594. *The Retardation of Benzaldehyde Autoxidation. Part V.* The Effects of Some Quinones.*

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A kinetic study has been made of the retarding actions of 15 quinones on the benzoyl peroxide-initiated autoxidation of benzaldehyde. Only quinones of high oxidation–reduction potential are effective retarding agents, but correlations between redox potentials and retarding ability are satisfactory only if applied to substances of similar structural type. Again, the activation energy of the chain-ending process cannot be correlated with the redox potential of the quinone used.

The preceding papers of this series (*J.*, 1952, 2420, 2427, 2432) showed that when 2 : 6 : 1-xylenol was used as a retarder of the autoxidation of benzaldehyde it was slowly oxidised to 3 : 5 : 3′ : 5′-tetramethyl-4 : 4′-diphenoquinone and then converted into 3 : 5 : 3′ : 5′-tetramethyl-4 : 4′-dibenzoyloxydiphenyl by the addition of benzoyl radicals to the oxygen atoms of the quinone. By this final action the quinone acted very effectively as a chain-stopping agent, and it was therefore decided to make a more comprehensive study of this action of quinones.

Though the relative efficacies of substituted phenols in inhibiting the autoxidations of hydrocarbons have been examined extensively in technical laboratories (Egloff, Morrell, Lowry, and Dryer, *Ind. Eng. Chem.*, 1932, **24**, 1375; 1933, **25**, 804; Rosenwald and Hoatson, *ibid.*, 1949, **41**, 914; Rosenwald, Hoatson, and Chenicek, *ibid.*, 1950, **42**, 162; Bolland and ten Have, *Discuss. Faraday Soc.*, 1947, **2**, 252) much less attention has been paid to the inhibiting powers of the quinones which may be derived from them. Milas (*Proc. Nat. Acad. Sci.*, 1929, **15**, 596; *Chem. Reviews*, 1932, **10**, 295) has reported that both *p*-benzoquinone and anthraquinone inhibit the autoxidation of anethole, Täufel and Arens (*Fette und Seifen*, 1944, **51**, 307; *Chem. Abs.*, 1950, **44**, 7567) have compared the efficiencies of a series of quinones in preventing the autoxidation of fats, and several workers have used quinones to inhibit vinyl polymerisation, but only by our previous work was the nature of the chain-stopping reaction made evident.

As the outcome of their studies of the inhibition of ethyl linoleate oxidation by quinols, Bolland and ten Have (*loc. cit.*) concluded that there was a linear relation between the chain-stopping power of a quinol and the oxidation–reduction potential for its reversible oxidation to a quinone, yet Egloff and his colleagues (*loc. cit.*) from the more cursory examination of many more phenols, had decided that a general relation between inhibiting actions and redox potentials of organic compounds could not be established. Dost (*Rec. Trav. chim.*, 1952, **71**, 857), however, concluded that the dehydrogenating powers of quinones were related to their redox potentials. In this connection Lopez Aparicio and Waters (*J.*, 1952, 4666) found that the ease of free-radical addition to the oxygen atoms of quinones could, in part, be correlated with their redox potentials, though steric effects of vicinal substituents were also significant. They pointed out that at most only approximate correlation between the free-radical reactivities of quinones and their redox potentials can be hoped for, since this is an attempt to relate the velocities of the irreversible reactions (1) and (2) with the equilibrium constants of the reversible systems (3) and (4) :

(1) $Ph\cdot CO\cdot + Q \longrightarrow Ph\cdot CO\cdot Q\cdot$ (3) $Q + e + H^+ \rightleftharpoons \cdot QH$

(2) $Ph\cdot CO\cdot + \cdot Q\cdot COPh \longrightarrow Ph\cdot CO\cdot Q\cdot COPh$ (4) $HQ\cdot + e + H^+ \rightleftharpoons H_2Q$

Again, the retarding action of a quinone depends initially on the velocity of reaction (1), which yields a semiquinone radical, whilst the measurement of a redox potential does not discriminate between the consecutive stages (3) and (4) of the reduction process.

Preliminary tests showed that only quinones of high redox potential were effective retarders of the benzoyl peroxide-initiated autoxidation of benzaldehyde, and we have therefore studied quinones of this group, including substituted 4 : 4′-diphenoquinones and

* Part IV, *J.*, 1952, 2432.

