

$K(\text{dissociation of sodium naphthalene}) = 1.7 \times 10^{-6}$ .<sup>16a</sup>

One would gather from the values of  $\Delta S^\circ$  obtained for reactions 10 and 11 that solvation changes accompanying reaction of a triple ion to give two ion pairs are roughly comparable with those accompanying dissociation of a single ion pair to free ions.

Table IV gives such estimates of  $K_{10}$  and  $K_{11}$  as our data afford. Values for Li and Na in 1,2-dimethoxyethane are based on plots similar to those of Figure 5, for which we must make the reservation that the scatter prohibits a very accurate separation of  $K_{10}$  and  $K_{11}$ , possibly due to the ionization of triple ions. For K and Cs we assume that ionization is not very significant so that  $K_F \approx K_{10}$ . The solvent effects on  $K_{10}$  and  $K_{11}$  are both in the expected direction. The metal ion effect on  $K_{10}$  appears to be generally opposite in direction from that which would be predicted on a strictly coulombic basis, a trend we view as reflecting solvation factors, discussed above.

Table IV. Estimated Values of  $K_{10}$  and  $K_{11}$  at 25°

Metal	$K_{10}$		$K_{11}$	
	DME <sup>a</sup>	THF <sup>b</sup>	DME	THF
Li	>2.4	...	$10^{-3}$ – $10^{-5}$	...
Na	1	42	$\sim 3 \times 10^{-4}$	$2 \times 10^{-6}$
K	45	6000	...	...
Cs	3000	Large	...	...

<sup>a</sup> 1,2-Dimethoxyethane. <sup>b</sup> Tetrahydrofuran.

*Extent of Disproportionation of MTPE.* Reference to eq. 12 discloses that a possible explanation for the unusually large extent of disproportionation of alkali adducts of TPE is that  $K_{11}$  is abnormally small, not that  $K_{10}$  is abnormally large. The comparison of  $K_{11}$  with the value found by Atherton and Weissman for dissociation of sodium naphthalene ion pairs (see above)<sup>16a</sup> suggests that this is not the case, and that  $K_{10}$  must be unusually large instead. Thus, while disproportionation probably would not occur in the absence of association, ion association in itself is probably not the cause for the unusual behavior of MTPE. Previous speculations as to this cause remain applicable.<sup>20,20a</sup>

(20) See ref. 2b and citations therein.

(20a) NOTE ADDED IN PROOF. Examples of directly measureable spontaneous disproportionation of monoalkali adducts of aromatic hydrocarbons in ethers have recently come to our attention from two groups.

J. Dieleman reports that monosodium *p*-terphenyl and monosodium *p,p'*-quaterphenyl disproportionate in methyltetrahydrofuran at room temperature with  $K$  (presumably analogous to our  $K_{10}$ ) values of 0.29 and 6.9, respectively. Disproportionation of the same species occurs in tetrahydrofuran to a lesser extent (J. Dieleman, Thesis, Free University, Amsterdam, 1962).

By employing selected metal ions and solvents, Shatenstein and co-workers found conditions under which the spontaneous disproportionation of naphthalene radical anion occurs, namely, with lithium in diethoxyethane or dioxane (A. I. Shatenstein, E. S. Petrov, and M. I. Belouseva, *Organic Reactivity* (Tartu State University, Tartu, Estonian S.S.R.), 1, 191 (1964). Since this publication is probably unavailable in most libraries, and since it is apparently bilingual, with a detailed English summary appearing in this case beginning on p. 199, we give here both the title of the paper, "Reaction Equilibria of Sodium and Lithium with Biphenyl and Naphthalene in Electron-donating Solvents," and the address, L. Y. Karpov Institute of Physical Chemistry, Moscow, of Prof. Shatenstein, from whom reprints can probably be obtained. We are grateful to Prof. Shatenstein for such a reprint.

## Equilibria of Substituted Semiquinones at High pH

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Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650. Received August 21, 1964

The equilibrium constants,  $K'$ , of a number of substituted semiquinones with the corresponding quinones and doubly ionized hydroquinones have been measured by a flow method. The calculation of  $K'$  necessitates the consideration of the reversible quinone-hydroxide addition reaction in some cases. Inductive effects have been shown to be an important factor in the position of equilibrium.

