

**623. Hydrogen Transfer. Part XI.\* The Dehydrogenation of Hydroaromatic Hydrocarbons by Quinones: The Effect of Quinone Shape.**

By (the late) E. A. BRAUDE, L. M. JACKMAN, R. P. LINSTEAD, and J. S. SHANNON.

The kinetics of the reactions of 1,2- and 1,4-dihydronaphthalenes with tetrachloro-1,2-benzoquinone, chloranil, and 3,3',5,5'-tetrachloro-4,4'-diphenoquinone have been studied and the Arrhenius parameters determined. The results allow a further refinement of the two-step ionic mechanism put forward in preceding papers.

In earlier papers<sup>1,2</sup> in this series a one-step concerted process was considered as a possible mechanism for the hydrogen transfer from hydroaromatic compounds to quinones, the two hydrogen atoms being transferred directly and simultaneously to the quinone oxygen atoms. It was suggested at the time that a crucial test for this mechanism lay in the relation of the rate of reaction to the relative internuclear separations of the two hydrogen atoms undergoing transfer and the two quinone oxygen atoms. An insensitivity to such steric considerations would vitiate the concerted mechanism. The preliminary results obtained in Part III<sup>2</sup> for the two hydrocarbons 1,2- and 1,4-dihydronaphthalenes against 1,4-benzoquinone and 1,2-naphthoquinone strongly indicated a lack of steric dependence. We now report a more detailed study which confirms our earlier findings and makes the concerted mechanism appear unlikely.

Three quinones have been used in this investigation, *viz.*, tetrachloro-1,2-benzoquinone, chloranil (tetrachloro-1,4-benzoquinone), and 3,3',5,5'-tetrachloro-4,4'-diphenoquinone. These provide adequate variation in O-O separation, the approximate values being 3.5, 5, and 8 Å, respectively. The unsubstituted quinones were not suitable for a kinetic investigation as, with the exception of 1,4-benzoquinone, they were too unstable. The two hydrocarbons used were 1,2- and 1,4-dihydronaphthalene in which the internuclear separations of the two transferable hydrogen atoms are 2.1 and 3.2 Å, respectively. Preparative experiments were carried out for all six combinations and the expected stoichiometry was found in each case.

The titrimetric methods developed in Part III<sup>1</sup> for studying the kinetics of similar reactions could not be used in the present experiments owing to the intense colour of tetrachloro-1,2-benzoquinone and the lability of the tetrachlorodiphenoquinone in acid. The kinetics could, however, be studied by following spectroscopically the disappearance of quinone, under suitable conditions, and two general techniques were developed. In the first, aliquot parts of the reaction mixture were removed, and diluted if necessary, and the concentrations were determined spectroscopically in the usual way. In the second,<sup>3</sup> which was the more convenient, the reactions were carried out in the actual absorption cell mounted in a specially designed thermostatic cell compartment. Comparable experiments by both methods gave a most satisfactory agreement.

The reactions with tetrachloro-1,2-benzoquinone were more or less straightforward. Phenetole was used as a solvent and introduced a minor complication in that the quinone underwent a slow thermal decomposition. However, by adjusting the hydrocarbon concentrations it was possible to render the decomposition reaction negligible.

The chloranil-1,4-dihydronaphthalene system proved more complicated. Although preparative experiments yielded 96% of the quinol and *ca.* 95% of naphthalene, preliminary experiments in phenetole with equimolecular concentrations of the two reactants revealed an intensely coloured by-product (Fig. 1). Even though present in as little as 1–2% this by-product, by virtue of its intense colour, caused large downward drifts in the second-

\* Part X, preceding paper.

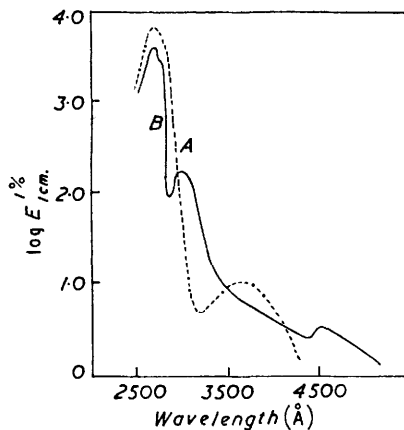
<sup>1</sup> Braude, Jackman, and Linstead, *J.*, 1954, 3548.