4 : 4′-stilbenequinones which (i) have particularly high redox potentials and (ii) are the probable intermediate products from those alkylated monohydric phenols which have been found to be the most effective inhibitors of hydrocarbon autoxidation (compare Cosgrove and Waters, *J.*, 1951, 1726). As Table 1 shows, the alkylated derivatives of *p*-cresol which could on oxidation yield derivatives of 4 : 4′-stilbenequinone, are better inhibitors of autoxidation of cracked "gasoline" than their respective isomers.

TABLE 1. *Relative efficiencies of alkylated phenols as inhibitors of hydrocarbon autoxidation* (based on the data of Rosenwald, Hoatson, and Chenicek, *loc. cit.*).

Substituent groups (OH = 1)	Relative efficiency	Substituent groups (OH = 1)	Relative efficiency	Substituent groups (OH = 1)	Relative efficiency
2-Bu^n, 4-Me	19	6-Bu^t, 2 : 4-Me$_2$	(100)	4-Bu^s, 2-Me	8
2-Bu^i, 4-Me	19	2 : 6-Bu$^t_2$, 4-Me	59	4-Bu^t, 2-Me	13
2-Bu^s, 4-Me	26	4-Bu^n, 2-Me	17	4-Bu^t, 2 : 6-Me$_2$	12
2-Bu^t, 4-Me	42	4-Bu^i, 2-Me	12	2 : 4-Bu$^t_2$, 6-Me	28

Our experimental procedure has been that described in Parts I—III (*locc. cit.*), and since the initial rate of autoxidation was regularly found to be proportional to the benzoyl peroxide concentration of the reaction mixture and to (1/[Quinone] — constant) (see Table 4), where the constant is always very small and often zero, we consider that in all cases the retarding action can be explained by the interventions of reactions (1) and (2) above (see Part II, *J.*, 1952, 2427). The minute constants referred to above would be explicable if traces of some of the quinones were being destroyed by an independent zero-order reaction, and possibly this may be due to an initial trace of perbenzoic acid, or other unidentified impurity in the reaction mixture, for the magnitude of the constant, though not that of the [Quinone]/(Inverse Rate) ratio, did vary with the batch of benzaldehyde used.

The relative retarding powers of the selected quinones have been expressed in col. 2 of Table 2 as the reciprocal of the number of moles of quinone required to reduce to a value of 1 ml. per minute (corrected to N.T.P.) the rate of oxygen uptake at 60° of a 10-ml. sample of benzaldehyde containing 1·5 g. of benzoic acid and 0·05 g. of benzoyl peroxide catalyst.

TABLE 2. *Efficiencies of quinones as retarders of the benzoyl peroxide-catalysed autoxidation of benzaldehyde.*

Quinone	Efficiency (10^4/M)	$\log_{10}$ efficiency	$E_{overall}$ (kcal.)	Redox potential, volt (+)
p-Benzoquinone	4·03 ± 0·14	0·6053	24·5	0·711
Toluquinone	5·89 ± 0·085	0·7701	—	0·653
p-Xyloquinone	4·61 ± 0·18	0·6607	—	0·597
2 : 5-Diethoxybenzoquinone	2·71 ± 0·18	0·4330	—	0·480
Chloranil	81·8 ± 2·2	1·1928	27·6 ± 1·0	0·703
1 : 4-Naphthaquinone	5·37 ± 0·11	0·7300	—	0·492
2-Methyl-1 : 4-naphthaquinone	3·51 ± 0·07	0·5453	27·8 ± 0·9	0·422
Phenanthraquinone	13·0 ± 0·6	1·1139	22·8 ± 0·2	0·471
Chrysenequinone	11·2 ± 0·3	1·0492	25·2 ± 0·6	0·465
4 : 4′-Diphenoquinone	1310·0 ± 22	3·1173	28·0	0·954
3 : 3′-Dimethyldiphenoquinone	812·0 ± 23	2·9076	—	(0·84)
3 : 3′ : 5 : 5′-Tetramethyldiphenoquinone	227·0 ± 3·0	2·3560	27·0	(0·73)
3 : 5 : 3′ : 5′-Tetramethyl-4 : 4′-stilbenequinone	356 ± 8·5	2·5514	26·4 ± 0·9	(0·63)
5 : 5′-Di-*tert.*-butyl-3 : 3′-dimethylstilbenequinone	160 ± 2·0	2·2041	—	(0·58)
3 : 5 : 3′ : 5′-Tetra-*tert.*-butylstilbenequinone ...	104 ± 3·5	2·0176	23·5	(0·54)

