Hydrogen Transfer. Part II. The Dehydrogenation of* 1 : 4-*Dihydronaphthalene by Quinones. Kinetics and Mechanism.*

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The dehydrogenation of 1 : 4-dihydronaphthalene by quinones has been studied kinetically in phenetole and other solvents in the range 50—160°. The principal findings are:

(i) The reactions are essentially bimolecular, though deviations from second-order kinetics are frequently observed owing to a variety of causes, which have been analysed.

(ii) The reactions are faster in polar than in non-polar solvents. Radical-producing agents, such as light or benzoyl peroxide, are without influence and no coupling products derived from the hydrocarbon are obtained.

(iii) The reactivity of quinones is enhanced by electron-attracting, and reduced by electron-donating substituents, and the rate constants as well as the energies of activation can be correlated with the reduction potentials of the quinones. *o*-Quinones are more reactive relatively to *p*-quinones than expected from their potentials.

(iv) With quinones of low potential, the reactions exhibit marked product catalysis which is due to the quinol formed. Similar catalytic effects are observed with other weak proton donors which form molecular complexes with quinones (*e.g.*, *p*-nitrophenol) and with very strong proton donors (*e.g.*, perchloric acid).

These observations are rationalised by a two-step heterolytic mechanism involving a rate-determining transfer of a hydrogen atom with its pair of bonding electrons from the hydrocarbon to the quinone, followed by rapid proton transfer between the resulting conjugate acid of the aromatic hydrocarbon and the quinol anion:

$$RH_2 + Q \xrightarrow[\text{Slow}]{} R{\cdot}H^+ + QH^- \xrightarrow[\text{Fast}]{} R + QH_2$$

Catalysis by proton donor is ascribed to the formation of the conjugate acid of the quinone, *i.e.*, the quinol cation QH^+, which has an even higher affinity for anionoid hydrogen than the quinone:

$$Q + HX \underset{\text{Fast}}{\rightleftharpoons} QH^+{\cdot}X^-,\ RH_2 + QH^+ \xrightarrow[\text{Slow}]{} R{\cdot}H^+ + QH_2,\ RH^+ + X^- \xrightarrow[\text{Fast}]{} R + HX$$

THIS paper is the first of a number which will deal with kinetic investigations of the dehydrogenation of hydroaromatic compounds by quinones. Such reactions are not only of practical interest, but also provide particularly attractive examples of thermal hydrogen transfer for quantitative study. Both reactants are readily capable of wide structural variation, a considerable amount of information concerning their thermodynamic properties is available, and convenient as well as accurate analytical methods can be devised. The majority of preparative applications of dehydrogenations with quinones refer to tetrahydro-compounds (for references, see Part I *), but, for the sake of simple stoicheiometry and ease of reaction, a dihydro-derivative was preferable for an initial study. We chose 1 : 4-dihydronaphthalene as a suitable donor and have examined the kinetics of its reaction with benzoquinone and a representative series of other quinones to give naphthalene and the quinols.

Transfer occurs at convenient speeds, and in most cases quantitatively, in the temperature range 50—160° in suitable solvents; in a preparative experiment, 1 : 4-dihydronaphthalene was heated with benzoquinone in diethylene glycol diethyl ether for 72 hr. at 131° and naphthalene was isolated in 90% yield. For the majority of kinetic experiments, phenetole, which has satisfactory solvent power for a wide range of quinones and quinols

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* Part I, preceding paper.

and is stable for prolonged periods at elevated temperatures, was used. Two methods were employed for determining reaction rates. In the first, the disappearance of quinone was followed by reduction of aliquot portions with titanous chloride. The direct estimation of quinones in this manner was first described by Knecht and Hibbert (" New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., London, 1910, p. 89) but a more accurate procedure consists in using excess of reducing agent and back-titration with ferric ammonium sulphate against an indicator of lower potential than the quinone. In order to obtain sharp end-points, the potential difference between quinone and indicator should be at least 0·2 v; methylene-blue was found suitable for quinones with $E^\circ > 0{\cdot}55$ v; and rosinduline ($E^\circ = -0{\cdot}28$ v) for quinones with $E^\circ < 0{\cdot}55$ v. In the second method, the appearance of quinol was followed by oxidation with ceric ammonium sulphate, with diphenylamine ($E^\circ = +0{\cdot}85$ v) as indicator. This method is not applicable to 1 : 2-quinols, since 1 : 2-quinones undergo rapid further oxidation; 1 : 4-quinones are also attacked by ceric ions but usually sufficiently slowly to allow a good end-point to be obtained. In a number of cases it was possible to combine the two methods, and thus obtain a check on the stoicheiometry of the reaction, by using ceric instead of ferric ammonium sulphate in the back-titration of titanous chloride against methylene-blue, and then continuing the titration after addition of diphenylamine until the second end-point was reached.

The reactions between dihydronaphthalene and 1 : 4-benzoquinone, toluquinone, chlorobenzoquinone, and tetrachlorobenzoquinone in phenetole and a number of other solvents were found to obey strictly second-order rate laws (first-order with respect to each reactant), both at equimolar concentrations of hydrocarbon and quinone and when one reactant was present in excess, provided aerial oxygen was excluded more or less rigorously (depending on the oxidation–reduction potential) to prevent re-oxidation of the quinols. The reactions with the other quinones studied also exhibited essentially second-order kinetics, but showed various types of deviations, as follows.

(1) With 2 : 6-dichloro- and trichloro-1 : 4-benzoquinone, a marked decrease in the second-order rate constants was observed as the reaction proceeded. Separate experiments showed that this was not due to the thermal instability of the quinones, quinols or quinhydrones, and that no reaction occurred between the quinols and either dihydronaphthalene or naphthalene under the conditions used. It is therefore probable that side-reactions between these quinones and dihydronaphthalene are responsible for the effect; two possibilities are the formation of (non-oxidisable) quinol diethers,* which has also been observed in other cases (Criegee, *Ber.*, 1936, **69**, 2758; Farmer, *Trans. Faraday Soc.*, 1942, **38**, 341) and the formation of naphthyl-substituted quinones or quinols which would result in more than equimolar consumption of dihydronaphthalene.

(2) The reaction with 1 : 4-naphthaquinone also exhibits a downward drift of the second-order rate constants when the reaction is followed by estimation of the quinol produced. Separate experiments showed that, in this case, the effect is at least partly due to thermal instability of 1 : 4-dihydroxynaphthalene. The fact that the ceric sulphate titre of the latter in phenetole decreases to a constant value corresponding to about 75% of the initial value suggests that reversible isomerisation to 1 : 4-dihydro-1-hydroxy-4-oxonaphthalene (Madinaveitia and Olay, *Anal. Fis. Quim.*, 1933, **32**, 1157 *et seq.*), analogous to the oxanthrol–oxanthrone rearrangement in the anthracene series, might be responsible.

(3) With 2 : 5- and 2 : 6-dimethylbenzoquinone, thymobenzoquinone (2-methyl-5-*iso*-propylbenzoquinone), 1 : 2-naphthaquinone, and 9 : 10-phenanthraquinone, all of which have oxidation–reduction potentials less than 0·6 v, the second-order rate constants, though accurately reproducible, increase as the reaction proceeds. The drifts are generally larger the lower the potential of the quinone, but they also decrease with increasing temperature and depend markedly on the solvent and other experimental conditions. Thus, for a 0·1M-solution in phenetole at 100°, the ratio k (after 50% reaction) : k (extrapolated to zero time) was 1·55 for thymoquinone (E° 0·589), 1·80 for 1 : 2-naphthaquinone (E° 0·579), and 2·00 for 9 : 10-phenanthraquinone (E° 0·471), while for thymoquinone at

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* Some quinol diethers are readily oxidisable; *e.g.*, 1 : 4-dimethoxybenzene.

155° the ratio was 1·2. The possibility that these effects might be due to the simultaneous occurrence of first-order reactions was eliminated in the following way. If the rate law were $dx/dt = k_2(a - x)^2 + k_1(a - x)$ (where a refers to the initial concentration of both reactants and x is the fraction which has undergone change at time t), then

$$k_2 = (1/\alpha t) \ln [a(a - x - \alpha)/(a + \alpha)(x - a)]$$

where $\alpha = k_1/k_2$. However, when this equation was solved for α from results of runs with thymoquinone at different values of a, a constant value for α was not obtained [See runs (xiv)—(xvi), p. 3561]. The upward drift in the second-order rate constants was eventually found to be due to a catalytic effect of the quinol produced; initial addition of 0·5 mol. of quinol increased the extrapolated rate constant by about 20%, while in the presence of 1·2 mols. of quinol, the rate constants were approximately doubled and little deviation from second-order kinetics was then observed during the first half of the reaction. On the other hand, the initial addition of the other reaction product, naphthalene, is without effect. The occurrence of product-catalysis due to quinol has important mechanistic implications and is further discussed below.