<sup>2</sup> Braude, Jackman, and Linstead, 1954, 3564.

<sup>3</sup> Cf. Barany, Braude, and Coles, *J.*, 1951, 2093.

order rate constants. In the hope that the by-product was formed from the quinone subsequently to the dehydrogenation, the reaction was made pseudounimolecular by using a hundred-fold excess of 1,4-dihydronaphthalene. This was successful in that the coloured compound was no longer produced. However the pseudounimolecular system failed to give satisfactory results, the first-order rate constants always exhibiting large irreproducible upward drifts, and extrapolation to zero time gave values which were erratic and often as much as twice the value found in Part II.<sup>1</sup> The cause of this behaviour was traced to the incorporation of significant concentrations of oxygen resulting from the use of a large excess of hydrocarbon. Liquid 1,4-dihydronaphthalene appears to dissolve appreciable quantities of oxygen as it releases gas noticeably on solidification or evacuation. It is known that a number of aromatic compounds form charge-transfer complexes with oxygen<sup>4,5</sup> and the inference is that 1,4-dihydronaphthalene is another example. Numerous experiments showed that oxygen was responsible for the observed high rate constants. Further, it was found that tetrachloroquinol in the presence of oxygen (but not in its

FIG. 1. Spectrum of (A) chloranil in ethyl acetate containing 2% of phenetole, and of (B) the solution (diluted with ethyl acetate) resulting from a kinetic experiment with 1,4-dihydronaphthalene and chloranil in phenetole.



absence) markedly enhanced the catalytic effect of the latter and the upward drift observed in the pseudounimolecular reactions may be attributed to the quinol which is formed in increasing concentrations as the reaction proceeds. These experiments are not reported in detail here (only a representative sample is given in the Experimental section) since more thorough examination is necessary for a rational interpretation.

Eventually a compromise was effected between formation of the coloured by-product and catalysis by oxygen. By working with 0.1M-quinone and 0.3M-hydrocarbon the downward drift due to the coloured by-product was sufficiently suppressed to permit reasonably accurate extrapolations to zero time and under these conditions the presence or absence of oxygen in the hydrocarbon did not alter the rate of reaction. The rate constants thus obtained were in reasonable agreement with those recorded in Part II.<sup>1</sup> A similar problem was encountered in the reaction of chloranil with 1,2-dihydronaphthalene. Here it was necessary to use a 1 : 5 ratio of quinone to hydrocarbon and when this was done oxygen catalysis did not occur.

Tetrachlorodiphenoquinone proved to be only sparingly soluble in phenetole and  $5 \times 10^{-4}$ M-concentrations had to be used. As a result it was impossible to purify phenetole sufficiently to yield reproducible kinetics. It was therefore necessary to use chlorobenzene as a solvent: when freshly purified this gave thermally stable solutions of the quinone. As the solvent effect in this type of reaction is small<sup>1</sup> and as we were primarily interested in comparing the rate ratios for the two hydrocarbons it is likely that the change in solvent is not critical. In chlorobenzene the tetrachlorodiphenoquinone gave satisfactory kinetics

<sup>4</sup> Evans, J., 1953, 345.

<sup>5</sup> Orgel, *Quart. Rev.*, 1954, 8, 422.

for both hydrocarbons and at the concentrations of hydrocarbons used (2:1) oxygen-catalysis was not observed.

#### EXPERIMENTAL

*Materials.*—The preparation and purification of 1,4- and 1,2-dihydronaphthalene, chloranil, and phenetole have been described in Parts II<sup>1</sup> and III.<sup>2</sup> Tetrachloro-1,2-benzoquinone was prepared by Brook's method<sup>6</sup> and purified (to m. p. 133°) by sublimation or repeated recrystallisation from light petroleum (b. p. 80—100°).

3,3',5,5'-Tetrachloro-4,4'-diphenoquinone was prepared from the quinol by oxidation with nitric acid<sup>7</sup> and could be recrystallised from chlorobenzene although the initial oxidation product was in fact spectroscopically identical with the recrystallised material.

Chlorobenzene was purified by drying (CaCl<sub>2</sub>) and distillation.