The oxidation of hydroquinones is known to involve semiquinone free-radical intermediates,<sup>1,2</sup> which themselves are stable at high pH, owing to the equilibrium with the corresponding quinone and doubly ionized hydroquinone (eq. 1).<sup>1,3-6</sup> However, most quinones

(1) L. Michaelis, M. P. Schubert, R. K. Reber, J. A. Kuck, and S. Granick, *J. Am. Chem. Soc.*, **60**, 1678 (1938).

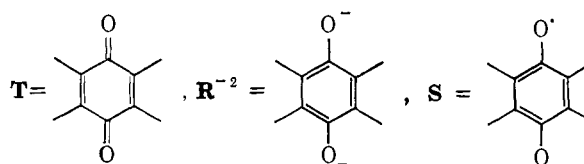
(2) T. H. James, J. M. Snell, and A. Weissberger, *ibid.*, **60**, 2084 (1938); G. Kornfeld and A. Weissberger, *ibid.*, **61**, 360 (1939); J. E. LuValle and A. Weissberger, *ibid.*, **69**, 1567 (1947).

(3) L. Michaelis, *Chem. Rev.*, **16**, 243 (1935).

(4) J. H. Baxendale and H. R. Hardy, *Trans. Faraday Soc.*, **49**, 1433 (1953).



where



react rapidly and irreversibly with hydroxide ion, causing the position of equilibrium to change with time and making quantitative determinations difficult. Tetramethylquinone (duroquinone) is one of the few exceptions, and the semiquinone equilibria were first investigated in this less reactive system by a static method.<sup>4</sup> More recently, the *p*-benzosemiquinone equilibria were

(5) N. K. Bridge and G. Porter, *Proc. Roy. Soc. (London)*, **A244**, 276 (1958).

(6) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

studied by a flow method,<sup>7</sup> where the system could be examined before any appreciable decomposition of the quinone had occurred. Many other substituted semiquinones have been shown to exist at high pH.<sup>8</sup> This paper reports a detailed investigation of several semiquinone equilibria by an improved technique in a flow system. In particular, the nature of substituents in the ring and the reversible quinone-hydroxide reaction<sup>9</sup> were shown to have sizable effects on these equilibria.

### Method

The equilibrium in eq. 1 was established in less than 10 msec., the shortest time limit of the apparatus; the semiquinone equilibrium constant,  $K'$ , can be expressed as shown in eq. 2. Experimentally, it is more con-

$$K' = \frac{[S]^2}{[T][R^{-2}]} \quad (2)$$

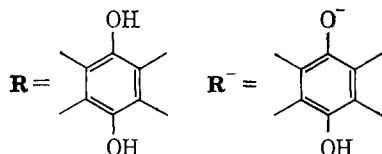
venient to measure the semiquinone concentration, S, and in the calculations to use the total concentrations of all species of hydroquinone, R, and quinone, T. This leads to an experimental formation constant

$$K = \frac{[S]^2}{[R][T]} \quad (3)$$

$K$  is dependent on pH since R consists of all the hydroquinone species

$$[R] = [R] + [R^-] + [R^{-2}] \quad (4)$$

where



which are related by their ionization constants,  $K_1$  and  $K_2$ .

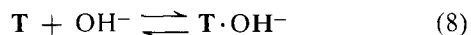
$$K_1 = \frac{[R^-][H^+]}{[R]} \quad (5)$$

$$K_2 = \frac{[R^{-2}][H^+]}{[R^-]} \quad (6)$$

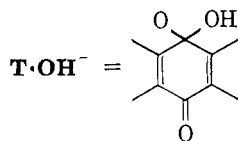
Therefore

$$[R] = [R^{-2}] \left( 1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 K_2} \right) \quad (7)$$

Some quinones containing electronegative substituents enter into a rapid, reversible equilibrium with hydroxide ion<sup>9</sup> according to eq. 8.



where



(7) H. Diebler, M. Eigen, and P. Matthies, *Z. Naturforsch.*, **16b**, 629 (1961).

(8) B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *J. Chem. Phys.*, **30**, 1006 (1959).