Second-order rate constants (extrapolated, where necessary, to zero time) for the reaction of 1 : 4-dihydronaphthalene and twelve quinones in phenetole are given in Table 1. In the four cases in which strict second-order kinetics were observed, the average deviation was about 1%; the accuracy of extrapolated rate constants is somewhat lower. In each case, the plots of log k_2 against $1/T$ were satisfactorily linear and the Arrhenius energies of activation (E_A), entropies of activation ($\Delta S^\ddagger$), and free energies of activation ($\Delta G^\ddagger$) are given in Table 2, together with the oxidation–reduction potentials (E°) of the quinones in ethanol at 25°, determined by Conant and Fieser (*J. Amer. Chem. Soc.*, 1923, **45**, 2194; 1924, **46**, 1858).

TABLE 1. *Second-order rate constants* (10^4k *in l. mole*$^{-1}$ *sec.*$^{-1}$) *for the reaction between* 1 : 4-*dihydronaphthalene and quinones in phenetole.*

	50°	60°	70°	80°	90°
Trichloro-1 : 4-benzoquinone	0·274	0·608	1·30	2·80	5·53
2 : 6-Dichloro-1 : 4-benzoquinone	0·313	0·687	1·47	2·94	5·90
1 : 2-Naphthaquinone	—	0·547	1·01	2·12	4·21

	90°	100°	110°	119°	131°	141°	155°
Tetrachloro-1 : 4-benzoquinone	7·85	15·7	28·3	59·4	100	—	—
Chloro-1 : 4-benzoquinone	2·37	4·57	8·48	14·4	28·3	—	—
1 : 4-Benzoquinone.........................	—	1·21	2·62	4·26	7·95	15·1	—
Toluquinone	—	0·399	0·825	1·42	3·27	5·90	—
2 : 6-Dimethyl-1 : 4-benzoquinone	—	0·140	—	—	1·25	—	5·28
2 : 5-Dimethyl-1 : 4-benzoquinone	—	0·0849	—	0·309	0·811	1·48	3·51
2-Methyl-5-*iso*propyl-1 : 4-benzoquinone	—	0·0633	—	0·254	0·610	1·15	2·81
1 : 4-Naphthaquinone	—	0·0157	—	0·0635	0·151	0·320	0·842
9 : 10-Phenanthraquinone	0·380	0·722	1·14	2·24	5·19	—	—

TABLE 2. *Thermodynamic quantities of activation for the reaction between* 1 : 4-*dihydronaphthalene and quinones in phenetole.*

No.		$-\log k_{100^\circ}$	E_A (kcal./mol.)	$\Delta S^\ddagger_{100^\circ}$ (e.u.)	$\Delta G^\ddagger_{25\cdot0^\circ}$ (kcal./mol.)	$E^\circ_{25\cdot0^\circ}$ (v)
1.	Tetrachloro-1 : 4-benzoquinone	2·80	18·2	−25·1	25·0	0·703
2.	Trichloro-1 : 4-benzoquinone	3·00 *	17·7	−27·3	25·1	0·726
3.	2 : 6-Dichloro-1 : 4-benzoquinone	3·00 *	17·0	−29·0	24·9	0·748
4.	Chloro-1 : 4-benzoquinone	3·34	17·7	−28·9	25·6	0·736
5.	1 : 4-Benzoquinone	3·92	18·9	−28·2	26·6	0·711
6.	Methyl-1 : 4-benzoquinone	4·40	20·3	−26·8	27·6	0·656
7.	2 :6 -Dimethyl-1 : 4-benzoquinone	4·85	21·1	−26·9	28·3	—
8.	2 : 5-Dimethyl-1 : 4-benzoquinone	5·07	21·8	−26·0	28·8	0·597
9.	2-Methyl-5-*iso*propyl-1 : 4-benzoquinone	5·20	22·0	−25·9	28·9	0·589
10.	1 : 4-Naphthaquinone	5·80	23·0	−26·1	30·0	0·493
11.	1 : 2-Naphthaquinone	3·14 *	16·6	−31·0	25·0	0·579
12.	9 : 10-Phenanthraquinone	4·14	18·5	−30·5	26·7	0·471

* Extrapolated from the k–T data by the method of least squares.

DISCUSSION

Only two previous quantitative investigations of thermal dehydrogenation processes with quinone acceptors are on record. The first was carried out by Dimroth and his pupils (*Angew. Chem.*, 1933, **46**, 571; 1938, **51**, 404) who employed diethyl 1 : 4-dihydrocollidine-2 : 6-dicarboxylate and *o*-tolylphenylsemicarbazide as donors. Only a summary of the results published shortly before Professor Dimroth's death is available, but it was established that the reactions exhibit the expected second-order kinetics and that an approximately linear relation obtains between log k_2 and the redox potentials of the quinones, determined in the same solvent, acetic acid. Since the preliminary report (*Nature*, 1952, **169**, 100) of our work, Dost (*Rec. Trav. chim.*, 1952, **71**, 857) has reported a study of the dehydrogenation of 1 : 2-dihydronaphthalene, acenaphthene, and certain other hydrocarbons by chloranil in chlorobenzene and also compared the reactivity of different quinones. He, too, found the reactions to be of the second order and obtained qualitative evidence for a correlation between dehydrogenating power and redox potential.

The present results confirm the conclusion that transfer reactions of this type are essentially bimolecular, though deviations from second-order kinetics due to catalytic effects of the quinols or side-reactions are frequently observed. The results in Table 2 also show that there is a roughly linear correlation between $\Delta G^{\ddagger}$ and the potentials of 1 : 4-quinones in ethanol solution (Fig. 1), but that the relation breaks down entirely in comparing 1 : 4-quinones with 1 : 2-quinones; the latter are far more reactive although their potentials are smaller. A similar difference, though surprisingly in the opposite direction, was noted by Dimroth (*loc. cit.*) who found that tetrabromo-1 : 2-benzoquinone was less reactive than would be expected from the plot of log k against $E°$ for 1 : 4-quinones.

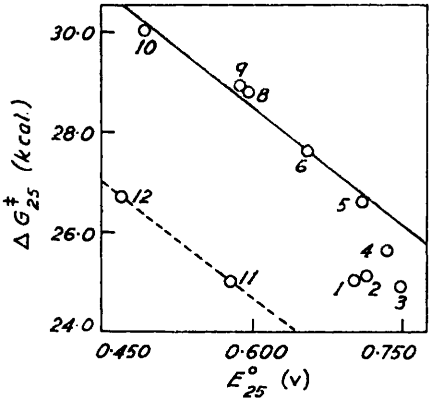


FIG. 1. *Plot of free energies of activation for dehydrogenation of* 1 : 4-*dihydronaphthalene in phenetole against oxidation–reduction potentials of quinones in ethanol. The numbers refer to the quinones listed in Table* 2.