*Preparative Experiments.*—A trial to establish the recovery of naphthalene from phenetole was carried out. A solution of naphthalene (3 g.) in phenetole (5 ml.) was fractionated through a 6" Stedman column to remove the phenetole as completely as possible. The column was rinsed with a little alcohol, and the washings were added to the distillation residue which was then made up to 20 ml. with alcohol. Picric acid (5.3 g.) was added and the mixture warmed until dissolution was complete. On cooling, naphthalene picrate (7.5 g., 87%), m. p. 146—149°, separated. One recrystallisation from ethanol gave the pure picrate (6.75 g., 78.5%), m. p. 150°.

*Tetrachloro-1,2-benzoquinone-1,4-Dihydronaphthalene.*—The quinone (5.7 g.) and the hydrocarbon (3.0 g.) were mixed in phenetole. The reaction was strongly exothermic and complete in 2—3 min. The quinol separated on cooling and was removed by filtration. The fine white crystals (5.5 g., 96%), m. p. 193—194°, were washed with light petroleum (b. p. <40°). The combined filtrate and washings were passed through a 5 in. × 1 cm. alumina column and eluted with more light petroleum. The light petroleum was removed by distillation, and the naphthalene recovered as its picrate from the phenetole by the above procedure. The crude picrate (7 g., 84%) had m. p. 145—148°, and on crystallisation from ethanol gave the pure compound (5.6 g., 67.2%), m. p. 150°.

*Tetrachloro-1,2-benzoquinone-1,2-Dihydronaphthalene.*—The quinone (5.5 g.) and hydrocarbon (2.9 g.) in phenetole (5 ml.) were heated at 100° for 5 min. and worked up as above. The reaction yielded the quinol (5.2 g., 94%), m. p. 193—194°, and picrate [6.9 g., 83% (crude); 5.9 g., 71% (pure)], m. p. 144—148° (crude), 150° (pure).

*Chloranil-1,4-Dihydronaphthalene.*—The quinone (5.7 g.) and hydrocarbon (3.0 g.) in phenetole (5 ml.) were heated at 100° for 1 hr. and worked up in the usual way, to give the quinol (5.4 g., 95%), m. p. 230°, and naphthalene picrate [6.5 g., 81% (crude); 5.85 g., 73% (pure)], m. p. 144—147° (crude), 150° (pure).

*Chloranil-1,2-Dihydronaphthalene.*—In the same quantities and under conditions as in the preceding experiment, this pair yield quinol (5.5 g., 96%), m. p. 230—231°, and picrate [6.6 g., 83% (crude); 5.6 g., 71% (pure)], m. p. 145—148° (crude), 150° (pure).

3,3',5,5'-Tetrachloro-4,4'-diphenoquinone-1,4-Dihydronaphthalene.—The quinone (3.2 g.) and hydrocarbon (1.3 g.) were refluxed for 5 min. in boiling chlorobenzene (15 ml.) during which the colour of the quinone disappeared. On cooling, the quinol separated and was recovered (3.0 g., 94%; m. p. 228—230°) by filtration and washing with light petroleum (b. p. <40°). The combined filtrate and washings were fractionated through a 6 in. helical column. After the removal of the chlorobenzene and cooling, the residue solidified (1.2 g.) and had m. p. 70—75°,  $\lambda_{\max}$  2750 Å ( $E_{1\text{cm}}^{1\%}$  416 in EtOH), which represented 95% of naphthalene and a corresponding overall yield of 87%.

3,3',5,5'-Tetrachloro-4,4'-diphenoquinone-1,2-Dihydronaphthalene.—The quinone (4.0 g.) and hydrocarbon (1.6 g.) were refluxed for 5 min. in chlorobenzene (15 ml.), and working up as in the preceding experiment gave the quinol (3.7 g., 92%), m. p. 228—230°, and crude naphthalene (1.4 g.), m. p. 60—70°. The light absorption in ethanol ( $\lambda_{\max}$  2750 Å;  $E_{1\text{cm}}^{1\%}$  415) of the naphthalene corresponded to an overall yield of 84%.

*Kinetic Methods.*—(a) The reactions were carried out in vessels described in Part II (method 1).<sup>1</sup> The rates of reaction were followed by determining spectroscopically the concentration of quinone at appropriate time intervals. The spectroscopic measurements were

<sup>6</sup> Brook, *J.*, 1952, 5040.

