true carbonium ion (*e.g.*, I); an alternative designation which emphasises the retention of ordinary single-bond character in the  $CH_2$  group is " $\sigma$ -complex" (Brown and Pearsall, *J. Amer. Chem. Soc.*, 1952, **74**, 191; Brown and Brady, *ibid.*, p. 3570; Brown and Wallace, *ibid.*, 1953, **75**, 6268). In the second, both the reactive carbon-hydrogen bonds in the donor undergo more or less synchronised changes, but whereas one hydrogen atom is actually transferred to the quinone acceptor in the form of a hydride ion, the other hydrogen atom is not subject to any marked nuclear displacement and remains within the orbit of the donor although the electronic nature of its attachment to the carbon skeleton is altered; the hybridisation of all the carbon atoms then changes simultaneously from  $sp^3$  to  $sp^2$  and the intermediate represents a  $\pi$ -complex (*e.g.*, II) (*cf.* Dewar, *J.*, 1946, 406; *Discuss. Faraday Soc.*, 1947, **2**, 50; "Electronic Theory of Organic Chemistry," Oxford Univ. Press, 1949). The distinction between the  $\sigma$ -complex and the  $\pi$ -complex type of intermediates, which are extremes of a continuous range (*cf.* Mulliken, *J. Phys. Chem.*, 1952, **56**, 801), is based on the following consideration: The gain in resonance stabilisation in converting a dihydro-compound into a  $\sigma$ -complex such as (I) will be derived mainly from charge-resonance and would be expected to increase in

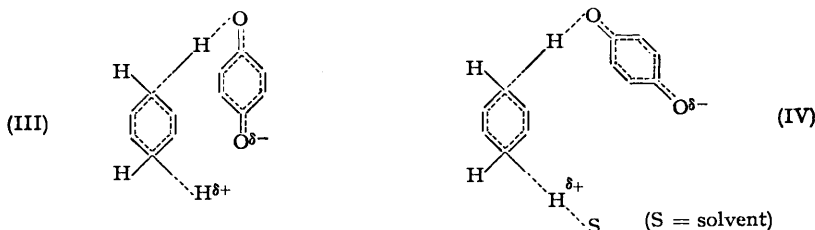


the sequence benzene < naphthalene < anthracene, as can be seen by considering, for example, the number of resonance forms (3, 7, and 16, respectively). Hence, on this hypothesis, the reactivities should increase in the same order, dihydrobenzene < dihydronaphthalene < dihydroanthracene, which is the reverse of that observed.\* On the other hand, the resonance stabilisation of  $\pi$ -complexes such as (II) will increase in the same order as that of the aromatic hydrocarbons from which they are derived (*cf.* Dewar, *loc. cit.*); and the sequence of resonance-energy gains predicted on this hypothesis therefore agrees with that observed, dihydrobenzene > dihydronaphthalene > dihydroanthracene.

The conclusion that the intermediates  $R\cdot H^+$  in hydrogen transfer by mechanism (2) are  $\pi$ - rather than  $\sigma$ -complexes is in harmony with the somewhat fragmentary evidence at present available concerning the range of existence of these limiting types of species in different environments. Sufficient is known to indicate that the bond type is strongly influenced by the nature of the anions and other proton-acceptors with which the species  $R\cdot H^+$  is in equilibrium; weakly basic surroundings favour a  $\sigma$ -complex, while strongly basic surroundings favour a  $\pi$ -complex. Thus, it has been demonstrated spectroscopically that anthracene in sulphuric-acetic acid (a strongly proton-donating, extremely weakly basic medium) is converted predominantly into the  $\sigma$ -complex in which a proton is attached and localised at the 9-position (Gold and Tye, *J.*, 1952, 2172); similarly, benzenoid hydrocarbons are converted into  $\sigma$ -complexes under the combined influence of hydrogen chloride and aluminium chloride, because the anion  $AlCl_4^-$  is very weakly basic (Brown and Brady, *loc. cit.*). On the other hand, hydrogen chloride alone appears to convert benzenoid hydrocarbons into  $\pi$ -complexes. This is indicated (Brown and Brady, *loc. cit.*) by the much closer relative basicities of toluene, *o*-xylene, and *m*-xylene towards HCl (1.00, 1.23, and 1.37, respectively) than towards  $HAlCl_4$  (1, 200, and 2000, respectively); unlike  $AlCl_4^-$ .