Since the potentials are a measure of the free-energy gain in converting the quinones into the quinols, some correlation with reactivity is to be expected independently of the reaction mechanism, though the precise relations will depend on the extent to which the additional resonance stabilisation of the quinol is effective in the transition state, as well as on a variety of other factors. A more detailed analysis of the results (Table 2) shows that the rate differences in the transfer reaction are mainly due to differences in the energies of activation E_A, whereas the entropies of activation $\Delta S^{\ddagger}$ exhibit small and irregular fluctuations. In relation to redox potentials, which are effectively a measure of the free-energy changes of the reduction of quinone by molecular hydrogen, the most comparable kinetic parameters are the free energies of activation $\Delta G^{\ddagger}$, and the values for five 1 : 4-quinones may be expressed within experimental error by the relation

$$\Delta G^{\ddagger}_{25^\circ} = 38{\cdot}0 - 0{\cdot}0016E^{\circ}_{25^\circ} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or, the potentials being converted into free energies,

$$\Delta G^{\ddagger}_{25^\circ} = 38{\cdot}0 - 0{\cdot}07\Delta G^{\circ}_{25^\circ} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where E° (in v) and ΔG° (in kcal.) refer to ethanol solutions (Conant and Fieser, *loc. cit.*). The only 1 : 4-quinones of known potentials which deviate from this relation are trichloro- and tetrachloro-benzoquinone, and it is significant that the potentials of these two quinones *in ethanol* are somewhat abnormal; whereas E° is increased by one and by two chlorine substituents, the third and fourth substituent each cause a decrease. This appears to be due to a specific solvent effect, for in benzene a decrease in E° occurs only with tetrachloro-1 : 4-benzoquinone, while the potentials referred to the gaseous state show a regular increase throughout the series (Conant, *J. Amer. Chem. Soc.*, 1927, **49**, 293; Hunter and Kvalnes, *ibid.*, 1932, **54**, 2869; Kvalnes, *ibid.*, 1934, **56**, 667, 670; Evans and De Heer, *Quart. Reviews*, 1950, **4**, 94). The free energies of the dehydrogenation of 1 : 4-dihydronaphthalene in phenetole exhibit a dependence on chlorine substitution in the quinone which is actually intermediate in type between that of the potentials in benzene and in ethanol (Fig. 2); since the solvating properties of phenetole are likely to be intermediate between those of benzene and ethanol, this suggests that the quinonoid species concerned in chemical and electrochemical hydrogen transfer are indeed closely similar, if not identical. The fact that, for a limited range of quinones, a straight-line relation between the free energies of the two processes obtains even in two different solvents indicates that, in the absence of several highly polar substituents, the differential effects of solvation are quite small. In this connection, it is of interest that the entropy changes in the electrochemical reduction of benzoquinone and toluquinone (the only two for which data are available) are very similar (*ca.* 30 e.u.; Conant and Fieser, *loc. cit.*) to those observed in the transfer reaction (Table 2).

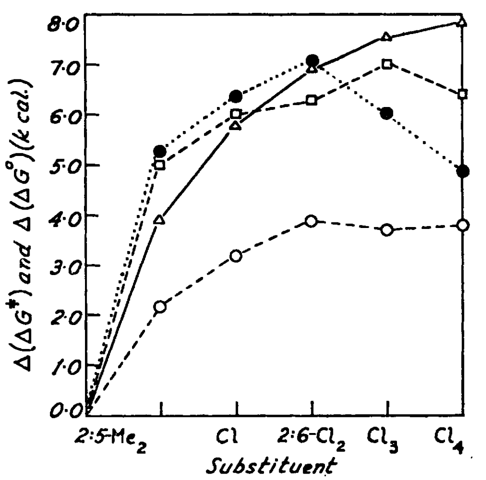


FIG. 2. *Effects of substituents in benzoquinone on the free energy of activation for dehydrogenation of* 1 : 4-*dihydronaphthalene in phenetole* (– – – ○ – – – ○ – – –), *and on the free-energy changes accompanying reversible reduction by hydrogen in ethanol* (· · · ● · · · ● · · ·), *in benzene* (– – – □ – – – □ – – –) *and in the gas phase* (——△——△——) (*calculated from oxidation–reduction potentials*).

We now turn to a consideration of the mechanism of the transfer reaction. It was suggested by Waters (*Trans. Faraday Soc.*, 1946, **42**, 184; "The Chemistry of Free Radicals," Oxford Univ. Press, 1946) that such processes are homolytic and involve the abstraction of a hydrogen atom by the quinone to give a semiquinone radical. The experimental basis of this suggestion was that the autoxidation of tetralin is inhibited by quinones and, although this fact can be explained in this manner, other interpretations are possible which do not involve homolytic hydrogen transfer to the quinone. Dost and van Nes (*Rec. Trav. chim.*, 1951, **70**, 403) also considered that dehydrogenation of hydroaromatic compounds by quinones proceeded by a free-radical mechanism, but their general arguments in favour of this view are not very convincing, and attempts to catalyse the reactions by ultraviolet light or by peroxides gave negative results. A similar lack of acceleration due to radical-producing agents has been observed here; thus the rate constant for the dehydrogenation of 1 : 4-dihydronaphthalene by thymoquinone in phenetole at 155° was unchanged within experimental error in the presence of 0·005M-benzoyl peroxide which undergoes rapid homolysis at this temperature (Bartlett and Nozaki, *J. Amer. Chem. Soc.*, 1946, **68**, 1686;

1947, **69**, 2299) or on illumination, and further examples are given in Part IV. As Dost and van Nes have rightly pointed out, such observations do not exclude a homolytic mechanism, though they do make it unlikely that a free-radical chain reaction is involved. Very recently, Moore and Waters (*J.*, 1953, 3405) showed that chloranil reacts under illumination with toluene and xylene to give the quinol and coupling products, and with excess of tetralin to give 1 : 2-dihydronaphthalene. They concluded that all these reactions were photochemical and, therefore, homolytic. However, no control experiments are recorded and although Moore and Waters's interpretation is probably correct for the alkylbenzenes, comparison with results obtained in the absence of illumination (Part IV) indicates that the photochemical effect was negligible for the hydroaromatic donor, tetralin; it is significant that no coupling products of the type expected from homolytic reactions were encountered in this instance. In any case, the existence of a photochemical reaction does not, in itself, prove that the corresponding thermal reaction is homolytic. The only indubitable example of thermal homolytic dehydrogenation by a quinone in solution appears to be the conversion of 3 : 3 : 4 : 4-tetraphenylhexane into diphenylethylene described by Ziegler and Deparade (*Annalen*, 1950, **567**, 123); this belongs to a different category since homolytic dissociation into diphenylpropyl radicals precedes transfer so that the actual donor is itself a free radical.

In agreement with the previous evidence, the kinetic features of the reactions studied here render a free-radical chain mechanism highly unlikely, although they do not as such exclude homolytic as opposed to heterolytic fission of the carbon–hydrogen bond in the donor. In order to obtain further evidence on this point, the influence of solvent was investigated in more detail (Table 3). An increase in rate with increasing polarity of the solvent is observed, which is larger than would be expected for a homolytic process (cf. Waters, *op. cit.*) and corresponds in order of magnitude to that generally encountered in bimolecular heterolytic reactions involving a high degree of charge-dispersal in the transition state (cf. Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, 1941; for a recent example, see Brown and Grayson, *J. Amer. Chem. Soc.*, 1953, **75**, 6285). Attempts to demonstrate a salt effect with thymoquinone and lithium chloride in dimethylformamide or propionic acid were not successful; the quinone, which is reasonably stable in these solvents alone, undergoes rapid changes in the presence of the salt (M) and although the reaction with dihydronaphthalene appeared to be accelerated even more strongly, the results are not considered reliable without more detailed investigation of these systems.

TABLE 3. *Solvent effects in the dehydrogenation of* 1 : 4-*dihydronaphthalene by quinones.* (*Second-order rate constants* × 10^4 *in l. mole*$^{-1}$ *sec.*$^{-1}$).

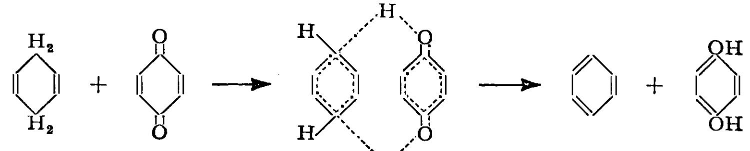
Solvent	Temp.	Thymoquinone	Benzoquinone	Chlorobenzoquinone
Decalin	100°	0·0623	—	—
Diethylene glycol diethyl ether	100	—	1·21	—
Phenetole	100	0·0633	1·21	4·43
o-Dichlorobenzene	100	0·102	1·85	6·55
Dimethylformamide	100	0·288	2·27	8·50

Solvent	Temp.	Thymoquinone
Phenetole	141°	1·21
Propionic acid	141	3·18
Propionic acid–water (19 : 1, v/v)	141	4·16
Propionic acid–water (9 : 1; v/v)	141	4·88
Phenetole	155°	2·93
o-Dichlorobenzene	155	3·20
Nitrobenzene	155	5·14