(9) C. A. Bishop and L. K. J. Tong, *Tetrahedron Letters*, **41-42**, 3043 (1964).

Then

$$K_c = \frac{[T \cdot OH^-]}{[T][OH^-]} \quad (9)$$

and in these cases

$$[T] = [T] + [T \cdot OH] = [T](1 + K_c[OH^-]) = [T] \left( 1 + \frac{K_c K_w}{[H^+]} \right) \quad (10)$$

where  $K_w$  is assumed to be  $10^{-14.00}$ . The value of  $K'$  can then be obtained from  $K$  by the use of eq. 2, 3, 7, and 10; *i.e.*

$$K \left( 1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 K_2} \right) \left( 1 + \frac{K_c K_w}{[H^+]} \right) = K' \quad (11)$$

At the high pH values used, the term [S] in eq. 3 was assumed to consist only of semiquinone anion. Tetramethylsemiquinone is reported to have a  $pK$  of 5.9<sup>5</sup>; the  $pK$  values of the other semiquinones should not differ from this by more than two or three orders of magnitude.

In many cases,  $K_1$ ,  $K_2$ , and  $K_c$  could be determined independently. However, occasionally either  $K_2$  or  $K_c$  was too small to be measured directly without the use of extremely high alkali concentrations, but still sufficiently large to influence the value of  $K$ . Then with the use of eq. 11 both  $K'$  and one other constant were calculated from a set of  $K$  values measured at several pH values. The application of this method will be described in a later section.

### Results

*Calculation of Experimental Formation Constants,  $K$ .* A hydroquinone solution of initial concentration,  $[R_0]$ , was oxidized to various degrees from 2 to 80%; the sum of concentrations (eq. 12) remains unchanged. A

$$[R_0] = [R] + [S] + [T] \quad (12)$$

plot of per cent oxidation of  $[R_0]$  vs.  $D$ , the density of the semiquinone at 420 or 430  $m\mu$ , gave a symmetrical curve with a maximum, as illustrated for hydroquinone in Figure 1a. The maximum in the curve is expected since, from the definition of  $K$  [S] is at a maximum when  $[R] = [T]$ , and eq. 12 holds. If we let  $Q$  be the normality of oxidant as added and assume that oxidation is complete by the time the measurement is made, then

$$[T] = \frac{Q - [S]}{2} \quad (13)$$

and from eq. 12

$$[R] = [R_0] - \frac{Q}{2} - \frac{[S]}{2} \quad (14)$$

Equations 3, 13, and 14 were combined to give eq. 15

$$\left( \frac{[S]}{[R_0]} + \frac{1}{A} \right)^2 = \frac{1 + A}{A^2} - \frac{1}{A} \left( \frac{Q}{[R_0]} - 1 \right)^2 \quad (15)$$

where  $A = (4/K) - 1$ . In eq. 15,  $[S]/[R_0]$  has a maximum at  $Q = [R_0]$  under the real physical conditions of  $0 < [S]/[R_0] < 1$  and  $K > 0$ . To calculate  $K$ ,  $\epsilon$ , the extinction coefficient of the semiquinone at the desired

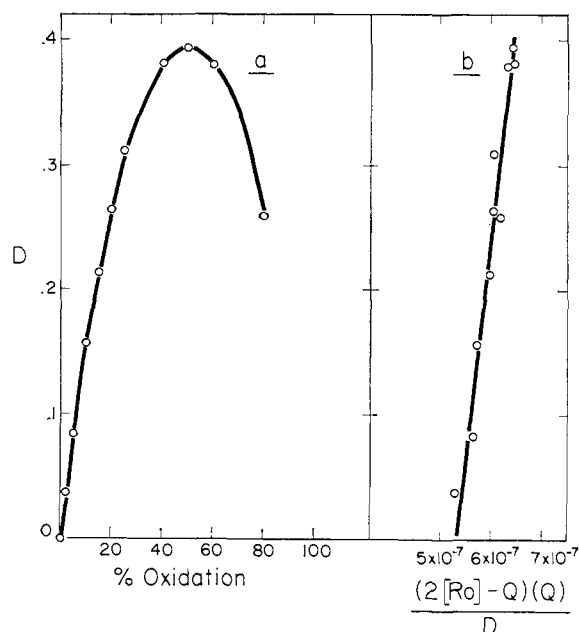


Figure 1. Change of density,  $D$ , due to  $p$ -benzoquinone with per cent oxidation (a) and with  $((2[R_0] - Q)Q)/D$  (b); circles represent data points.