Col. 5 of Table 2 gives the available values of the redox potentials of the quinones, as measured at 25° in ethanol containing N-hydrogen chloride. Unfortunately, the substituted diphenoquinones and stilbenequinones are too sparingly soluble in this solvent for accurate potential determination to be possible. Consequently, the redox potentials given in parentheses are calculated from the recorded redox potentials of unsubstituted 4 : 4′-diphenoquinone and 4 : 4′-stilbenequinone on the assumption that the alkyl substituents lower these potentials by the same amount as they do in the *p*-benzoquinone series. The relevent data have been taken from the measurements of Conant and Fieser (*J. Amer. Chem.*

Soc., 1923, **45**, 2208; 1924, **46**, 858; Fieser, *ibid.*, 1930, **52**, 5204) and of Lopez Aparicio and Waters (*loc. cit.*), but the computed potentials for the *tert.*-butyl-substituted compounds may well be too high since the only available reference compound is 2 : 5-di-*tert.*-butyl-1 : 4-benzoquinone which has only one alkyl group *ortho* to each quinonoid oxygen.

It is clear from Table 2 that there is no general relation between the redox potential of a quinone and its efficiency as an inhibitor, or to the logarithm of this quantity. However, although *p*-benzoquinone is an exception, the inhibiting powers of quinones of similar ring structure do appear to increase with increasing redox potential.

In accordance with the results of Wittig and Pieper (*Annalen*, 1947, **558**, 207), chloranil is a much better inhibitor than is benzoquinone, although its redox potential in alcohol is somewhat less. However, benzaldehyde is a much less polar solvent than ethanol, and Kvalnes (*J. Amer. Chem. Soc.*, 1934, **56**, 667) has found that the redox potential of chloranil in benzene, which may be a more comparable solvent, is 0·742 v when referred to 0·711 v for benzoquinone in this solvent. But even when due allowance is made for the possible higher redox potential of chloranil, its efficiency as an inhibitor is still very high. This may be attributed to the combined inductive effect of four chlorine atoms which, by withdrawing electrons from the ring system, reduce the electron density at the quinonoid oxygen atoms and thereby increase their affinity for free radicals.

We would suggest that, within any one group of aromatic compounds of similar nuclear type, correlations between inhibitor efficiency and redox potential may be due to the fact that substituent groups will have similar effects upon both types of measurement. Alkyl groups would be expected to lower the inhibitor efficiencies of quinones, since they will increase the electron availability in the nucleus and so will lower the (electrophilic) affinity of the quinonoid oxygens for free radicals : in the phenol series the reverse will be true (see Table 1) since the alkyl groups will then, by electron donation, facilitate hydrogen-atom release. Evidently the alkylation of both positions *ortho* to the quinonoid oxygen atoms lowers the inhibitor efficiency by a relatively greater amount than the substitution of only one *ortho*-position, and this may be attributed to steric hindrance of the attack by the bulky benzoyl group (equation 1). Again, in the stilbenequinone series the replacement of methyl by *tert.*-butyl groups leads to a further marked decrease in inhibitor efficiency, though the corresponding change of redox potential is small.

When quinones of different aromatic nuclei are compared it becomes evident that there is no pervading connection between redox potential and inhibiting power. Tetramethyldiphenoquinone and benzoquinone have closely similar redox potentials, yet the former is 50 times more efficient as an inhibitor. Tetramethylstilbenequinone, which should have a redox potential about 0·1 v lower than that of tetramethyldiphenoquinone, is a slightly more efficient inhibitor. Again, the retarding powers of *p*-benzoquinone and 1 : 4-naphthaquinone are much more alike than their redox potentials would indicate, and the efficiencies of phenanthraquinone and chrysenequinone are much greater than would have been expected.