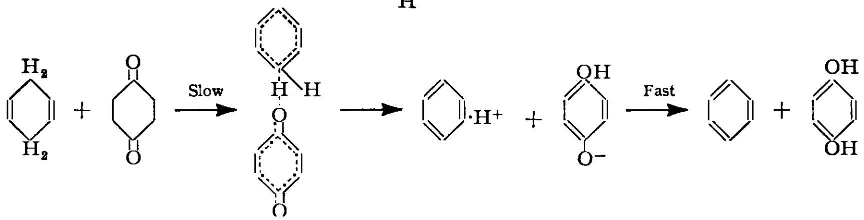
The criteria so far applied being inconclusive, the effects of structure on the reactivity of quinones can next be invoked in attempting to classify the reaction. The close parallelism expressed in relations (1) and (2) (p. 3551) between equilibrium in electrochemical reduction and reaction rate in thermal hydrogen transfer indicates that the quinones act as electron-acceptors in both types of processes. That this is indeed the case can be seen, without considering redox potentials, from the fact that the reactivity is increased by electron-attracting substituents (*e.g.*, Cl) and decreased by electron-donating substituents (*e.g.*, Me). From this viewpoint, the correlation with redox potentials is due to the circumstance that electron-attracting substituents decrease, and electron-donating substituents increase, the stability of the quinone relative to the quinol, because the double-bonded oxygen atoms in the former are electron-demanding ($C{=}C{-}C{=}O \longleftrightarrow C^{+}{-}C{-}C{=}O^{-}$) while the single-bonded oxygen atoms in the latter have a mesomeric effect ($C{=}C{-}\ddot{O}H \longleftrightarrow C^{-}{-}C{=}O^{+}H$) of the opposite sign. Although the qualitative effects of substituents thus leave no doubt that the quinone acts as an electrophilic reagent, they do not necessarily exclude a homolytic process in which the quinone is an electron-acceptor (cf. Breitenbach and Folly, *Monatsh.*, 1953, **84**, 319; Lopèz Aparicio and Waters, *J.*, 1952, 4666; Dunn and Waters, *J.*, 1953, 2993; Dunn, Waters, and Roitt, *J.*, 1954, 584, and earlier papers). The quantitative relations, however, favour a heterolytic process and, summarising, we may say that the absence of side-reactions involving the hydrocarbon, the effects of reaction medium, and the influence of substituents in the quinone all point in the same direction.

The conclusions so far reached can be accommodated in two types of mechanism. In the first (1), the two hydrogen atoms are transferred more or less simultaneously from the hydrocarbon to the quinone, through a pseudocyclic transition state. In the second (2), one hydrogen atom with its electron pair is transferred through a linear transition state to give the conjugate acid of the dehydrogenation product and the quinol anion, and this is followed by the rapid transfer of the other hydrogen atom in the form of a proton, not necessarily to the same acceptor molecule. The two mechanisms represent the extremes of a range characterised by the varying time-sequence of the two C–H bond fissions; in the one-step mechanism (1), the two events are linked to a high degree, while in the two-step mechanism (2) they are essentially independent. In both mechanisms, a rapid reversible association of the reacting partners might precede the rate-determining step. (For simplicity, the two schemes have been written for 1 : 4-dihydrobenzene and benzoquinone.) In scheme (1) (below) the two rings are supposed to be in different but approximately parallel planes in the transition state.

(1)



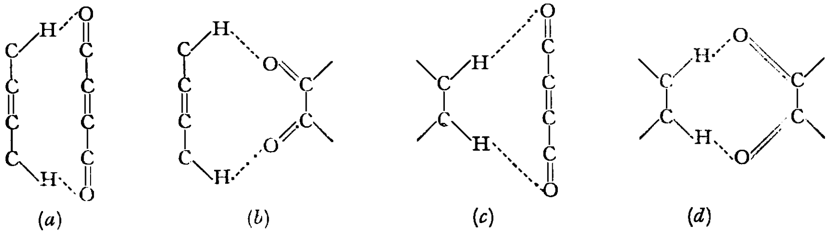
(2)



In the one-step mechanism (1), the quinone is a bifunctional reagent, with one carbonyl group displaying electrophilic, and the other nucleophilic, reactivity. If the time-sequence of hydrogen transfer to both carbonyl groups were completely synchronised, the electronic classification of the reagent would lose its meaning and the influence of substituents would have to be ascribed almost entirely to the change in stabilisation of the quinol which would be partly effective in the transition state. In addition, any differential effect of substituents on the two carbonyl groups, which would facilitate a bipolar condition, might make itself felt, and the somewhat higher reactivity of unsymmetrically as compared with symmetrically substituted methyl- and chloro-quinones (Table 1) might be explained in this way. A diagnostically sharper consequence of the single-step mechanism (1) is that the ease of reaction should be closely dependent on the geometrical relations between the donor and the acceptor; the spatial arrangement of the hydrogen and oxygen atoms must be such as to allow the formation of the pseudocyclic transition state without appreciable strain. It is not immediately obvious in the case of a donor of 1 : 4-dihydrobenzene type whether this condition is better fulfilled by a 1 : 2-quinone or a 1 : 4-quinone (Fig. 3*a* and *b*); but in the case of a donor of 1 : 2-dihydrobenzene type, it is certainly better fulfilled by a

1 : 2-quinone (Fig. 3*c* and *d*). The fact that the ratios of the rate constants for the reactions of 1 : 2- and 1 : 4-naphthaquinone with 1 : 2-dihydronaphthalene and 1 : 4-dihydronaphthalene are similar (Part III) is strong evidence against a single-step mechanism and further evidence is provided by the high reactivity of 1 : 8-diphenoquinones (Braude, Brook, Linstead, and Shannon, unpublished work). On the other hand, on the basis of mechanism (2), the relatively high reactivity of 1 : 2-quinones is understandable since, in contrast to 1 : 4-quinones, both carbonyl groups can participate in the removal of hydride ion in the rate-determining step, and the resulting quinone anion will be stabilised to a greater extent than quinol itself by intramolecular hydrogen bonding. The existence of such additional stabilisation is clearly indicated by the fact that, even in aqueous solution, catechol (p*K* 9·1) is a stronger acid than either phenol or quinol (p*K* 9·9) (Abichandani and Jatkar, *J. Indian Inst. Sci.*, 1938, **21**, *A*, 417; Gawron, Duggan, and Grelecki, *Analyt. Chem.*, 1952, **24**, 969).

FIG. 3. *Schematic representation (side views) of transition states for synchronised hydrogen-transfer between* 1 : 4- *and* 1 : 2-*dihydro-donors and* 1 : 4- *and* 1 : 2-*quinones.*



We are thus led, by a process of elimination, to adopt the two-step mechanism (2).* Additional confirmation is provided by the observation (p. 3550) that quinols catalyse transfer to low-potential quinones. Since low-potential quinones are particularly prone to quinhydrone formation (cf. Hunter and Northey, *J. Phys. Chem.*, 1933, **37**, 875), it was suspected that the catalytic effect might be associated with this phenomenon. The catalytic effect does not merely depend on molecular complex-formation by the quinone, however, for, although *p*-nitrophenol and picric acid proved to be strong catalysts, *p*-nitroanisole was ineffective (Table 4); yet all these compounds may be expected to form molecular compounds of the same type with quinones (cf. Wallwork and Harding, *Nature*, 1953, **171**, 40). An attempt to establish whether the quinol dimethyl ether is a catalyst failed because the ether is, somewhat unexpectedly, oxidised by ceric sulphate, but the clear-cut difference between nitrophenol and nitroanisole indicates that the catalytic effect is specific to proton-donors. In phenetole as a solvent, it appears that both complex-forming and acidic properties are needed, for no accelerating influence was shown by acetic or benzoic acid at comparable concentrations. Phenetole, however, is a relatively basic solvent and the absence of general acid catalysis could be due to the fact that the very weakly basic quinone is unable to compete successfully for the proton donor. Some experiments were therefore carried out in propionic acid solution. The considerably increased rate of reaction, compared with that in phenetole, could be a general solvent effect and does not necessarily signify acid catalysis, but a further slight, though significant, acceleration is observed with quite low concentrations of chloroacetic acid in propionic acid, and an enormous acceleration (representing a rate factor of *ca.* 10^3) is produced by perchloric acid, known to be a particularly powerful proton donor under such conditions (cf. Hall, *Chem. Reviews*, 1931, **8**, 191; Kolthoff, *J. Amer. Chem. Soc.*, 1934, **56**, 1007; Mackenzie and Winter, *Trans. Faraday Soc.*, 1948, **44**, 159). Unfortunately, side-reactions occur in this highly acidic solvent and hydrogen transfer could only be followed to about 20% completion. The side-reactions probably include acid-catalysed isomerisation of 1 : 4- to 1 : 2-dihydronaphthalene (which undergoes dehydrogenation much less readily; Part III) as well as addition of propionic acid to the ethylenic double bond (cf. Tilichenko,

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* The precise state of the conjugate acid of the aromatic hydrocarbon produced in the rate-determining step has been deliberately left undefined at this stage. Further evidence concerning this detail is presented in Part III.

