New Aromatic Anions. X. Dissociation Constants of Substituted Oxocarbon Acids[1]

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Abstract: Dissociation constants of several substituted oxocarbon acids have been measured spectrophotometrically: phenylhydroxycyclopropenone, pK = 2.01; phenylhydroxycyclobutenedione, pK = −0.22; methylhydroxycyclobutenedione, pK = 0.24; and phenylhydroxycyclopentenetrione, pK = 1.64. The possible effect of "aromatic" electron delocalization in the anions of these species and of the unsubstituted oxocarbons is discussed. Values of H_-, useful in studying the dissociation of very strong uncharged acids, have been determined as a function of sulfuric acid concentration.

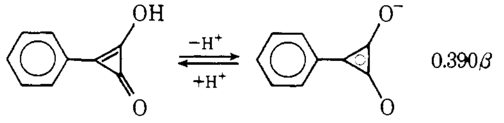
The cyclic anions of the simple oxocarbons, $C_nO_n^{-m}$, have been described as a new class of aromatic substances.[2] Evidence from vibrational spectroscopic[3] and X-ray[4-6] studies indicates that they are planar and symmetrical, implying complete π-electron delocalization, in agreement with MO calculations. The stability of these anions is demonstrated most dramatically by the very low pK's of the parent hydroxides which resemble inorganic rather than organic acids (Table I).

Table I. Dissociation Constants of Oxocarbon Acids[a]

Compd	pK_1	pK_2	Method	Ref
$H_2C_4O_4$	0.5	3.48	c	*b*
$H_2C_5O_5$	0.32	1.51	s	*c*
$H_2C_6O_6$	<1	<4.72	s	1b
1	**2.01 ± 0.03**		s	a
	2.0 ± 0.5		s	*d*
2	**−0.22 ± 0.1**		s	a
	+0.37 ± 0.04		s	*e*
3	**1.64 ± 0.09**		s	a
	1.75		p	*f*
4	**0.24 ± 0.1**		s	a
	0.69 ± 0.03		p	*g*

[a] a = this work; c = conductometric; s = spectrophotometric; p = potentiometric. Best values for **1–4** are in boldface. [b] L. M. Schwartz and L. O. Howard, *J. Phys. Chem.*, **74**, 4374 (1970); **75**, 1798 (1971). [c] D. J. Carlquist and D. Dyrssen, *Acta Chem. Scand.*, **16**, 94 (1962). [d] D. G. Farnum, J. S. Chickos, and P. E. Thurston, *J. Amer. Chem. Soc.*, **88**, 3075 (1966). [e] E. J. Smutney, M. C. Caserio, and J. D. Roberts, *ibid.*, **82**, 1793 (1960). [f] T. Yamazaki, T. Oohama, T. Doiuchi, and T. Takizawa, *Chem. Pharm. Bull.*, **20**, 238 (1972). [g] J. Chickos, *J. Amer. Chem. Soc.*, **92**, 5794 (1970).

Molecular orbital calculations suggest that phenyl-substituted oxocarbons may also be stabilized by π-electron delocalization. Using the parameters $\alpha_0 = \alpha_c + 0.3\beta$ and $\beta_0 = 1.4\beta$ suggested by the work of Baenziger and Hegenbarth on the structure of the croconate ion,[5] HMO calculations give the delocalization energies per π electron listed below for the anions of phenylhydroxycyclopropenone (**1**), phenylhydroxycyclobutenedione (**2**), and phenylhydroxycyclopentenetrione (**3**). Similar delocalization is proposed for the anion of methylhydroxycyclobutenedione (**4**) recently synthesized by Chickos.[7]



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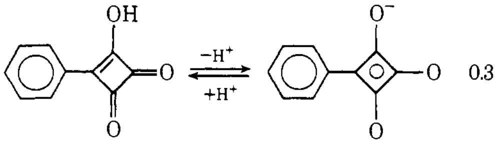

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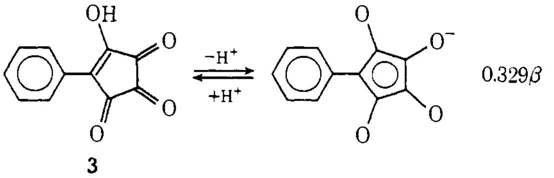

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Some information was already available about the acid dissociation constants of these substituted oxocarbons indicating that they are indeed quite strong acids (Table I). However, most of the literature values were either determined under poorly controlled conditions or were intended only to be approximate. Accordingly we have redetermined the dissociation constants of **1–4** spectrophotometrically. Our new values are given in Table I, along with earlier data on dissociation constants for these and related compounds.

Measurement of dissociation constants for several of these compounds posed special experimental problems. The dissociation constants of **1** and **3** were determined by spectrophotometric measurements as a function of pH, measured using a glass electrode. However, for **1** the maxima for the acid and its anion differ by only 10 nm, so that the bands overlap seriously. Precise results were obtained only by exceptionally careful calibration of the spectrometer. The ratio of dissociated to undissociated acid was measured at ten different wave-

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(1) Previous papers in this series: (a) E. Patton and R. West, *J. Phys. Chem.*, 77, 2652 (1973); (b) E. Patton and R. West, *ibid.*, **74**, 2512 (1970).