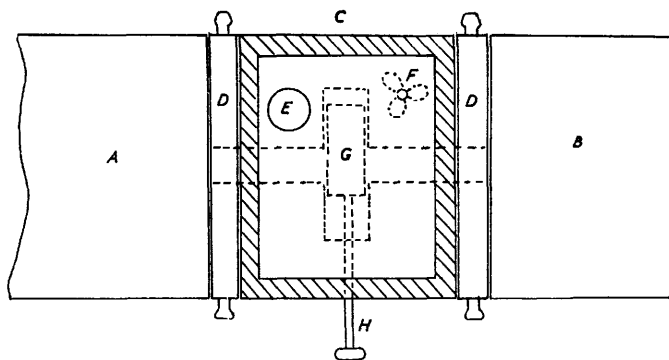
<sup>7</sup> Magatti, *Ber.*, 1880, 13, 227.

made at a suitable point on the long-wavelength bands of the quinones. For this purpose aliquot parts were withdrawn and diluted to a known volume if necessary.

(b) In method (b) the reactions were carried out directly in a thermostatic spectroscopic cell. For this purpose a self-contained thermostat-controlled cell compartment was designed for use with a Beckman D.U. spectrophotometer and a Unicam S.P. 500. The general lay-out is shown diagrammatically in Fig. 2. The cell compartment was fitted between the monochromator (A) and the photocell housing (B). Heat-insulation was provided for by the sindanyo plates (C), and the instrument itself was further protected by the water jackets (D). The free space of the thermostat was filled with oil which was electrically heated. Two heaters were employed; one being controlled by a contact thermometer thermoregulator (E) and a Sunvic E.A.3. relay, the other by a booster heater manually adjusted by means of a Variac. Uniformity of heating was ensured by an efficient belt-driven stirrer (F). The cell carriage (G) was of the conventional type and manipulated by a push-rod (H).

This apparatus could be conveniently used in the range 45–120°. It was necessary to adjust the flow of water through the jackets D such that the effluent temperature was somewhat above room temperature, otherwise condensation occurred and, in the case of the Beckman D.U. spectrophotometer, caused instrumental instability.

FIG. 2. Thermostatic cell compartment.



After being mounted in the thermostat, the cells and their contents required at least  $\frac{1}{2}$  hr. to reach thermal equilibrium. For this reason it was necessary to fill the reaction cell with a solution of one of the reactants and allow the system to reach the equilibrium temperature. The second reactant was then added either in the solid state by means of a small platinum cup or as a very concentrated solution from a syringe fitted with an "Aglá" micrometer. Even so the addition of the second component caused a fall in temperature of as much as 4°. In practice it was found that this temperature drop could be accurately anticipated and largely overcome by initially setting the thermostat at the appropriate value above the desired temperature. The thermostat was re-adjusted immediately after the addition and mixing of the second reactant. The error thus introduced was negligible. The actual temperature for a given run was determined directly on the solution at the end of the experiment as there was a significant lag between the thermostat and the cell.

*Results of Chloranil Experiments.*—Unless otherwise stated rate constants are given in  $l. \text{ mole}^{-1} \text{ min.}^{-1}$ .

(1) Chloranil (0.100M)—1,4-dihydronaphthalene (0.100M) in phenetole at 110° [method (a)]. This experiment illustrates the downward drift caused by coloured by-product formation.

$t$ (min.)	0	54	70	181	223	394	2000
$E$ (3640 Å)	0.554	0.460	0.434	0.396	0.383	0.360	0.610
$10^3k$	—	37.8	39.5	22.0	20.0	13.6	—

(2) Chloranil (0.10M)—1,4-dihydronaphthalene (1.00M) in phenetole at 60.9° [method (a)]. This and the succeeding run (3) show the form and irreproducibility caused by oxygen incorporated by a large excess of hydrocarbon. The uncatalysed rate constant obtained later is  $10^3k = 0.50$ .

$t$ (min.) .....	0	6	20	27	35	44
$E$ (4400 Å) .....	0.720	0.672	0.518	0.449	0.356	0.232
$10^2k$ .....	—	1.13	1.64	1.74	1.98	3.3

(3) As in (2)

$t$ (min.) .....	6.7	13.7	21.3	45	53.3	59
$E$ (4400 Å) .....	0.896	0.814	0.746	0.489	0.321	0.192
$10^2k$ .....	—	1.36	1.25	1.58	2.28	2.95

(4) As in (2) and (3) except that tetrachloroquinol (0.010M) was added initially.