Two theoretical considerations are relevent to this subject : (*a*) The redox potential of a quinone is a measure of its free energy of reduction, and will only be a corresponding measure of its heat of reduction within a series of compounds in which the entropy of reduction can be regarded as constant. According to Evans (*Trans. Faraday Soc.*, 1946, **42**, 113), this will be so for substances of the same structural type, but it is most unlikely that the entropies of reduction of benzoquinone and diphenoquinone will be the same, since 4 : 4′-dihydroxydiphenyl is capable of free rotation about the bond between the two aromatic rings. (*b*) The efficiency of radical capture by a quinone is due essentially to reaction (1) (p. 2993), *i.e.*, to the reduction of a quinone to a semiquinone radical. Although for quinones of similar structure the free-energy change for this step may be a constant proportion of the free-energy change for the complete two-electron reduction, this is certainly not true for quinones of different series, as has been shown by Fieser (*loc. cit.*). Unfortunately, he determined the free-energy change for the first stages of the reductions of only benzoquinone and diphenoquinone, and data for the other quinones now examined are not available.

Col. 4 of Table 2 gives the overall activation energies for a number of the quinone-inhibited autoxidations of benzaldehyde as computed, by the Arrhenius equation, from

3 or 4 sets of measurements in the temperature range 50—75°. For the chain reaction concerned in this autoxidation:

$$E_{\text{overall}} = E_{\text{initiation}} + E_{\text{propagation}} - E_{\text{chain-ending}}$$

$E_{\text{propagation}}$ refers to the reaction

$$\text{Ph·CO·O·O·} + \text{Ph·CHO} \longrightarrow \text{Ph·CO·O·OH} + \text{Ph·CO·}$$

which has been found by Ingles and Melville (*Proc. Roy. Soc.*, 1953, *A*, **218**, 163, 175) to be $1{\cdot}8 \pm 0{\cdot}5$ kcal. $E_{\text{initiation}}$ can be taken as the activation energy of benzoyl peroxide decomposition, which, though it has not been studied in benzaldehyde, was found by Bawn and Mellish (*Trans. Faraday Soc.*, 1951, **47**, 1216) to be 29·6 kcal. in a number of other solvents. From these figures we derive the values given in Table 3 for the activation energies of chain termination. Clearly, these activation energies cannot be correlated mathematically either with redox potentials or with inhibiting efficiencies, as would be the case if entropy factors remained constant.

TABLE 3. *Activation energies of inhibition of benzaldehyde autoxidation by quinones.*

Quinone	*E* (kcal.)	Efficiency	Redox potential, v.
Diphenoquinone	3·0	1310	0·954
2-Methyl-1 : 4-naphthaquinone	3·0	3·51	0·422
Chloranil	3·0	81·8	0·703
3 : 5 : 3′ : 5′-Tetramethyldiphenoquinone	4·0	227·0	(0·73)
3 : 5 : 3′ : 5′-Tetramethylstilbenequinone	5·0	356·0	(0·63)
Chrysenequinone	6·0	11·2	0·465
p-Benzoquinone	7·0	4·03	0·711
3 : 5 : 3′ : 5′-Tetra-*tert.*-butylstilbenequinone	8·0	104·0	(0·58)
Phenanthraquinone	9·0	13·0	0·471

Throughout, the computed standard deviations of our measurements are so low that, although our actual figures for activation energies and inhibitor efficiencies may be subject to systematic errors associated with either the technique or the theoretical computations, yet the relative orders of the figures of Table 3 can be relied on unless minute traces of impurities (*e.g.*, quinols) in certain of the quinones have an overwhelming effect even when present in traces too small to have been revealed by our criteria for purity.

Thus from our results we conclude, in general agreement with Egloff and his colleagues, that there is no *general* correlation between redox potentials and inhibitory effect of quinones on benzaldehyde autoxidation. There seems, however, to be some correlation between inhibitor efficiency and redox potential amongst quinones of the same structural type, and we suggest that this may be due to the fact that the " induced polarity " of substituent groups would affect both molecular properties in a similar way.