wave length, must first be determined so that  $[S]$  can be evaluated from the spectrophotometric measurements. This was done graphically (Figure 1b), with a set of density measurements from Figure 1a obtained after the addition of known quantities,  $Q$ , of oxidant. The plot of  $D$  vs.  $((2[R_0] - Q)Q)/D$  was based on eq. 16, which was derived by substitution of  $[S] = D/\epsilon$  into eq. 15.

$$D = \frac{(2[R_0] - Q)Q \epsilon^2}{D A} 2[R_0] \frac{\epsilon}{A} \quad (16)$$

The linear relationship of eq. 16 is suitable for graphical determination of  $\epsilon$  as well as  $K$  at a given pH. If we let

$$a = \lim_{D \rightarrow 0} \frac{(2[R_0] - Q)Q}{D} \quad (17)$$

and  $b = \text{slope}$ , then  $\epsilon = 2[R_0]/a$  and  $A = 4[R_0]^2/a^2b$ . Although, in principle, both  $\epsilon$  and  $K$  can be obtained from one plot, the optimum conditions for obtaining  $\epsilon$ , *i.e.*, a large slope, are not accurate for obtaining  $A$ . In practice, then, eq. 3 was used to calculate  $K$  at several pH values after  $\epsilon$  was determined at a single pH.

**The pH Dependence of Semiquinone Equilibrium.** The variation of  $K$  with pH is illustrated for  $p$ -benzoquinone in Figure 2 and Table I. The experimental formation constants were calculated from 50% oxidized mixtures with  $\epsilon = 1880$  l./mole at 420 m $\mu$  (0.25-cm. cell) obtained from the plot in Figure 1b. The value of  $K$  is seen to increase, as predicted, up to pH 12, but then decreases again at higher pH (solid line) instead of remaining constant, as expected (dotted line). The decrease at high pH can be attributed to formation of a reversible quinone-hydroxide addition product,<sup>9</sup> *i.e.*,  $K_c$  is large enough to affect  $K$  in this case. This interpretation was supported by spectrophotometric examination of the absorption due to  $p$ -benzoquinone at pH 13, which showed a drop in density compared to that

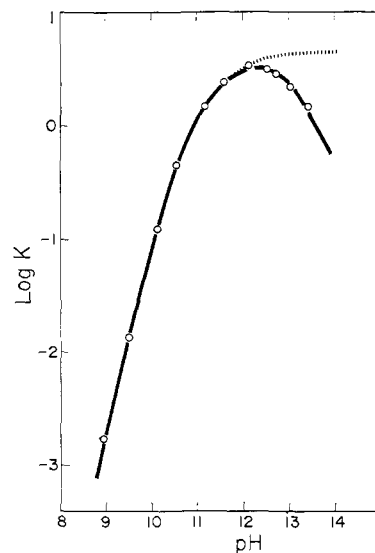


Figure 2. Variation of  $\log K'$  with pH for  $p$ -benzoquinone: O, data points; —, calculated from separate constants; ·····, calculated assuming  $K_c = 0$ .

at lower pH; such a drop is characteristic of a reversible carbonyl addition reaction.<sup>9,10</sup> Above pH 12.7,  $K_1$  and  $K_2$  were negligible, so  $K_c = 8.3$  and  $K' = 4.2$  were calculated from eq. 11. By using these constants and the data from pH 11.15 to 12.5,  $pK_2 = 11.4$  was calculated, and agrees with the value reported by Baxendale and Hardy.<sup>11</sup> Finally, with these constants and  $pK_1 = 9.85$ ,<sup>11</sup> the variation in  $K$  was calculated for the pH range of 8.8 to 13.4 from eq. 11. The solid line in Figure 2 is  $\log K$  vs. pH determined in this way and demonstrates the excellent fit of the data over the pH range.