$t$ (min.) .....	6.0	14.0	22.0	29.0	33.0
$E$ (4400 Å) .....	0.768	0.519	0.303	0.143	0.072
$10^2k$ .....	—	4.91	5.81	7.31	8.75

(5) Chloranil (0.010M)-1,4-dihydronaphthalene (1.00M) in phenetole at 60.9° [method (a)]. In this experiment the solution of the hydrocarbon was refluxed "in vacuo" for  $\frac{1}{2}$  min. to remove dissolved gases. Nitrogen was then admitted and the quinone added.

$t$ (min.) .....	3.5	15.6	27.0	42	90.0	110	190
$E$ (4400 Å) .....	0.960	0.899	0.853	0.790	0.623	0.571	0.420
$10^2k$ .....	—	0.53	0.50	0.51	0.50	0.49	0.44

(6) As in (5) except that oxygen was admitted instead of nitrogen.

$t$ (min.) .....	3.5	15.6	55	85	109	132
$E$ (4400 Å) .....	0.942	0.876	0.610	0.379	0.260	0.192
$10^2k$ .....	—	0.68	0.84	1.12	1.22	1.24

(7) As in (5) except that tetrachloroquinol (0.010M) was added.

$t$ (min.) .....	3.5	15.6	30	45	85	105	155
$E$ (4400 Å) .....	0.934	0.826	0.707	0.596	0.386	0.323	0.234
$10^2k$ .....	—	1.03	1.05	1.09	1.09	1.05	0.91

(8) Chloranil (0.100M)-1,4-dihydronaphthalene (0.309M) in phenetole at 95° [method (a)]. This is representative of the experiments from which the extrapolated rate constants recorded in Table I were obtained.

$t$ (min.) .....	0	4	7.7	12.5	18	28	82
$E$ (5920 Å) .....	0.842	0.775	0.729	0.670	0.618	0.530	0.395
$10^2k$ .....	—	6.85	6.20	6.09	5.81	5.75	3.86

(9) Chloranil (0.100M)-1,2-dihydronaphthalene (0.500M) in phenetole at 145° [method (a)]. A representative run with 1,2-isomer from which the extrapolated values of  $k$  were obtained.

$t$ (min.) .....	0	15	21	30	45	65	90	125
$E$ (6150 Å) .....	0.780	0.692	0.678	0.608	0.542	0.478	0.434	0.384
$10^2k$ .....	—	1.60	1.40	1.70	1.67	1.58	1.37	1.21

Results of Experiments with Tetrachloro-1,2-benzoquinone and 3,3',5,5'-Tetrachloro-4,4'-diphenoquinone.—(10) Tetrachloro-1,2-benzoquinone (0.0102M)-1,4-dihydronaphthalene (0.0102M) in phenetole at 60.2° [method (a)].

$t$ (min.) .....	0	8	13	20	30	45	1600
$E$ (5400 Å) .....	0.880	0.490	0.390	0.300	0.223	0.157	0.014
$k$ .....	—	9.75	9.46	9.47	9.61	9.80	—

(11) As in (10) but method (b).

$t$ (min.) .....	0	3	7	10	15	30	45	1000
$E$ (6050 Å) .....	1.050	0.814	0.633	0.540	0.434	0.271	0.197	0.016
$k$ .....	—	9.63	9.40	9.45	9.46	9.55	9.60	—

(12) Tetrachloro-1,2-benzoquinone (0.0100M)-1,2-dihydronaphthalene (0.0500M) in phenetole at 50° [method (a)].

$t$ (min.) .....	0	30	71	121	182	233	300	1600
$E$ (5400 Å) .....	0.862	0.740	0.610	0.472	0.363	0.274	0.224	0.014
$k$ .....	—	0.101	0.100	0.105	0.102	0.107	1.00	—

(13) 3,3',5,5' - Tetrachloro - 4,4' - diphenoquinone ( $5.00 \times 10^{-4}M$ ) - 1,4 - dihydronaphthalene ( $5.00 \times 10^{-4}M$ ) in chlorobenzene at 100° [method (b)]. In all experiments with this quinone it was necessary to redistil the solvent just before use.

<i>t</i> (min.) .....	0	12	25	35	80	112	150	220
<i>E</i> (5020 Å) .....	0.890	0.784	0.697	0.645	0.477	0.396	0.336	0.264
<i>k</i> .....	—	22.7	22.1	21.8	21.5	22.3	22.0	21.5

(14) 3,3',5,5' - Tetrachloro - 4,4' - diphenoquinone ( $5.00 \times 10^{-4}M$ ) - 1,2 - dihydronaphthalene ( $10.0 \times 10^{-4}M$ ) in chlorobenzene at 100°.

