694. *Addition of Methyl Radicals to Quinones. Part II.* The Reaction Centre.*

By R. P. Buckley, A. Rembaum, and M. Szwarc.

The relative rate constants of addition of methyl radicals to substituted benzo- and naphtha-quinones were determined. They are considered as evidence for the addition of methyl radicals to the C=C and not to the C=O double bond of quinones.

Reaction of radicals with quinones is undoubtedly by addition, which may involve the C=O or the C=C double bond of the quinone. The literature indicates that both are attacked, although by different types of radical: the C=O double bond of benzoquinone by polystyryl,[1] poly(methyl methacrylate),[2a] poly(methyl acrylate),[2b] and 2-cyano-2-propyl radicals,[3] and the C=C double bond of naphthaquinone by methyl.[4,5] In all these investigations the centres of addition were identified by examining the products. The shortcomings of such a method have been discussed [6] and an alternative method based on kinetic evidence was outlined. The results reported indicated that methyl radicals add to the C=C double bonds of quinones, confirming Fieser and Oxford's findings.[4] We now report new results which confirm this conclusion, though we emphasize that our results are pertinent only to the methyl radicals.

As in our earlier work,[6,7] results are given as the ratio k_2/k_1; the subscripts refer to the hydrogen abstraction reaction (1):

$$CH_3 + \text{Solvent} \longrightarrow CH_4 + \text{Solvent radical} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and to the addition reaction (2)

$$CH_3 + Q \longrightarrow Q{\cdot}CH_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where Q denotes a molecule of a quinone.

* Part I, *J. Amer. Chem. Soc.*, 1955, **77**, 4468.

[1] Cohen, *J. Amer. Chem. Soc.*, 1947, **69**, 1057.
[2] Kice, (*a*) *ibid.*, 1954, **76**, 6274; (*b*) *J. Polymer. Sci.*, 1956, **19**, 123.
[3] Bickel and Waters, *J.*, 1950, 1746; Aparicio and Waters, *J.*, 1952, 4666.
[4] Fieser and Oxford, *J. Amer. Chem. Soc.*, 1942, **64**, 2060.
[5] Kvalnes, *ibid.*, 1934, **56**, 2478.
[6] Rembaum and Szwarc, *ibid.*, 1955, **77**, 4468.
[7] Levy and Szwarc, *ibid.*, p. 1949 and subsequent papers.

We have shown [6,8] that a carbon atom to which a methyl radical might be added can be " blocked " by substituting methyl groups or chlorine atoms for hydrogen atoms. Apart from the " blocking " effect a methyl group only slightly affects the reactivity. On the other hand, a chlorine atom powerfully activates the C=C double bond, although a completely chlorinated double bond is unreactive owing to the " blocking " effect of the chlorine atoms. These observations were considered in the previous paper [6] as crucial in deciding which centre was attacked by methyl radicals. It was pointed out that the decrease in the reactivity (*i.e.*, in k_2/k_1) along the series benzoquinone, toluquinone, 2 : 5-xyloquinone, and duroquinone reflects the " blocking " effect of methyl groups. Supporting evidence was provided by the series, naphthaquinone, 2-methylnaphthaquinone and 2 : 3-dimethylnaphthaquinone, where the value of k_2/k_1 also decreases. On the other hand, the reactivity of 2 : 7-dimethyl- differs little from that of 2-methyl-naphthaquinone, showing that a methyl group substituted away from the relevant C=C double bond has negligible effect on the reactivity.

It may be argued, however, that the methyl groups sterically hinder the addition to the C=O bonds. Indeed, the methyl groups in the substituted benzoquinones and the corresponding naphthaquinones are adjacent to the C=O bonds, and they might therefore interfere with the addition to this centre. If so, reactivities of methylated quinones do not allow us to differentiate between the two alternative modes of addition. It should be stressed that the results in Table 1 clearly show 2 : 3-, 2 : 5-, and 2 : 6-dimethylquinones to be equally reactive in respect to methyl-radical addition. Furthermore, their reactivities (*i.e.*, k_2/k_1's) are approximately half that of unsubstituted benzoquinone ($k_2/k_1 = 2020$, see ref. 6), indicating that the two methyl groups " blocked " two of the four centres of addition.

TABLE 1. *Reaction of quinones in toluene at* 65° ($Ac_2O_2 = \sim 0{\cdot}02$M).

Mole (%)	k_2/k_1	Mole (%)	k_2/k_1	Mole (%)	k_2/k_1	Mole (%)	k_2/k_1
2 : 5-Dimethyl-benzoquinone		2 : 6-Dimethyl-benzoquinone		2 : 3-Dimethyl-benzoquinone		2 : 5-Dichloro-benzoquinone	
0·1	1100	0·1	1100	0·1	910	0·02	5130
0·1	910	0·1	1200	0·1	1150	0·03	4860
0·1	970	0·1	1300	Average 1030 ± 85		0·04	5560
0·1	990	0·1	1150			0·05	5340
0·5	1160	Average 1190 ± 80				Average 5220 ± 300 †	
Average 1030 ± 90 *							
2 : 3-Dichloro-benzoquinone		2-Chloro-1 : 4-naphthaquinone		6 : 7-Dichloro-1 : 4-naphthaquinone		2 : 6-Dimethoxy-benzoquinone	
0·02	1460	0·041	2390	0·039	880	0·032	317
0·04	1270	0·061	2240	0·098	1010	0·046	386
0·09	1500	0·102	1870	0·157	1030	0·064	299
0·10	1520	0·163	2180	Average 970 ± 80		0·096	360
0·10	1690	Average 2170 ± 220				Average 340 ± 40	
0·10	1330						
0·10	1110						
0·16	1490						
0·17	1600						
Average 1330 ± 300							

Averages reported in Part I are * 870, † 5240.