Table I. Values of  $K$  for  $p$ -Benzoquinone at Different pH Values

pH	$K$
8.95	0.0016
9.52	0.0131
10.12	0.124
10.55	0.453
11.15	1.47
11.56	2.41
12.10	3.41
12.5	3.04
12.7	2.90
13	2.13
13.4	1.47

**The pK Values of Hydroquinones.** Table II includes the pK values for the first and second ionizations of the hydroquinones as well as the  $\lambda_{D_{max}}$  for each ionic species. Some of the data were taken from the literature, as indicated in the footnote. Both the first and the second ionization constants show the expected effect of ring substitution. The  $\lambda_{D_{max}}$  shifts to longer wave lengths as successive protons are removed, in agreement with the observations of Baxendale and Hardy.<sup>11</sup> The extinction coefficients at  $\lambda_{D_{max}}$  increase

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

(11) J. D. Baxendale and H. R. Hardy, *Trans. Faraday Soc.*, **49** 1140 (1953).

**Table II.** Hydroquinone Ionization Constants and Semiquinone Equilibrium Constants

$$R \xrightarrow{K_1} R^- \xrightarrow{K_2} R^{2-}$$

Substituents	$\lambda_{D_{\max}}(R)$	$pK_1$	$\lambda_{D_{\max}}(R^-)$	$pK_2$	$\lambda_{D_{\max}}(R^{2-})$	$K'$
None (hydroquinone)	288 <sup>a</sup>	9.85	307 <sup>a</sup>	11.4 <sup>b</sup>	319 <sup>a</sup>	4.2
2-Methyl	289 <sup>a</sup>	10.05 <sup>a</sup>	307 <sup>a</sup>	11.5 <sup>b</sup>	317 <sup>a</sup>	2.0
2-Methoxy	283	9.91	307	11.9	319	1.5
2-Chloro	219	8.90	312	11.0	328	10.7
2-Sulfonate	300	9.57	324	11.9	343	41.0
2,3-Dimethyl	287	10.43	306	12.6 <sup>b</sup>	319	3.6
2,5-Dimethyl	288	10.38	309	12.5 <sup>b</sup>	320	6.0
2,6-Dimethyl	284	10.35	300	12.4 <sup>b</sup>	319	3.0
2-Octyl-5-sulfonate	300	9.90	323	11.8	338	30.0
2,5-Dichloro	296	7.90	320	10.0	336	17.3
2,3,5-Trimethyl	284	10.8	304	12.9 <sup>b</sup>	319	3.3
Tetramethyl	283 <sup>a</sup>	11.25 <sup>a</sup>	302 <sup>a</sup>	13.2 <sup>a,b</sup>	317	1.3 <sup>c</sup>

<sup>a</sup> Ref. 11,  $\mu = 0.65$ . <sup>b</sup> From semiquinone data. <sup>c</sup> Ref. 4,  $\mu = 0.65$ .

in the same order, ranging from 2600–4000 l./mole cm. for the hydroquinones to 4000–5500 l./mole cm. for the doubly ionized hydroquinones.

**Semiquinone Formation Constants,  $K'$ .** The constants,  $K'$ , for semiquinones other than *p*-benzosemiquinone were calculated from a series of  $K$  values at different pH values, by means of eq. 11 (Table II). The pH range for  $K$  was high enough in all cases that  $K_1$  did not enter into the calculations. For the methyl and methoxy substituted semiquinones,  $K_c$  was negligibly small up to pH 13.4, but  $K_2$  was small enough to interfere with the calculation and had to be determined, along with  $K'$ . For the other semiquinones, which are listed in Table III,  $K_c$  was either known,<sup>9</sup> or was determined from the semiquinone data, along with  $K'$ . In these latter cases  $K_2$  was large enough to be determined independently.

### Discussion

The variation in the semiquinone equilibrium constants,  $K'$ , must be due to relatively different free energies of the species involved in the equilibria represented in eq. 1. Electronegative substituents on the ring should have stabilizing effects on these species in the order of neutral quinone, singly ionized semiquinone, and doubly ionized hydroquinone. Table II shows that higher values of  $K'$  were obtained as electronegative groups were added to the ring. Therefore, the combined lowering of the free energy of the two semiquinone anions must outweigh the free-energy change for the doubly ionized hydroquinone, resulting in a shift of the equilibrium to the semiquinone side. In general, the reverse effect was found with electron-donating groups. The anomalous higher values of the dimethyl and trimethyl semiquinone constants are probably due to operation of other effects which override the comparatively small inductive effect of methyl groups.