EXPERIMENTAL

Initial rates of oxygen uptake were measured as described by Waters and Wickham-Jones (Part II, *loc. cit.*), using 10-ml. samples of benzaldehyde containing 1·5 g. of benzoic acid. Both the benzaldehyde and the benzoyl peroxide were purified by their method. The inhibitor efficiency of each quinone, as previously defined (p. 2994), was calculated as

$$\frac{\text{g.-mol. weight of quinone}}{(\text{mg. of quinone taken}) \times (\text{O}_2 \text{ uptake rate in ml./min. at } 60°)}$$

In Table 4, ***n*** gives the number of observations, upon different weights of quinones, from which the product 1/(mg. of quinone × absorption rate) of the following column has been calculated. The standard deviations for these products have been computed by Birge's method (*Phys. Review*, 1932, **40**, 207). Except for the 3 diphenoquinones marked *, the data refer to mixtures containing 0·0500 g. of benzoyl peroxide catalyst. For these diphenoquinones, however, measurements were made with 0·2500 g. of benzoyl peroxide, but since with each of them it was found experimentally that the oxygen uptake rate was directly proportional to the first power of the benzoyl peroxide concentration (see Part III) the experimental data can all be reduced to the standard values used in Tables 2 and 3.

Preparation and Purification of Quinones.—*p*-Benzoquinone was steam-distilled and then crystallised from light petroleum to constant m. p. (112·5°). *p*-Xyloquinone was prepared from *p*-xylidene sulphate as described by Kehrmann and Stiller (*Ber.*, 1912, **45**, 3348), distilled in steam, and dried in a vacuum; it had m. p. 123°. Toluquinone, 2 : 5-diethoxybenzoquinone, and chloranil were pure materials that had been prepared by Dr. Lopez Aparicio. 1 : 4-Naphthaquinone, prepared by Conant and Freeman's method (*Org. Synth.*, Coll. Vol. I, p. 376),

TABLE 4.

Quinone	Temp., °K	*n*	1/(O_2 uptake rate) (mg. quinone taken)	Intercept on concn. axis (mg. quinone)
Benzoquinone	328	6	0·0667 ± 0·0022	—
	333	9	0·0373 ± 0·0013	—
	338	6	0·0232 ± 0·0008	—
Toluquinone	333	10	0·0483 ± 0·0007	—
p-Xyloquinone	333	9	0·0340 ± 0·0013	—
Chloranil	333	10	0·3328 ± 0·0088	0·0203 ± 0·0007
	338	5	0·1750 ± 0·0034	0·0203 ± 0·0009
	343	5	0·1000 ± 0·0051	0·0228 ± 0·0007
	348	5	0·0575 ± 0·0048	0·0228 ± 0·0007
2 : 5-Diethoxybenzoquinone	333	8	0·0138 ± 0·0009	0·0291 ± 0·0002
1 : 4-Naphthaquinone	333	11	0·0340 ± 0·0007	—
2-Methyl-1 : 4-naphthaquinone	328	6	0·0366 ± 0·0004	—
	333	8	0·0204 ± 0·0004	—
	338	6	0·0104 ± 0·0003	—
	343	6	0·0055 ± 0·0002	—
Phenanthraquinone	328	6	0·1075 ± 0·0017	0·0053 ± 0·0002
	333	7	0·0653 ± 0·0028	0·0068 ± 0·0004
	338	6	0·0400 ± 0·0010	0·0082 ± 0·0002
	343	6	0·0236 ± 0·0003	0·0100 ± 0·0001
Chrysenequinone	328	6	0·0764 ± 0·0025	—
	333	10	0·0436 ± 0·0012	—
	339	6	0·0216 ± 0·0004	—
	343	6	0·0144 ± 0·0003	—
* 4 : 4′-Diphenoquinone	328	6	2·670 ± 0·093	0·0011 ± 0·0007
	333	8	1·420 ± 0·0243	0·0028 ± 0·0004
	338	7	0·725 ± 0·031	0·0047 ± 0·0006
* 3 : 3′-Dimethyl-4 : 4′-diphenoquinone	333	9	0·766 ± 0·022	0·0025 ± 0·0002
* 3 : 3′ : 5 : 5′-Tetramethyl-4 : 4′-diphenoquinone	333	10	0·189 ± 0·0025	—
	338	5	0·1058 ± 0·0025	—
	343	5	0·0562 ± 0·0018	—
3 : 5 : 3′ : 5′-Tetramethyl-4 : 4′-stilbenequinone	333	9	1·262 ± 0·032	0·0019 ± 0·0004
	338	5	0·666 ± 0·057	0·0033 ± 0·0009
	343	5	0·381 ± 0·021	0·0051 ± 0·0007
	348	5	0·233 ± 0·014	0·0079 ± 0·0007
5 : 5′-Di-*tert.*-butyl-3 : 3′-dimethylstilbenequinone	333	9	0·455 ± 0·006	0·0025 ± 0·0001
3 : 5 : 3′ : 5′-Tetra-*tert.*-butylstilbenequinone	333	8	0·256 ± 0·0086	0·0104 ± 0·0001
	338	6	0·149 ± 0·0059	0·0127 ± 0·0003
	343	6	0·0889 ± 0·0061	0·0206 ± 0·0004