\* The same applies to mechanisms involving free-radical intermediates  $RH\cdot$  (*cf.* Part II, *loc. cit.*).

the more strongly basic anion  $\text{Cl}^-$  can compete effectively with the hydrocarbon for a proton, and the  $\pi$ -complex can be regarded as a hydrogen-bonded ion-pair,  $\text{R} \dots \text{H}^+ \dots \text{Cl}^-$ . Now, in hydrogen transfer from a hydroaromatic donor to a quinone, the intermediate  $\text{R}\cdot\text{H}^+$  is generated simultaneously with a strongly basic quinol anion  $\text{QH}^-$  which provides precisely the type of environment conducive to  $\pi$ -complex formation; even if the distance between the hydrogen atom in  $\text{R}\cdot\text{H}^+$  and the charged oxygen atom in  $\text{QH}^-$  considerably exceeds the covalent-bond length, it will still be well within the range of electrostatic forces at the completion of the rate-determining step. We may thus further refine the formulation of the intermediate by representing it as  $\text{RH}^+ \dots \text{QH}^-$  in which an electrovalent bond exists between  $\text{RH}^+$  and  $\text{QH}^-$ . The second, fast step then becomes the conversion of this electrovalent bond into a covalent one, to give  $\text{R} + \text{QH}_2$ . This implies that both hydrogen atoms are eventually transferred to the same quinone acceptor and the distinction between such a process and the one-step mechanism (1) considered in Part II is a subtle one, depending, as it does, on the detailed geometry of the transition states and the time-sequence of electron re-distributions as well as of nuclear displacements. Moreover, the degree of electrovalent interaction between the reactants will be influenced by the solvent and it is highly probable that in a strongly basic solvent such as phenetole the positive "end" of the transition state will be surrounded by solvent molecules which will intervene as acceptors. Under such conditions of indirect proton transfer, the proton need not necessarily go to the quinone molecule involved in the rate-determining step, but may be taken up by a different quinol anion. The unsolvated and solvated transition states of the rate-determining step are schematically represented in (III) and (IV); it has been assumed that the preferred  $\text{H}-\text{O}-\text{C}$  angle is about  $120^\circ$ , but that it is distorted to about  $90^\circ$  if there is strong attraction between the opposite ends of the transition state, as in (III). The actual configuration in a particular case will obviously depend not only on the solvent, but also on the electronic and steric properties of the donor and acceptor.



One consequence of this model is that the geometrical correspondence between the labile hydrogen atoms in the donor and the oxygen atoms in the acceptor will have *some* influence on the ease of transfer, though less than predicted for the one-step mechanism (1) (Part II, *loc. cit.*, p. 3554). Such an effect is indicated by the differing ratios of the rate constants for the dehydrogenation of 1 : 4- and 1 : 2-dihydronaphthalene by 1 : 4-benzoquinone (160) and 1 : 2-naphthaquinone (80). An even smaller ratio would be expected with a quinone in which the two carbonyl functions are so far apart that the electrovalent interaction present in a transition state of type (III) is very weak; furthermore, with such a quinone, solvent effects would be expected to be relatively large. Work in progress with 1 : 8-diphenoquinones as acceptors (cf. Part IV) indicates that these expectations are fulfilled.

#### EXPERIMENTAL

*Materials.*—1 : 4-Dihydrobenzene, b. p.  $81^\circ/763$  mm.,  $n_D^{24}$  1.4707, was prepared from benzene according to Wibaut and Haak (*Rec. Trav. chim.*, 1948, **67**, 85) and purified through its tetrabromide. 1 : 2-Dihydrobenzene, b. p.  $80^\circ/762$  mm.,  $n_D^{25}$  1.4712, was prepared from cyclohexene (Ziegler *et al.*, *Annalen*, 1942, **551**, 80; Arbusov and Mastryukova, *Izvest. Akad. Nauk U.S.S.R. Otdel. Khim. Nauk*, 1952, 665). Dioxan and anisole were purified by refluxing with sodium and fractionation. The other materials were those described in Part II (*loc. cit.*).

*Isolation of Reaction Products.*—(i) 1 : 2-Dihydronaphthalene (1.30 g.), 1 : 2-naphthaquinone (1.58 g.), and chlorobenzene (100 ml.) were refluxed under nitrogen for 8 days. On cooling, a purple solid (0.80 g.), m. p.  $160-170^\circ$  (cf. Part II), separated and was filtered off. The filtrate

was diluted with light petroleum (100 ml.; b. p. 40–60°), filtered again, and chromatographed on alumina, with more light petroleum (100 ml.) as an eluant. The combined solutions were concentrated by slow distillation through a column until the volume was 3 ml. This was treated with a hot, saturated solution of picric acid (2.3 g.) in ethanol, giving naphthalene picrate (2.15 g., 60%), m. p. 148–149°.