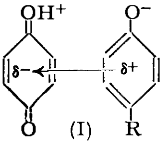
Zhur. Obshchey Khim., 1950, **20**, 2152; Braude and Forbes, *J.*, 1953, 2208; Knight, Coos, and Swern, *J. Amer. Chem. Soc.*, 1953, **75**, 6212) and self-condensation of the quinone (cf. Ioffé and Sukhina, *Zhur. Obshchey Khim.*, 1953, **23**, 1370). As a check, the general acid catalysis of hydrogen transfer was tested with 9 : 10-dihydroanthracene in which prototropic rearrangement is unlikely to occur. The more than two-fold acceleration produced by 0·1M-trichloroacetic acid in propionic acid provides clear evidence of proton catalysis.

TABLE 4. *Effects of various addenda on the rate of dehydrogenation of* 1 : 4-*dihydronaphthalene by thymoquinone* (both reactants 0·1M).

Solvent	Temp.	Addendum	10^4k_2 (l. mole^{-1} sec.$^{-1}$)
Phenetole	155°	None	2·93
,, ...	,,	Naphthalene, 0·1M	2·88
,, ...	,,	Thymoquinol, 0·05M	3·43
,, ...	,,	,, 0·12M	5·50
,, ...	,,	*p*-Nitrophenol, 0·058M	6·13
,, ...	,,	*p*-Nitroanisole, 0·058M	2·90
,, ...	,,	Acetic acid, 0·058M	2·87
,, ...	,,	Benzoic acid, 0·058M	2·78
,, ...	,,	Picric acid, 0·058M	3·8
,, ...	,,	Benzoyl peroxide, 0·045M	2·70
Propionic acid	141	None	3·18
,, ...	,,	Chloroacetic acid, 0·058M	3·33
,, ...	23	Perchloric acid, 0·070M	0·92
Propionic acid	141 *	None	0·97
,, ...	,, *	Trichloroacetic acid, 1M	2·27

* With 9 : 10-dihydroanthracene in place of dihydronaphthalene as donor.

Since addition of a proton to the hydrocarbon could not possibly assist its dehydrogenation, the catalytic effect clearly depends on the partial conversion of the quinone into its conjugate acid. The latter would indeed be expected to be a far more powerful reagent than the quinone itself for dehydrogenation by the two-step mechanism; the presence of a positive charge will greatly increase the electrophilic reactivity of the carbonyl group and the abstraction of a hydride ion from the donor will convert the acceptor directly into the quinol (2*a*). The reactivity of the conjugate acids of the quinones must exceed that of the quinones by many powers of ten, for the extent of conversion when the catalytic effect first becomes noticeable must be extremely small. It is highly probable that in a basic solvent such as phenetole where only proton donors which form molecular complexes with the quinone are effective, the proton transfer is only partial, to give an ion pair in which the charge resonance due to π-bonding (cf. Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811) is reinforced by charge resonance due to proton transfer, as represented in (I). The fact that product-catalysis due to the quinol is observed only with quinones of low potential indicates that electron-donating substituents increase the basicity of the quinone more than they reduce the acidity of the quinol (cf. Hunter and Northey, *J. Phys. Chem.*, 1933, **37**, 875). This picture is also in accord with the fact that product-catalysis decreases with increasing temperature which will reduce the extent of molecular-complex formation (cf. Gibson and Loeffler, *J. Amer. Chem. Soc.*, 1940, **62**, 1324) and with increasing ionising properties of the solvent, which will have the same effect since they favour charge dispersal.*



(I)

Reactions involving displacement of hydrogen in an anionoid condition (hydride ion),

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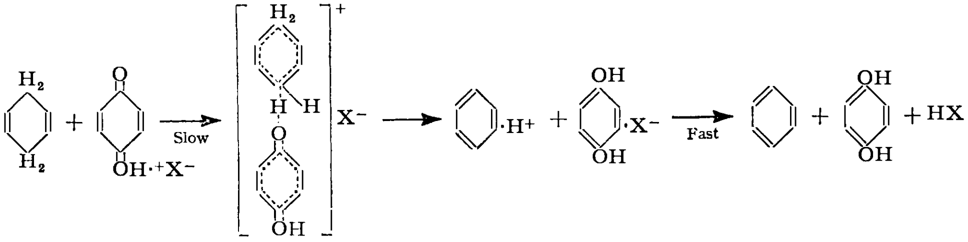
* It should be mentioned that, in isolation, proton catalysis could conceivably be accounted for by the homolytic variant of mechanism (2*a*), as was first pointed out to us by Professor J. D. Roberts (California). In such a scheme, the conjugate acid of the quinone would be converted into a radical cation in the rate-determining step:

$$RH_2 + QH^+ \longrightarrow RH\cdot + QH_2{\cdot}^+,\ QH_2{\cdot}^+ \longrightarrow QH\cdot + H^+,\ RH\cdot + QH\cdot \longrightarrow R + QH_2$$

Evidence has recently been reported for the stabilisation of quinone diradicals in strongly acid media (Hirshon, Gardner, and Fraenkel, *J. Amer. Chem. Soc.*, 1953, **75**, 4115) but, except possibly under such conditions, the above mechanism, like other homolytic mechanisms, is unlikely for the reasons already given (p. 3553).

as postulated here for thermal hydrogen transfer between hydroaromatic donors and quinones, are comparatively rare in organic chemistry. They normally occur only under the influence of reagents with a strong tendency to increase their covalency and to acquire a negative charge. Amongst inorganic reagents, certain metal halides, *e.g.*, aluminium chloride, display such properties, and steps involving transfer of hydride ion have been proposed for various reactions of Friedel–Crafts type (cf. Baddeley, Wrench, and Williamson, *J.*, 1953, 2112; Baddeley and Pickles, *ibid.*, p. 3726; Pines, Aristoff, and Ipatieff, *J. Amer. Chem. Soc.*, 1953, **75**, 4775); in most cases it is a positively charged carbonium ion formed under the agency of aluminium halides, rather than the halide itself, which is regarded as the hydride-ion acceptor. Amongst primary organic reagents, the carbonyl group is ourstanding in conferring the required properties and the transfer of hydride ions has been postulated in the Cannizzaro reaction (cf. Alexander, " Principles of Ionic Organic Reactions," Wiley, New York, 1950) and in the reduction of ketones by metal alkoxides (Alexander, *op. cit.*; cf. Jackman and Macbeth, *J.*, 1952, 3252; Doering and Ashner, *J. Amer. Chem. Soc.*, 1953, **75**, 393), Grignard reagents (cf. Mosher and LaCombe, *ibid.*, 1950, **72**, 3994, 4991; Percival, Wagner, and Cook, *ibid.*, 1953, **75**, 3731), and metal hydrides (Trevoy and W. G. Brown, *ibid.*, 1949, **71**, 1675; H. C. Brown and Mead, *ibid.*, 1953, **75**, 6267). The azomethine group is less effective, but transfer of hydride ion has been suggested in the Sommelet and certain other reactions involving methyleneimines (Angyal, Penman, and Warwick, *J.*, 1953, 1742). Quinones, quinone imides, and similar compounds are exceptional, in not only possessing two suitable functional groups, but also acquiring increased resonance stabilisation through the addition of hydrogen. Thus, it is not altogether surprising that such compounds appear to represent neutral acceptors *par excellence* for hydride ion.

(2*a*)



EXPERIMENTAL

Materials.—1 : 4-Dihydronaphthalene, prepared by Bamberger and Lodter's method (*Ber.*, 1887, **20**, 1705), was purified through its addition compound with mercuric acetate (m. p. 121°; Sand and Gennsler, *Ber.*, 1903, **36**, 3705) and had m. p. 25·5°; it was stored *in vacuo* at 0°. 9 : 10-Dihydroanthracene, m. p. 109°, was prepared by Wieland's method (*Ber.*, 1912, **45**, 492).

