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THE REVERSIBLE ADDITION OF HYDROXIDE ION TO QUINONES

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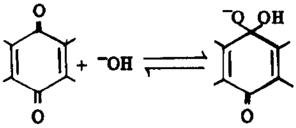
The reversible 1,2-addition of bisulfite to carbonyl groups of quinones was reported recently.[1] We are reporting here the reaction believed to be the reversible addition of hydroxide ion to a quinone carbonyl according to Equation 1. This reaction is promoted by strong



(1)

electronegative groups attached to the ring. Figure 1 shows that the ultraviolet absorption of chloro-*p*-benzoquinone (Curve 1) in aqueous solution gradually diminished with increasing pH and became constant beyond pH 12.2 (Curve 6). These typical absorption curves were obtained in a flow machine[1] 25 milliseconds after mixing phosphate

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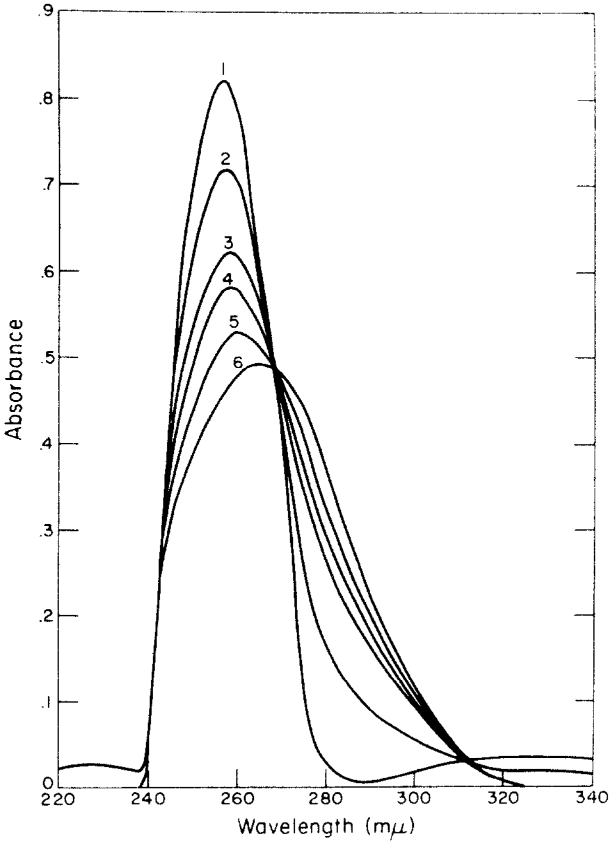
[1] C. A. Bishop, R. F. Porter, and L.K.J. Tong, *J. Am. Chem. Soc.*, *85*, 3991 (1963).

FIG. 1

Change in absorption of chloro-p-benzoquinone (5×10^{-5}M) at high pH: pH = 8.93(1); 11.03(2); 11.52(3); 11.75(4); 12.10(5); 12.30(6).



buffers with quinone solution to adjust the pH and giving a final ionic strength of 0.375. The chloro-p-benzoquinone as well as the 2,5-dichloro-p-benzoquinone and benzoquinonemonosulfonate were prepared in the flow machine just prior to the addition of buffer by oxidation of the corresponding hydroquinone with ferricyanide. Even neutral aqueous solutions of these quinones start to decompose within a few minutes, whereas chloranil and trichlorohydroxyquinone are stable under the same conditions for much longer periods.

The formation of adduct was complete in less than 12 milliseconds, the shorter time limit of our equipment. No further change in absorption was observed up to 300 milliseconds. Furthermore, agreement with calculations using Equation 2 justifies the assumption that each curve

$$K_c = \frac{(T\cdot OH)}{(T)(OH^-)} \qquad (2)$$

in Figure 1 is due to the absorption of an equilibrium mixture of quinone (T) and quinone-hydroxide adduct (T·OH) having a formation constant, K_c. If a solution of adduct which had been formed and kept at high pH over a period of 25 milliseconds was acidified, the absorption due to the quinone was completely regenerated. Thus, the reversibility of the reaction was demonstrated.