was purified by vapour distillation and dried in a vacuum (over P_2O_5), had m. p. 123°. 2-Methyl-1 : 4-naphthaquinone (Light & Co.) was crystallised from methanol to constant m. p. (105·5°). Phenanthraquinone, made from pure phenanthrene, was crystallised to constant m. p. (208°) from hot benzene. Chrysenequinone, prepared from chrysene by Graebe and Hönigsberger's method (*Annalen*, 1900, **311**, 262), was crystallised to constant m. p. (236°) from glacial acetic acid and dried in a vacuum.

Diphenoquinone. 4 : 4′-Dihydroxydiphenyl, prepared from benzidine (Hirsch, *Ber.*, 1889, **22**, 1335), was oxidised to the quinone with lead dioxide (Willstätter and Kelb, *Ber.*, 1905, **38**, 202), and the quinone crystallised from benzene; it had m. p. 160° (decomp.).

3 : 3′-*Dimethyldiphenoquinone.* 4 : 4′-Dihydroxy-3 : 3′-dimethyldiphenyl, m. p. 156°, was prepared from *o*-tolidine (Gerber, *Ber.*, 1888, **21**, 749; Hobbs, *ibid.*, p. 1067; Winston, *Amer. Chem. J.*, 1904, **31**, 119) and then oxidised to **3 : 3′-*dimethyl*-4 : 4′-*diphenoquinone*** with lead

dioxide, though in poor yield. After crystallisation from benzene the quinone had m. p. 165° (decomp.) (Found: C, 78·9; H, 5·7. $C_{14}H_{12}O_2$ requires C, 79·3; H, 5·6%).

3 : 5 : 3′ : 5′-Tetramethyldiphenoquinone, m. p. 203—204° (decomp.), was prepared by Mr. R. F. Moore (see Part IV). 3 : 5 : 3′ : 5′-Tetramethyl-4 : 4′-stilbenequinone, prepared by oxidation of mesitol by silver oxide (Porter and Thurber, *J. Amer. Chem. Soc.*, 1921, **43**, 1194), was crystallised from boiling xylene; it had m. p. 218—220° (decomp.).

5 : 5′-*Di*-tert.-*butyl*-3 : 3′-*dimethyl*-4 : 4′-*stilbenequinone*. 6-*tert.*-Butyl-2 : 4-dimethylphenol (5 g.) in benzene (200 ml.) was warmed at 50° for 4 hr., with occasional shaking, with freshly prepared silver oxide (25 g.). The mixture was then heated to boiling and filtered hot, and the residue extracted with more benzene. After evaporation, the extracts left a tarry product which on trituration with a little petroleum (b. p. 100—120°) yielded an orange-red solid. This *quinone* was crystallised to constant m. p. (225°) from petroleum (b. p. 100—120°) (Found: C, 82·1; H, 8·4; $C_{24}H_{30}O_2$ requires C, 82·3; H, 8·6%).

3 : 5 : 3′ : 5′-Tetra-*tert.*-butylstilbenequinone was prepared by a similar method from 2 : 6-di-*tert.*-butyl-4-methylphenol and was crystallised to constant m. p. (302°) from petroleum. The yield was about double that of Cosgrove and Waters (*J.*, 1951, 388) who used benzoyl peroxide as the oxidiser.

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