Error in  $K'$  is due primarily to the error in the determination of  $\epsilon$ , since a small change in the latter can lead to much larger changes in  $K$ . The reliability of the method used for obtaining  $\epsilon$  is shown in Figure 1b by the conformity of the data to a theoretical straight line. The several data points were obtained conveniently from one set of solutions by changing only the normality of the oxidant. Thus, the error in  $K'$  was estimated as less than 10%. The value of  $\epsilon$  for *p*-benzosemiquinone anion reported by Diebler, Eigen, and Matthies<sup>7</sup> to be 6400 l./mole cm. at 420 m $\mu$  had been

calculated by using a quinone concentration uncorrected for quinone-hydroxide complex formation. When this correction was made, the value became 7500 l./mole cm. in agreement with the figure found in this work. Likewise,  $\epsilon$  at 430 m $\mu$  became 8700 l./mole cm. instead of 7400 l./mole cm., and  $K = 2.3$  at pH 13 would be obtained instead of 4.7 as reported.

Finally, the need for a knowledge of the quinone equilibria at high pH in order to treat the semiquinone data properly is obvious from the above discussion. If a small value of  $K_c$ , *i.e.*, 1–10, is exhibited by a quinone, it can be detected by a study of the dependence of  $K$  on pH. In such a study of durosemiquinone,<sup>4</sup> no quinone-hydroxide reaction was observed up to pH 13.3. Some quinone-hydroxide adduct formation constants,  $K_c$ , have been determined independently and reported elsewhere,<sup>9</sup> but two of those in Table III had to be calculated from the pH dependence of semiquinone formation.

**Table III.** Quinone-Hydroxide Adduct Formation Constants at 25°

Quinone	$K_c$
<i>p</i> -Benzoquinone	8.3
2-Chloro- <i>p</i> -benzoquinone	364 <sup>a</sup>
2,5-Dichloro- <i>p</i> -benzoquinone	1700 <sup>a</sup>
<i>p</i> -Benzoquinonemonosulfonate	125 <sup>a</sup>
2-Octyl-5- <i>p</i> -benzoquinonesulfonate	6 <sup>b</sup>

<sup>a</sup> From ref. 9. <sup>b</sup> Determined as described for *p*-benzoquinone.

### Experimental

All quinones and hydroquinones were either commercially available or prepared by known methods. All were purified and the physical constants were checked with reported values.

All equilibria were measured at 25 ± 0.1°. Phosphate buffers were prepared by mixing appropriate volumes of K<sub>2</sub>HPO<sub>4</sub> and K<sub>3</sub>PO<sub>4</sub> solutions to give a final ionic strength of 0.375 in the reaction solution. When KOH was used, the ionic strength was adjusted with KCl. Nitrogen was bubbled through all solutions at least 15 min. before use to exclude oxygen.

The pH of equilibrium mixtures when buffers were used was measured on a Beckman Model G pH meter with a glass electrode. At pH above 12, standardized KOH solutions were used and the [H<sup>+</sup>] was calculated.

Ionization constants of the hydroquinones  $K_1$  and  $K_2$  were calculated from the ultraviolet spectra at various pH values. A  $10^{-3}$  M solution of the desired hydroquinone was prepared with deaerated water. Some hydroquinones are slow to dissolve in water, so they were first dissolved in a small volume of alcohol and this solution was added to water. The alcohol was never more than 0.5% of the total volume of the reaction solution. The hydroquinone solution was mixed in the volume ratio of 1:1 with various phosphate buffers or KOH solutions in a flow machine<sup>10</sup> and the ultraviolet absorption spectra were measured in the region of 220 to 400 m $\mu$ . A flow system was not actually necessary for this phase of the study since all of the hydroquinone species are stable at high pH. However, the apparatus was convenient in these cases since the deaerated solutions could be kept from contact with the air until the spectra were measured.