$10^{-2}t$ (min.) .....	0	2	4	7	11	17
<i>E</i> (5000 Å) .....	1.000	0.874	0.773	0.646	0.517	0.380
<i>k</i> .....	—	0.702	0.681	0.689	0.696	0.702

Arrhenius Parameters.—Table 1 lists *k*-*T* data for the six systems studied. From these the Arrhenius parameters were computed by the method of least squares. Standard deviations have been calculated from the following formulæ relating to an equation  $y = a + bx$ :

$$\sigma_a = s\sqrt{\sum x^2/D}; \quad \sigma_b = s\sqrt{n/D}; \quad \sigma_y = s\sqrt{\sum(x - x_0)^2/D}$$

where  $s = \sqrt{\frac{(y_{\text{obs.}} - y_{\text{calc.}})^2}{n - 2}}$ ;  $D = n\sum x^2 - (\sum x)^2$ .

Table 2 gives  $\ln A$ ,  $E_A$ , and  $k_{100^\circ}$  for the six systems.

TABLE 1. Data <sup>a</sup> for the dehydrogenation of 1,4-dihydronaphthalene (1,4-DHN) and 1,2-dihydronaphthalene (1,2-DHN) by quinones.

Tetrachloro-1,2-benzoquinone				Chloranil				Tetrachlorodiphenoquinone			
1,4-DHN <sup>b</sup>		1,2-DHN		1,4-DHN <sup>c</sup>		1,2-DHN <sup>c</sup>		1,4-DHN		1,2-DHN	
Temp. (K)	10 <sup>3</sup> <i>k</i>	Temp. (K)	10 <sup>3</sup> <i>k</i>	Temp. (K)	10 <sup>4</sup> <i>k</i>	Temp. (K)	10 <sup>4</sup> <i>k</i>	Temp. (K)	10 <sup>3</sup> <i>k</i>	Temp. (K)	10 <sup>3</sup> <i>k</i>
273°	0.228	318°	1.18	353°	4.27	408°	1.35	353°	0.86	373°	1.16
314.4	4.43	323	1.68	358	5.75	413	1.90	358	1.22	378	1.59
323.3	8.63	328	2.40	363	8.50	418	2.65	363	1.73	383	2.38
333	15.9	333	3.40	368	13.0	423	3.57	378	3.63	388	3.35
353	45.3	338	4.93	373	17.75	428	5.05	383	6.33	343	4.65

<sup>a</sup> *k* in l. mole<sup>-1</sup> sec.<sup>-1</sup>. <sup>b</sup> A further five results were obtained in this range and were subsequently used in the calculation of  $E^\ddagger$ . <sup>c</sup> Extrapolated data.

TABLE 2. Arrhenius parameters and  $k_{100^\circ}$ .

System	$k_{100^\circ}$ (l. mole <sup>-1</sup> sec. <sup>-1</sup> )	$\ln A$	$E_A$ (kcal. mole <sup>-1</sup> )
Tetrachlo-1,2-benzoquinone-1,4-DHN	1.18 ± 0.06	17.3 ± 0.2	12.8 ± 0.15
1,2-DHN	4.06 (± 0.17) × 10 <sup>-2</sup>	17.3 ± 0.35	15.3 ± 0.2
Chloranil-1,4-DHN	1.78 (± 0.06) × 10 <sup>-3</sup>	19.5 ± 1.0	19.3 ± 0.7
1,2-DHN	9.80 (± 0.65) × 10 <sup>-6</sup>	19.1 ± 0.4	22.8 ± 0.3
Tetrachlorodiphenoquinone-1,4-DHN	3.44 (± 0.25) × 10 <sup>-1</sup>	23.4 ± 0.6	18.3 ± 0.35
1,2-DHN	1.14 (± 0.03) × 10 <sup>-2</sup>	23.2 ± 0.9	20.7 ± 0.5

DISCUSSION

The relative reactivities of quinones towards 1,4-dihydronaphthalene are conveniently assessed by means of linear free-energy equations relating oxidation potentials to ease of dehydrogenation. In Part II the equation\* (1) was derived for 1,4-quinones where  $\Delta G^\ddagger$  is in

$$\Delta G^\ddagger_{25^\circ} = 38 - 16E^\circ_{25} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

kcal./mole and  $E^\circ_{25}$  in volts. A similar expression (2) can be derived for the 1,2-quinones:

$$\Delta G^\ddagger_{25^\circ} = 34 - 16E^\circ_{25} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

\* The gradient of the equation for 1,4-quinones is 16.0 and not 0.0016 as given in Part II.