The quinones were prepared according to the following procedures and were purified by crystallisation from light petroleum (b. p. 60—80°) (cf. Braude, *J.*, 1945, 490) unless otherwise stated. 1 : 4-Benzoquinone (Underwood and Walsh, *Org. Synth.*, Coll. Vol. II, p. 553), m. p. 113°; chloro-1 : 4-benzoquinone (Levy and Schultz, *Annalen*, 1881, **210**, 138), m. p. 57°; 2 : 6-dichloro-1 : 4-benzoquinone (Conant and Fieser, *J. Amer. Chem. Soc.*, 1923, **45**, 2194), m. p. 121°; trichloro-1 : 4-benzoquinone (Knapp and Schultz, *Annalen*, 1881, **210**, 174), purified by sublimation, m. p. 169°; tetrachloro-1 : 4-benzoquinone, commercial sample crystallised from benzene, m. p. 286—287°; toluquinone (Clark, *Amer. Chem. J.*, 1892, **14**, 553), m. p. 68°; 2 : 5-dimethyl-1 : 4-benzoquinone (Nölting, Witt, and Forel, *Ber.*, 1885, **18**, 2667), m. p. 124°; 2 : 6-dimethyl-1 : 4-benzoquinone (Nölting and Forel, *ibid.*, p. 2673), m. p. 71—72°; 2-methyl-5-*iso*propyl-1 : 4-benzoquinone (Kremers, Wakeman, and Hixon, *Org. Synth.*, Coll. Vol. I, 2nd edn., p. 511), m. p. 45°; 1 : 2-naphthaquinone (Fieser, *ibid.*, Coll. Vol. II, p. 430), purified by sublimation, m. p. 146° (decomp.); 1 : 4-naphthaquinone (Braude and Fawcett, *J.*, 1951, 3117; *Org. Synth.*, **33**, 50), m. p. 124°; 9 : 10-phenanthraquinone (Underwood and Kochmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2069), m. p. 204°.

Phenetole was refluxed over sodium and then distilled; it had b. p. 170°, n_D^{20} 1·5085. Diethylene glycol diethyl ether and decalin were similarly purified. *o*-Dichlorobenzene and dimethylformamide were fractionated. Nitrobenzene was dried over phosphoric oxide, distilled, and finally purified by fractional freezing, to m. p. 5·7° (Cohen and Bockhorst, *Z. physikal. Chem.*, 1934, *B*, **24**, 241). Propionic acid was refluxed over chromic oxide and fractionated from boron tripropionate (Eichelberger and LaMer, *J. Amer. Chem. Soc.*, 1933, **55**, 3633).

Isolation of Reaction Products.—(i) 1 : 4-Dihydronaphthalene (1·0 g.), benzoquinone (0·83 g.), and diethylene glycol diethyl ether (50 ml.) were heated in a sealed tube for 72 hr. at 131°. The mixture was then poured into water (250 ml.). An oil separated, which rapidly solidified and was filtered off. The crude material (0·91 g.) showed $\lambda_{max.}$ 2200 Å, $E_{1\,cm.}^{1\%}$ 8200 in EtOH, corresponding to a naphthalene content of 96% and a total yield of 87%. Recrystallisation from aqueous ethanol raised the m. p. to 79°, undepressed on admixture with naphthalene.

(ii) In a similar experiment with chloranil (0·12 g.) in phenetole (10 ml.), tetrachloroquinol (0·11 g.) separated on cooling of the reaction mixture.

(iii) 1 : 4-Dihydronaphthalene (1·30 g.), 1 : 2-naphthaquinone (1·58 g.), and toluene (100 ml.) were heated in a sealed tube for 48 hr. at 100°. On cooling, a purple solid (0·41 g.), m. p. 165—168°, separated and was filtered off. A further quantity (0·15 g.) of this material, presumably a mixture of the oxidation products known to be readily formed from 1 : 2-dihydroxynaphthalene (Stenhouse and Groves, *Annalen*, 1878, **194**, 208; Straus, Bernoully, and Mautner, *ibid.*, 1925, **444**, 165) was precipitated on dilution of the filtrate with pentane (100 ml.). The solution was then worked up as above, giving naphthalene picrate (2·9 g., 80%), m. p. 148—149°.

(iv) 1 : 4-Dihydronaphthalene (1·30 g.), 9 : 10-phenanthraquinone (2·08 g.), and chlorobenzene (100 ml.) were heated in a sealed tube for 6 days at 100°. On cooling and dilution with pentane, 9 : 10-dihydroxyphenanthrene, contaminated with a little unchanged quinone, separated and was filtered off; the m. p. was 142—145° (the pure quinol has m. p. 147°). The filtrate was worked up as above, giving naphthalene picrate (3·10 g., 86%), m. p. 148—149°.

Kinetic Experiments. General Procedures.—The ease of aerial oxidation of the quinol varies greatly from compound to compound and with the temperature. Oxidation could be rigorously prevented by a sealed-ampoule technique, but this is tedious and was only employed with quinones of low potential ($E° < 0·6$ v) where it is essential. With quinones of higher potential, more convenient procedures usually proved adequate and two different general methods with individual variations were therefore adopted.

Method 1. The reactions were carried out in long-necked flasks of the type described by Braude, Jones, and Stern (*J.*, 1946, 396) but provided with cold-fingers containing a narrow, central, inlet tube through which a very slow stream of dry nitrogen [purified by successive washing with alkaline pyrogallol, with sodium anthraquinone-2-sulphonate and sodium dithionite (hydrosulphite), and with sulphuric acid] could be passed. The nitrogen pressure was controlled by a simple mercury-filled overflow-valve and adjusted to *ca.* 0·5 cm. above atmospheric pressure; under such conditions slow outward leakage of nitrogen occurs, without the cold-fingers being " lifted " out of their seats. For runs up to 100°, thermostatic control was effected by means of an oil-bath controlled within ±0·05°. For runs at higher temperatures, jacketed vessels adapted from an earlier design (Waight, Thesis, London, 1950) were employed. The outer bulb was half-filled with the jacketing liquid and a few porcelain chips, and was heated to slow reflux with an electric mantle. For adequate temperature control, it was important that the outer bulb should be pear-shaped, that the inner bulb should be at least 3 cm. above the level of the liquid, and that the latter should be at least 2 cm. above the level of the heating mantle. The jacketing liquids used and the approximate temperatures measured in the inner bulbs were: methyl*cyclo*hexane (101°), toluene (110°), ethyl *n*-butyrate (119°), *iso*amyl alcohol (131°), xylene (141°), anisole (155°). The operational temperatures could be adjusted over a range of 0·5° by altering the temperature of the heating mantle, but were constant within ±0·1° for prolonged periods once equilibrium had been attained and provided fluctuations in atmospheric pressure did not exceed 20 mm.

Before a run was carried out, the empty vessel was flushed with nitrogen by slightly raising the cold-finger. A solution of dihydronaphthalene (or quinone) in phenetole or other solvent (usually 25 ml., 0·1M) was then introduced and the cold-finger was replaced. (In this and subsequent operations, the cold-finger was never completely removed, so that a nitrogen atmosphere was continuously maintained in the flask.) After thermal equilibrium had been attained (*ca.* 2 hr.), a small, open, glass capsule containing the finely ground quinone (or hydrocarbon) was dropped into the flask which was immediately shaken vigorously until all the quinone had dissolved (this normally required *ca.* 30 sec.). Subsequently, 1 ml. samples were withdrawn at appropriate intervals by means of a long-stem graduated pipette and titrated, as described below.

Method 2. In this method, 1-ml. aliquot portions of reaction mixture were placed in ampoules at room temperature, and the ampoules were sealed after evacuation (to 10 mm.) in such a manner that only *ca.* 0·2 ml. of free space remained. All the ampoules were then placed simultaneously into an oil-bath or in a jacketed vessel similar to that used in method 1, and, at appropriate intervals, were removed and rapidly cooled. A correction was applied to the reaction time to allow for the initial period during which the ampoules attained thermal equilibrium. The maximum correction needed was 4 min.; fortunately the reactions with quinones of low potential are relatively slow, so that the necessary corrections were small compared with the reaction half-times.