The pK values could be determined from plots of log (singly ionized hydroquinone/hydroquinone) or log (doubly ionized hydroquinone/singly ionized hydroquinone) vs. pH. However, we used the ratios of density differences instead of the ratios of concentrations<sup>12</sup> of the species. The analyses were made at wave lengths at which the difference in density between the two species was greatest.

The use of strong alkali necessary for the complete ionization of some hydroquinones had to be avoided in order to protect the quartz optics of the flow machine. Where pK<sub>2</sub> was very large, then, it was calculated along with  $K'$  from analysis of the pH dependence of  $K$ , as described in another section.

(12) C. A. Bishop and L. K. J. Tong, *J. Phys. Chem.*, **66**, 1034 (1962).

*Semiquinone Formation Data.* The semiquinones were produced in a jet mixing machine<sup>13</sup> by partial oxidation of a deaerated solution of hydroquinone with ferricyanide solutions of predetermined concentrations. The hydroquinone, ferricyanide, and buffer (or KOH) solutions were mixed in volume ratio of 1:1:2 and examined 16 msec. after mixing by measuring the per cent transmission through an interference filter at 420 or 430 m $\mu$  in a 0.25-cm. cell. In the time scale we used, the equilibrium according to eq. 1 was established instantaneously. No change in semiquinone concentration could be detected in the interval 16–100 msec., showing that irreversible side reactions were negligible.

The hydroquinone stock solutions were made up by dissolving  $2 \times 10^{-3}$  mole in 1 l. of water, so that the initial hydroquinone concentration,  $[R_0]$ , was  $5 \times 10^{-4}$  M after mixing in the flow machine. In most cases, the concentration was checked by showing that the maximum occurred in the  $D$  vs. per cent oxidation curve when precisely one-half of the calculated amount of oxidant required to oxidize  $R_0$  completely was added. In a few cases, e.g., the hydroquinonesulfonates, the solid hydroquinone was hydrated, so the weighed amount was something less than  $2 \times 10^{-3}$  mole. In these cases, the maxima in the  $D$  vs. per cent oxidation curves occurred when less than the expected amount of oxidant was added, but from the normality of the oxidant and the amount added at the maximum, the precise value of  $[R_0]$  was calculated.<sup>14</sup>

(13) W. R. Ruby, *Rev. Sci. Instr.*, **26**, 460 (1955).

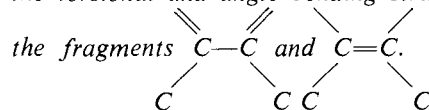
(14) NOTE ADDED IN PROOF. A similar treatment for *p*-phenylenediamines has appeared recently: L. K. J. Tong and M. C. Glesmann, *Phot. Sci. Eng.*, **8**, 319 (1964).

## Strain Effects. I. The Hydroxymethylene Ketone–Aldo Enol Equilibrium

Edgar W. Garbisch, Jr.<sup>1</sup>

Contribution from the Department of Chemistry of the University of Chicago, Chicago, Illinois 60637. Received June 12, 1964

Directions of enolizations of  $\alpha$ -formyl cyclic ketones relative to the cyclohexyl system ( $K_n/K_6$ ) have been estimated by considering strain energy differences between I and II. The good qualitative agreement between the calculated and observed values of  $K_n/K_6$  that is found suggests that the major effects that influence the relative directions of enolizations of  $\alpha$ -formyl cyclic ketones are the torsional and angle bending strains associated with



The effects of strain on chemical reactivities and equilibria are most pronounced in cyclic structures

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where molecular geometry takes on various forms of constraint. An understanding of the fundamental origin of reactivity of equilibrium differences in ring systems requires knowledge of the structures of the systems being compared, and this is a most formidable requirement particularly for the medium-sized and seven-membered rings whose basic structures might be expected to depend largely on the degree and nature of substitution.

The concept of I-strain<sup>2,3</sup> has led in some instances to rather quantitatively striking correlations between relative reactivities of chemically divergent processes involving a common change in carbon hybridization

(2) H. C. Brown and M. Gerstein, *J. Am. Chem. Soc.*, **72**, 2926 (1950).

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