Substitution in (2) of the value  $^8 E_{25}^\circ = 0.87$  for tetrachloro-1,2-benzoquinone gives  $k_{25} = 1.4 \times 10^{-2}$  l. mole $^{-1}$  sec. $^{-1}$ , in excellent agreement with the value  $1.6 \times 10^{-2}$  obtained by extrapolation of the  $1/T - \ln k$  curve.

Tetrachloro-1,4-benzoquinone has been discussed in Part II. The experimental data obtained here are in fair agreement with those found by the titrimetric method although there is a discrepancy of 1.0 kcal. mole in the computed activation energies. The activation energy obtained in the present investigation is of low accuracy, the standard deviation being 0.7 kcal.

The value of  $E_{25}^\circ$  for tetrachlorodiphenquinone has not been determined. However, that for the parent quinone<sup>9</sup> is 0.954 v, and if it is assumed that the introduction of four chlorine atoms into the diphenquinone nucleus alters  $\Delta G^\ddagger$  by the same amount as does similar substitution of 1,4-benzoquinone (*viz.*, 1.6 kcal. mole $^{-1}$ ) equation (1) gives  $k_{25} = 2.7 \times 10^{-3}$  which is of the same order as the extrapolated value of  $k_{25} = 0.73 \times 10^{-3}$ .

That tetrachlorodiphenquinone is accommodated by the same  $E^\circ - \Delta G^\ddagger$  relation as for 1,4-quinones strongly suggests that at least for these two types of quinone, a synchronous removal of two hydrogen atoms does not occur. The abnormal reactivity of 1,2-quinones on the other hand might be in part due to synchronisation although, as pointed out previously,<sup>1</sup> hydrogen bonding in the transition state leading to a catechol monoanion can account for this increased reactivity.

A more sensitive test for synchronisation is provided by the relative rates of dehydrogenation of 1,4- and 1,2-dihydronaphthalene by the three quinones (Table 3). These data

TABLE 3. *Relative rates of dehydrogenation of 1,4- and 1,2-dihydronaphthalene at 100°.*

	Tetrachloro- <i>o</i> -benzoquinone	Chloranil	Tetrachlorodiphenquinone
$k(1,4\text{-DHN})/k(1,2\text{-DHN}) \dots$	$29.1 \pm 1.7$	$182 \pm 10$	$30.2 \pm 2.4$

provide strong evidence that even with the 1,2-quinone simultaneous removal of both hydrogen atoms does not occur to a significant extent. Models indicate that the transition state for a one-step process should be most favourable for the reaction of a 1,2-dihydro-system with a 1,2-quinone whereas in practice the 1,2-quinone actually favours the 1,2-dihydro-system to the same extent as does the dipheno-quinone. The 1,2- and the dipheno-quinone show comparable relative reactivities, whereas the 1,4-quinone in accordance with its lower dehydrogenating power is more discriminating.

In the preceding paper attention was drawn to the fact that 1,4- and 1,2-dihydronaphthalene should yield the same ionic intermediate and that the difference in activation energies for the two reactions should therefore be approximately equal to the difference in resonance energies of the two hydrocarbons. The latter quantity, as determined by heats of hydrogenation, is *ca.* 3.0 kcal., which agrees with differences in activation energies determined from the data in Table 2 (*viz.*,  $2.5 \pm 0.3$ ,  $3.5 \pm 0.8$ , and  $2.4 \pm 0.6$ ).

The results recorded in this and other relevant papers in this series are best accommodated by a two-step ionic mechanism in which the intermediate is a  $\sigma$ -complex. There does not appear to be any need to invoke the modified intermediates described in Part III although a knowledge of the exact kinetic significance, if any, of the "second" hydrogen atom must await further experiment.

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

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<sup>8</sup> Fieser and Conant, *J. Amer. Chem. Soc.*, 1924, **46**, 1873.

<sup>9</sup> Fieser, *J. Amer. Chem. Soc.*, 1930, **52**, 4915.