Estimation of Quinones and Quinols.—(*a*) One ml. of reaction mixture was introduced into a 10-ml. glass-stoppered conical flask, either by pipetting or by crushing a sealed glass ampoule (washed free from jacketing liquid) with a glass rod which was then rinsed with a little phenetole. The appropriate amount of titanous chloride (2—3 ml., *ca.* 0·1N) was then added from an enclosed, self-filling burette in which the reagent was stored under hydrogen. Water (1 ml.) and the indicator were added and the stoppered flask was shaken until the colour of the indicator disappeared. The excess of titanous chloride was then estimated by back-titration with ferric ammonium sulphate solution (*ca.* 0·04N) until the colour of the indicator was no longer discharged by shaking. Generally the value of the back-titre was known approximately and it was found desirable to add immediately all but 0·2 ml. of the required volume so as to reduce the chance of aerial oxidation. Methylene-blue (1% in methanol) was employed as an indicator for quinones with potentials greater than 0·55 v and rosinduline (0·1% in methanol) or phenosafranine (0·1% in methanol) for quinones with potentials below this value. Titrations with rosinduline and phenosafranine were rendered tedious by the slow rate of reaction of the indicators with titanous chloride. The titanous chloride solution required daily standardisation against the ferric ammonium sulphate solution.

(*b*) One ml. of the reaction mixture, acetic acid (1 ml.), water (2 ml.), and one drop of 0·1% sodium diphenylaminesulphonate were placed in a glass-stoppered, 10-ml. conical flask, and ceric ammonium sulphate solution (*ca.* 0·04N) was run in slowly from a burette with constant shaking, until a permanent violet colour persisted on shaking for ½ min. The method is general for 1 : 4-quinones and an accuracy of 1% or better is readily obtained, provided high local concentrations of reagent, which slowly attacks the quinones, are avoided. 1 : 2-Quinols cannot generally be estimated by this method as the quinones readily undergo further oxidation, but with 9 : 10-dihydroxyphenanthrene it was just possible to obtain a " flash " end-point.

(*c*) These titrations were performed as described in method (*a*) except that ceric ammonium sulphate was used as the back-oxidant. When the first end-point was reached, sodium diphenylaminesulphonate indicator and acetic acid (2 ml.) were added and the titration was continued as in method (*b*). The difference between the two titres should be equivalent to the initial concentration of the quinone provided quinol and naphthalene are the only reaction products.

Individual Runs.—One or more representative runs are recorded below for each quinone, so as to illustrate the procedures selected in different cases, the accuracies attained, and the various types of deviations from second-order kinetics which are encountered. Concentrations of quinone (*a*) and hydrocarbons (*b*) are 0·1M unless otherwise stated. x = ml. of reagent. Second-order rate constants k are given in l. mole^{-1} min.$^{-1}$; the values differ from those in the Tables which are in different units. The precision index employed is the standard deviation of the mean.

(i) Benzoquinone in phenetole at 100°.
Method 1*b*. $[Ce^{4+}]$ = 0·0452N.

t (min.)	118	180	287	396	427	1458
x	0·35	0·51	0·76	0·96	1·06	2·29
10^2k	0·727	0·722	0·722	0·700	7·35	0·735

$$10^2k = 0{\cdot}723 \pm 0{\cdot}005$$

(ii)—(iv) Benzoquinone in phenetole at 100°.

a	0·050	0·100	0·200
b	0·100	0·050	0·100
10^2k	0·701 ± 0·013	0·710 ± 0·008	0·705 ± 0·010

(v) Benzoquinone in phenetole at 131°.

Method 1*c*. 2 ml. of 0·0995N-$\mathrm{TiCl_3}$ back-titrated with 0·0467N-Ce^{4+}. x' refers to the second end-point.

t (min.)	0	27·6	43·6	68·5	112	143	182	224	301	680	2650
x	0·02	0·60	0·76	1·05	1·54	1·78	2·04	2·29	2·62	3·37	4·12
x'	4·31	4·82	5·04	5·31	5·82	6·03	6·35	6·60	6·86	7·61	8·32
$x' - x$	4·29	4·22	4·28	4·26	4·28	4·25	4·31	4·31	4·24	4·24	4·20
Reaction (%)	—	11·9	17·3	23·3	35·2	40·1	47·5	53·4	59·5	77·0	93·5
10^2k	—	4·90	4·74	4·44	4·85	4·68	4·98	5·10	4·87	4·90	—

10^2k = 4·83 ± 0·07

(vi) Toluquinone in phenetole at 131°.

Method 1*b*. $[\mathrm{Ce}^{4+}]$ = 0·0445N.

t (min.)	77	96	120	161	214	295	309	410	1358
x	0·58	0·70	0·85	1·09	1·31	1·66	1·70	2·02	3·29
10^2k	1·93	1·92	1·94	1·98	1·92	1·99	1·97	1·99	2·00

10^2k = 1·96 ± 0·02

(vii) Chloro-1 : 4-benzoquinone in phenetole at 90·0°.

Method 1*b*. $[\mathrm{Ce}^{4+}]$ = 0·0465N.

t (min.)	64·5	146	210	310	447	537	754
x	0·37	0·74	0·98	1·31	1·70	1·85	2·22
10^2k	1·46	1·42	1·41	1·41	1·46	1·41	1·43

10^2k = 1·42 ± 0·01

(viii) 2 : 6-Dichloro-1 : 4-benzoquinone in phenetole at 119°.

Method 1*b*. $[\mathrm{Ce}^{4+}]$ = 0·0465N. This run illustrates the marked deviations from second-order kinetics observed with this quinone.

t (min.)	9	19	30	52	65	122
x	0·60	1·14	1·42	1·80	1·98	2·43
10^2k	23·9	19·0	16·5	13·9	13·1	10·7

(ix) 2 : 6-Dichloro-1 : 4-benzoquinone in phenetole at 80·2°.

Method 1*b*. $[\mathrm{Ce}^{4+}]$ = 0·0465N. This run illustrates that second-order kinetics are observed with this quinone during the first 10% of the reaction (cf. previous run).

t (min.)	19	25	30	35	40	46	52	59
x	0·14	0·18	0·22	0·25	0·29	0·32	0·37	0·39
10^2k	1·77	1·75	1·80	1·77	1·81	1·75	1·81	1·70

10^2k = 1·79 ± 0·02 (up to 52 min.)

(x) Trichloro-1 : 4-benzoquinone in phenetole at 69·8°.

Method 1*b*. $[\mathrm{Ce}^{4+}]$ = 0·0465N.

t (min.)	17	34	54	78	100	126	158	221
x	0·06	0·125	0·17	0·265	0·34	0·41	0·49	0·61
10^2k	0·833	0·880	0·762	0·842	0·860	0·877	0·815	0·750

10^2k = 0·837 ± 0·030 (up to 158 min.)

(xi) Tetrachloro-1 : 4-benzoquinone in phenetole at 100·5°.

Method 1*b*. $[\mathrm{Ce}^{4+}]$ = 0·0455N.

t (min.)	66·5	85	111	122	144·5	178	250
x	1·82	2·05	2·31	2·45	2·68	2·84	3·15
10^2k	10·03	10·03	10·00	10·03	10·08	10·03	10·02

10^2k = 10·03 ± 0·01

(xii) 2 : 6-Dimethyl-1 : 4-benzoquinone in phenetole at 154·5°.

Method 2*b*. $[\mathrm{Ce}^{4+}]$ = 0·0484N. This run illustrates the upward drift in k due to product catalysis.

t (min.)	46	94	126	153	212	264	330	370
x	0·505	1·00	1·23	1·44	1·83	2·09	2·37	2·53
10^2k	3·03	3·40	3·37	3·50	3·76	3·88	4·08	4·27

10^2k = 3·07 (graphical extrapolation)

(xiii) 2 : 5-Dimethyl-1 : 4-benzoquinone in phenetole at 140·8°.

Method 2*b*. [Ce^{4+}] = 0·0465N. This run illustrates the upward drift in k due to product catalysis.

t (min.)	67	136	228	310	420	505	1522	3208
x	0·24	0·46	0·74	0·94	1·20	1·42	2·85	3·60
10^2k	0·882	0·881	0·913	0·904	0·920	0·975	1·32	1·61

10^2k = 0·88 (graphical extrapolation)

(xiv) Thymoquinone in phenetole at 100·0°.

Method 2*b*. [Ce^{4+}] = 0·0484N.

t (min.)	1190	2695	4050	5385	6805	8220
x	0·18	0·40	0·62	0·84	1·05	1·25
10^2k	0·0383	0·0398	0·0437	0·0474	0·0500	0·0528

10^2k = 0·038 (graphical extrapolation)

(xv) Thymoquinone in phenetole at 154°.

Method 2*b*. [Ce^{4+}] = 0·0484N. Comparison with run (xiv) illustrates the decrease in product catalysis with increasing temperature.

t (min.)	80	162	240	301	399
x	0·49	0·85	1·25	1·47	1·79
10^2k	1·68	1·62	1·82	1·84	1·92

(xvi) Thymoquinone in phenetole at 154°. Concentration of reactants, 0·2M.