In Table I are listed the adduct formation constants along with the λ_{Dmax} and log ϵ for both quinones and quinone-hydroxide adducts for five quinones with electronegative substituents. Since chloranil is not soluble in water, the hydroxide addition had to be studied in 50% ethanol. The constant K_c in this case is an estimate due to uncertainty of the pH scale in 50% ethanol using a glass electrode. Nevertheless, it is within a factor of five at the most and shows that replacement of one chlorine atom on the ring with a hydroxy group lowers K_c by 100-fold or more. In general, the data in Table I show that more electron withdrawal from the quinone ring leads to tighter bonding in the adduct.

TABLE I

Quinone-Hydroxide Adduct Formation Constants at 25°C.

		Quinone		Adduct	
Quinone	K_c(l/mole)	λ_{Dmax}	log ϵ	λ_{Dmax}	log ϵ
Benzoquinone-monosulfonate[a]	125	253	4.20	253	3.86
Chloro-p-benzoquinone[a]	364	257	4.22	267	4.00
2,5-Dichloro-p-benzoquinone[a]	1,700	272	4.25	250	4.00
Trichlorohydroxy-p-benzoquinone[b]	210	294	4.07	250 365	3.75 3.70
Chloranil[a]	100,000[c]	290[c]	4.17[c]	285[c]	3.83[c]

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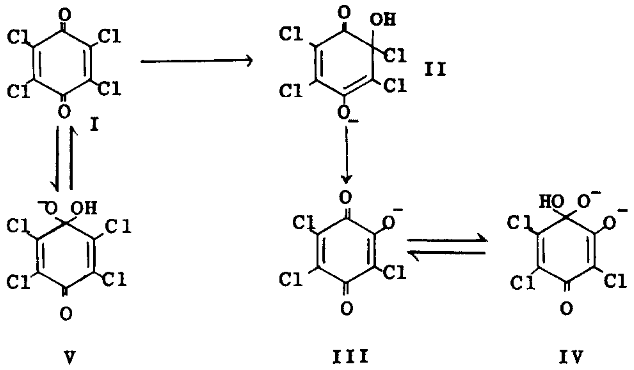
[a] Commercially available samples of quinones or hydroquinones were recrystallized before use.

[b] Prepared according to Reference 2.

[c] In 50% ethanol-water.

Hydroxide has been found to be a poorer nucleophile than sulfite for displacement of halides from the quinone ring.[1] This work shows that it is also weaker than sulfite in adduct formation with quinones. At the same concentration of hydroxide and sulfite, only the latter will add reversibly to quinones without electronegative substituents.

Though insoluble in water, chloranil (I) dissolved in cold 1<u>N</u> KOH, giving a pale yellow solution of a compound (A) with a spectrum identical with that of the hydroxide adduct of trichlorohydroxy-p-benzoquinone. Hancock, Morrell, and Ruhm also obtained the same yellow solution from chloranil,[2] but attributed the absorption to the



ring-addition intermediate (A = II), since acidification of this solution gave a quantitative yield of trichlorohydroxy-p-benzoquinone, III.

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[2] J. W. Hancock, C. E. Morrell, and D. Ruhm, Tetrahedron Letters, No. 22, 987 (1962)

However, we found that when this solution of III was made basic again, the same absorption was obtained as that from the original chloranil-KOH solution (A). Therefore, except for the improbable coincidence that II and IV have similar absorption spectra, II could not be the initial product, A, because hydroxide addition to III could not give a compound with four chlorine atoms in the ring. Furthermore, acidification of II would not be expected to give a quantitative yield of III, but rather a mixture of I and III; the former was not found.

The first displacement reaction probably does go through an intermediate similar to II, but this process must be quite fast in this case, since the first observed product under these conditions is A, now assumed to be IV. As a side reaction, I also undergoes reversible hydroxide addition $(\mathrm{I} \rightleftharpoons \mathrm{V})$ before displacement. One further product, 2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone, results from solutions of III, or mixtures of III and IV at high pH on longer standing.

The hydroxide adducts had spectrophotometric characteristics quite similar to the bisulfite adducts.[1] For the same reasons as cited previously, the adducts are believed to be carbonyl addition compounds. Nevertheless, the structures have not been rigorously established because the adducts were not isolated.