(ii) 9 : 10-Dihydroanthracene (1.8 g.), benzoquinone (2.16 g.), and phenetole (100 ml.) were heated under nitrogen for 60 hr. at 130°. The solution was then evaporated to dryness under reduced pressure and the residue extracted with hot water to remove quinol. There remained the anthracene-benzoquinone adduct which, after crystallisation from xylene, formed pale yellow needles (2.36 g., 82%) which sintered at 207° (cf. Clar, *Ber.*, 1931, **64**, 1676).

*Kinetic Measurements.*—These were carried out by the methods described in Part II. In most cases, method A was used (reduction of unchanged quinone with excess of titanous chloride, followed by back-titration with ferric ammonium sulphate). One typical run for each hydrocarbon is reproduced below. In each case, the stated volume of titanous chloride was added to 1 ml. of reaction mixture and  $x$  is the volume of ferric salt solution consumed. The limits of error of the second-order rate constants ( $k$ , l. mole<sup>-1</sup> min.<sup>-1</sup>) are given as standard deviations of the mean.

(i) 1 : 4-Dihydrobenzene (0.2M) and 1 : 4-benzoquinone (0.2M) in dioxan at 80°. 4 ml. of 0.0975 N-Ti<sup>3+</sup> back-titrated with 0.0407N-Fe<sup>3+</sup>.

$t$ (min.)	0	123	244	339	420	1525
$x$ (ml.)	0.06	0.41	0.80	1.09	1.20	2.95
$10^4k$	—	15.9	17.5	17.8	16.4	14.5

$$10^4k = 16.5 \pm 0.6$$

(ii) 1 : 2-Dihydrobenzene (0.1M) and 1 : 4-benzoquinone (0.1M) in dioxan at 80°. 2.5 ml. of 0.0970N-Ti<sup>3+</sup> back-titrated with 0.0407N-Fe<sup>3+</sup>

$t$ (min.)	0	120	225	315	1370
$x$ (ml.)	1.25	1.99	2.48	2.70	4.36
$10^4k$	—	15.8	15.7	14.0	13.7

$$10^4k = 14.8 \pm 0.8$$

This rate constant refers almost entirely to the Diels-Alder addition reaction, for isolation of the products after 3 days at 100° gave an 86% yield of the adduct as pale yellow plates, m. p. 94–96°, raised to 97° by one recrystallisation (Diels, Alder, and Stein, *Ber.*, 1929, **62**, 2337; Alder and Stein, *Annalen*, 1933, **501**, 247, give m. p. 98°).

(iii) 1 : 4-Dihydronaphthalene (0.1M) and 1 : 4-benzoquinone (0.1M) in anisole at 130°. 5.0 ml. of 0.059N-Ti<sup>3+</sup> back-titrated with 0.0509N-Fe<sup>3+</sup>.

$t$ (min.)	0	16.3	32	38	47	58	96
$x$ (ml.)	1.99	2.34	2.66	2.72	2.90	2.99	3.35
$10^4k$	—	61.8	67.1	61.1	66.2	61.4	58.2

$$10^4k = 64 \pm 0.2$$

(iv) 1 : 2-Dihydronaphthalene (0.1M) and 1 : 4-benzoquinone (0.1M) in anisole at 130°. 2.5 ml. of 0.0970N-Ti<sup>3+</sup> back-titrated with 0.0407N-Fe<sup>3+</sup>.

$t$ (min.)	0	1230	8380	11,500	14,400
$x$ (ml.)	1.16	1.42	2.36	2.61	3.00
$10^4k$	—	4.36	4.00	3.98	4.20

$$10^4k = 4.14 \pm 0.09$$

(v) 9 : 10-Dihydroanthracene (0.1M) and 1 : 4-benzoquinone (0.1M) in dioxan at 80°. 2.5 ml. of 0.0970N-Ti<sup>3+</sup> back-titrated with 0.0407N-Fe<sup>3+</sup>.

$t$ (min.)	0	8460	11,740	25,000	72,000
$x$ (ml.)	1.27	2.10	2.96	4.02	5.21
$10^4k$	—	2.5	3.9	5.6	7.0

$$10^4k = \text{ca. } 2.5 \text{ (extrapolated)}$$

This extrapolated rate-constant may be too high by a factor of up to 2, depending on the undetermined rate of Diels-Alder addition which is higher than with thymoquinone.