Method 2*b*. [Ce^{4+}] = 0·0484N. Comparison with run (xv) illustrates the increase with reagent concentration of the upward drift due to product catalysis. α is defined by the equation $k_2 = (1/\alpha t) \ln [a(a - x - \alpha)/(a + \alpha)(x - a)]$ (see p. 3550) which is clearly not obeyed.

t (min.)	80	162	240	301	399
x	1·77	3·10	4·10	4·66	5·36
10^2k	1·70	1·86	2·06	2·16	2·32
α	0·17	2·0	2·4	2·5	2·9

(xvii) Thymoquinone in nitrobenzene at 155·5°.

Method 2*b*. [Ce^{4+}] = 0·0465N. In this solvent product catalysis is absent, at least over the first half of the reaction.

t (min.)	40	63	80	100	120	182	333
x	0·52	0·70	0·89	1·05	1·20	1·59	2·24
10^2k	3·44	3·09	3·27	3·23	3·23	3·22	3·27

$10^2k = 3·25 \pm 0·04$

(xviii) Thymoquinone in 0·120M-thymoquinol in phenetole at 155·0°.

Method 2*b*. [Ce^{4+}] = 0·0484N.

t (min.)	0	43	75	134	182	249
x	4·96	5·45	5·86	6·30	6·67	7·07
10^2k	3·14	3·72	3·60	3·69	3·90	4·20

10^2k = 3·30 (graphical extrapolation)

(xix) Thymoquinone in 0·058M-*p*-nitrophenol in phenetole at 155°.

Method 2*b*. [Ce^{4+}] = 0·0465N.

t (min.)	15	30	60	90	105	120	135	210
x	0·28	0·48	0·79	1·08	1·17	1·29	1·39	1·70
10^2k	3·60	3·81	3·71	3·72	3·74	3·74	3·74	3·37

$10^2k = 3·68 \pm 0·05$

(xx) Thymoquinone in 0·058M-*p*-nitroanisole in phenetole at 155·4°.

Method 2*b*. [Ce^{4+}] = 0·0465N.

t (min.)	76	118	134	183	235	275	348
x	0·52	0·77	0·86	1·09	1·34	1·50	1·78
10^2k	1·81	1·85	1·87	1·85	1·93	1·96	2·08

10^2k = 1·75 (graphical extrapolation)

(xxi) Thymoquinone in 0·058M-picric acid in phenetole at 155·0°.

Method 2*b*. $[Ce^{4+}]$ = 0·0465N.

t (min.)	11	29	63	135	249	382
x	0·10	0·21	0·40	0·60	0·75	0·80
10^2k	2·16	1·96	1·63	1·20	0·85	0·60

10^2k = 2·2 (graphical extrapolation)

(xxii) Thymoquinone in phenetole containing 0·0045M-benzoyl peroxide at 154·6°.

Method 2*b*. $[Ce^{4+}]$ = 0·0484N.

t (min.)	116	140	178	243	337
x	0·66	0·80	0·96	1·25	1·57
10^2k	1·64	1·72	1·71	1·79	1·83

10^2k = 1·60 (graphical extrapolation)

(xxiii) Thymoquinone in propionic acid at 141·1°.

Method 2*b*. $[Ce^{4+}]$ = 0·0465N.

t (min.)	30	42	70	90	120	165	210	255	391	468
x	0·23	0·32	0·48	0·62	0·78	1·04	1·22	1·49	1·81	1·96
10^2k	1·90	1·92	1·80	1·87	1·85	1·93	1·89	2·08	1·86	1·79

10^2k = 1·90 ± 0·04

(xxiv) Thymoquinone in 90% (v/v) aqueous propionic acid at 141·1°.

Method 2*b*. $[Ce^{4+}]$ = 0·0465N.

t (min.)	20	40	125	173	240	290
x	0·24	0·45	1·16	1·31	1·89	2·08
10^2k	2·96	2·92	2·96	3·13	3·27	3·23

10^2k = 3·09 ± 0·07

(xxv) Thymoquinone in 0·07M-perchloric acid in propionic acid at *ca.* 23·4°.

Method 2*b*. $[Ce^{4+}]$ = 0·0465N.

t (min.)	117	262	395	1380
x	0·26	0·38	0·45	0·57
10^2k	0·55	0·37	0·30	0·11

(xxvi) Thymoquinone and 9 : 10-dihydroanthracene in propionic acid at 141·0°.

Method 2*b*. $[Ce^{4+}]$ = 0·0465N.

t (min.)	120	209	337	424	956	1053	1170	1292
x	0·28	0·47	0·79	0·95	1·82	1·89	1·92	2·12
10^2k	0·581	0·589	0·569	0·670	0·760	0·745	0·690	0·752

10^2k = 0·58 (graphical extrapolation)

(xxvii) Thymoquinone and 9 : 10-dihydroanthracene in propionic acid containing trichloroacetic acid (1·0M) at 141·0°.

Method 2*b*. $[Ce^{4+}]$ = 0·0465N.

t (min.)	45	77	156	219	285
x	0·25	0·40	0·75	1·04	1·24
10^2k	1·37	1·34	1·36	1·45	1·42

10^2k = 1·36 (graphical extrapolation)

(xxviii) 1 : 4-Naphthaquinone in phenetole at 132·0°.

Method 2*b*. $[Ce^{4+}]$ = 0·0484N.

t (min.)	150	322	388	940	1400	3140	5250
x	0·06	0·12	0·145	0·40	0·61	0·89	1·11
10^2k	0·099	0·094	0·097	0·114	0·123	0·088	0·070

Further readings were impossible as the end-point was obscured by a coloured by-product.

(xxix) Isomerisation of 1 : 4-dihydroxynaphthalene (0·05M) in phenetole at 131°. Method 2*b*. [Ce^{4+}] = 0·0439N.

t (min.)	0	990	1800	7550
x	2·28	1·79	1·68	1·70

(xxx) 1 : 2-Naphthaquinone in phenetole at 99·8°

Method 2*a*. 3 Ml. of 0·0804N-TiCl$_3$ back-titrated with 0·0552N-Fe^{3+}

t (min.)	0	61	89	152	214	283	314
x	0·73	1·61	2·01	2·69	3·25	3·70	3·76
10^2k	—	5·20	6·04	7·65	8·70	11·5	16·2

(xxxi) 1 : 2-Naphthaquinone in phenetole at 70·0°

Method 2*a*. 3 Ml. of 0·0723N-TiCl$_3$ back-titrated with 0·0545N-Fe^{3+}

t (min.)	0	62	80	100	121	140	180
x	0·30	0·57	0·64	0·74	0·80	0·91	1·09
10^2k	—	1·26	1·24	1·34	1·29	1·42	1·51

10^2k = 1·26 (graphical extrapolation)

(xxxii) 9 : 10-Phenanthraquinone in phenetole at 122·0°.

Method 2*b* (flash end-point). [Ce^{4+}] = 0·0484N.

t (min.)	33	60	114	200	248	309	360
x	0·22	0·41	0·84	1·55	1·84	2·16	2·40
10^2k	1·71	1·83	2·24	3·00	3·24	3·56	3·86

(xxxiii) 9 : 10-Phenanthraquinone in phenetole at 99·6°.

Method 2*b* (flash end-point). [Ce^{4+}] = 0·0484N.

t (min.)	80	106	121	151	180	214
x	0·14	0·17	0·22	0·28	0·33	0·39
10^2k	0·439	0·405	0·465	0·464	0·483	0·489

10^2k = 0·422 (graphical extrapolation)

Arrhenius energies of activation E_A were calculated by the method of least squares; they are estimated to be accurate to ±0·1—0·4 kcal. in most cases, but with 1 : 2-naphthaquinone and 9 : 10-phenanthraquinone the spread of individual values was somewhat greater. Entropies of activation $\Delta S^‡$ were calculated from the equation $\log k = \log (e\boldsymbol{R}T/\boldsymbol{N}h) - E_A/2{\cdot}3\boldsymbol{R}T + \Delta S^‡/2{\cdot}3\boldsymbol{R}$, E_A being expressed in cal./mole, and free energies of activation from $\log k = \log (\boldsymbol{R}T/\boldsymbol{N}h) - \Delta G^‡/2{\cdot}3\boldsymbol{R}$.

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