On the other hand, by investigating the reactivities of chlorinated quinones the two modes of addition can be distinguished. Earlier in this paper it was noted that a chlorine atom substituted at a double bond has a strongly activating effect although dichlorination of such a bond results in complete " blocking " and consequent decrease in reactivity.

The reactivity of monochlorobenzoquinone was 3450 (ref. 6), compared with 2020 for benzoquinone itself. If it is assumed that one of the C=C double bonds of the chloroquinone remains as reactive as a C=C double bond of the unsubstituted quinone, the effect of a

[8] Szwarc and his co-workers, *J. Amer. Chem. Soc.*, p. 5493; 1956, **78**, 5696; 1957, **79**, 5621, 6343.

chlorine atom on the reactivity of the other C=C bond is given by a factor of 2·4. In 2 : 5- and 2 : 6-dichlorobenzoquinone both double bonds are activated by chlorine atoms and k_2/k_1 values were 5240 and 5130 (see ref. 6). The value of k_2/k_1 for 2 : 5-dichlorobenzoquinone was redetermined in the present work and found to be 5220 (see Table 1), in

TABLE 2. *Reactivity of naphthaquinone in toluene at* 65°.

Mole % of quinone	CH_4	CO_2	CH_4/CO_2	k_2/k_1
Series A				
—	0·458	0·683	0·669	—
0·052	0·575	1·050	0·546	433
0·130	0·320	1·150	0·278	1082
0·156	0·287	0·806	0·324	683
0·208	0·211	0·855	0·247	821
Series C				
—	0·406	0·591	0·687	—
—	0·402	0·601	0·669	—
0·051	0·362	0·803	0·451	986
0·128	0·200	0·676	0·296	1009
0·154	0·184	0·688	0·267	999
0·205	0·139	0·670	0·207	1110
			Average 1080 ± 100	

Mole % of quinone	CH_4	CO_2	CH_4/CO_2	k_2/k_1
Series B				
—	0·392	0·598	0·656	—
—	0·432	0·617	0·700	—
0·051	0·501	1·110	0·451	986
0·127	0·310	1·130	0·274	1161
0·153	0·275	1·120	0·246	1148
0·204	0·212	1·100	0·193	1232

Series *A*: recryst. from ligroin.
Series *B*: recryst. from ligroin, then from EtOH; m. p. 124°.
Series *C*: recryst. from EtOH, then sublimed *in vacuo*; m. p. 124—125°.

Apparently series A was carried out with insufficiently pure compound. The results of series B and C were reproducible and self-consistent in CH_4/CO_2 ratio and therefore in k_2/k_1. However, it seems that the compound used in the series B contained some impurities which induced the decomposition of the peroxide, increasing the amounts of CH_4 and of CO_2 formed, although apparently they did not affect the ratio CH_4/CO_2; this impurity seems to be largely removed in series C.

agreement with the previous value. On this basis the effects of chlorine atoms in these compounds can be calculated to be 2·6 and 2·5 per double bond respectively, in agreement with the other value.

The reactivity of 1 : 4-naphthaquinone was redetermined in the present work. The relevant data (Table 2) show that the extent of purification of the compound appears to be critical. On the basis of the values obtained in series *B* and *C*, the k_2/k_1 for 1 : 4-naphthaquinone is 1080 ± 90, *i.e.*, the same as k_2/k_1 per double bond of benzoquinone or 2 : 3-dimethylbenzoquinone. The same value (970 ± 80) was obtained for 6 : 7-dichloronaphthaquinone (see Table 1), indicating that chlorine atoms remote from the centre of reaction affect its reactivity very slightly. The k_2/k_1 for 2-chloro-1 : 4-naphthaquinone was found to be 2170 ± 220; thus, the effect of a chlorine atom on the reactivity of the particular C=C double bond amounts to a factor of 2·0.

In contrast to all these observations k_2/k_1 for 2 : 3-dichlorobenzoquinone was found to be 1330 ± 300 (*i.e.*, a value corresponding to one C=C double bond only). Hence, this result shows convincingly that the addition of methyl radicals to quinones takes place on a C=C double bond and not on a C=O double bond. If the latter bond were involved in the reaction then a low value would be observed for 2 : 6-dichlorobenzoquinone, which contradicts the actual observations. Apparently the two chlorine atoms in 2 : 3-dichlorobenzoquinone " block " one of the C=C double bonds and have a negligible effect on the reactivity of the other C=C bond. In this respect 2 : 3-dichlorobenzoquinone behaves like 6 : 7-dichloronaphthaquinone.

Finally, the reactivity of 2 : 6-dimethoxybenzoquinone deserves comment. The methoxy-group deactivates the C=O double bond for methyl-radical addition. Accepting the previous approach it is concluded that a methoxy-group deactivates a C=C double bond of benzoquinone by a factor of 0·17. A similar result can be obtained from the reactivity of 2-methoxybenzoquinone (k_2/k_1 1060). Assuming that only one C=C bond in this compound was deactivated affords a value of 0·05. Here the deactivating effect of the

methoxy-group can only be given as an order of magnitude since it was obtained as a small difference between two large numbers.

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DEPT. OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY,
SYRACUSE UNIVERSITY, SYRACUSE 10, N.Y., U.S.A. [*Received, April 9th,* 1958.]