(2) R. West and J. Niu in "Non-benzenoid Aromatic Compounds," Vol. I, J. Snyder, Ed., Academic Press, New York, N. Y., 1969, p 312.

(3) M. Ito and R. West, *J. Amer. Chem. Soc.*, **85**, 2580 (1963).

(4) W. M. MacIntyre and M. S. Werkema, *J. Chem. Phys.*, **40**, 3563 (1964).

(5) N. C. Baenziger and J. J. Hegenbarth, *J. Amer. Chem. Soc.*, **86**, 3250 (1964).

(6) M. A. Neuman, Thesis, University of Wisconsin, 1966; *Diss. Abstr.*, **26**, 6394 (1966).

(7) J. Chickos, *J. Amer. Chem. Soc.*, **92**, 5794 (1970).

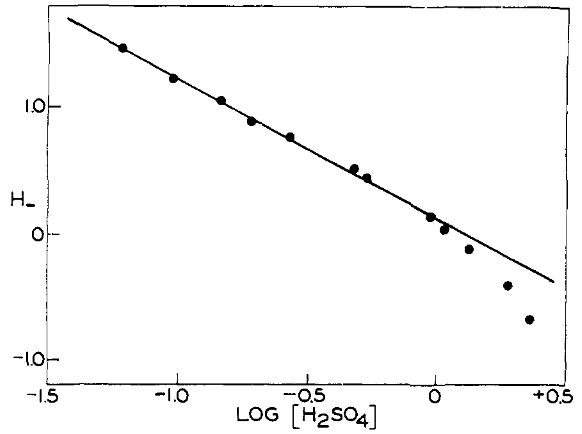

Figure 1. Values for H_- in aqueous sulfuric acid solutions as a function of concentration.

lengths and the average values were used to calculate p*K*. (Details of the determinations and calculations are given in the Experimental Section.)

Both **2** and **4** are such strong acids that solutions with pH between 0 and 1 are necessary to study their dissociation. Glass electrodes cannot be used in this region, so a procedure using the H– function was employed.[8] Previous studies of dissociation constants of very strong acids by this method were limited by the accuracy with which H_- was known. To obtain accurate H_- values for sulfuric acid, we made use of the recent, extremely careful redetermination of the p*K* for picric acid by Davis and Paabo.[9] The amount of dissociation of picric acid in various concentrations of sulfuric acid was determined spectrophotometrically and used to calculate the H_- values shown graphically in Figure 1. These should be the most reliable H_- values currently available, and are recommended for use in studying other very strong acids.

The measurement of the dissociation constants for **2** and **4** is further complicated by the fact that it is not possible to determine the spectrum of the undissociated acids, D_{HA}, exactly. At acid concentrations high enough so that the anions are fully protonated, slight solvent shifts appear (see Figures 4 and 5). However, by careful selection of the proper acid concentration to give complete protonation with minimum solvent shift we were able to minimize this problem and obtain data of good reproducibility.

Experimental Section

Spectrophotometric Determination of p*K*'s. Dissociation contants were determined using the relationship

$$\mathrm{p}K = \mathrm{pH} + \log [\mathrm{HA}]/[\mathrm{A}^-]) + \log (\gamma_{\mathrm{HA}}/\gamma_{\mathrm{A}^-}) \quad (1)$$

The ratio $[\mathrm{HA}]/[\mathrm{A}^-]$ is equal to $(D_{\mathrm{A}^-} - D)/(D - D_{\mathrm{HA}})$, where D_{A^-} is the optical density of the anion of a specific wavelength and concentration, D_{HA} is the optical density of the acid at the same wavelength and concentration, and D is the optical density of the mixture of these two at the same wavelength and total concentration of chromophore. A Cary Model 14 spectrophotometer was used for all measurements which were carried out at concentrations of $3\text{-}5 \times 10^{-5}$ *M*. The phenyloxocarbon anion spectra are given in Figure 2.

Activity coefficient corrections were calculated using the Debye–Hückel relationship, $-\log \gamma_{\mathrm{A}^-} = 0.509\sqrt{\mu}/(1 + 0.3A\sqrt{\mu})$, where A is the ionic diameter in Å, assumed to be 3 Å for **1** and 5 Å for **3**. The ionic strength of the sulfuric acid solutions, μ, was calculated in the following manner

$$\mu = {}^1/_2([\mathrm{H}^+] + [\mathrm{HSO_4}^-] + 4[\mathrm{SO_4}^{2-}])$$

The first dissociation of H_2SO_4 is assumed to be complete and the second partial

$$\mathrm{H_2SO_4} \rightleftharpoons \mathrm{H}^+ + \mathrm{HSO_4}^-$$

$$\mathrm{HSO_4}^- \rightleftharpoons \mathrm{H}^+ + \mathrm{SO_4}^{2-}$$

If $[\mathrm{H_2SO_4}]_0$ is the initial concentration of acid added to the solution, then

$$[\mathrm{SO_4}^{2-}] = [\mathrm{H}^+] - [\mathrm{H_2SO_4}]_0$$

$$[\mathrm{HSO_4}^-] = [\mathrm{H_2SO_4}]_0 - [\mathrm{SO_4}^{2-}]$$

$$= 2[\mathrm{H_2SO_4}]_0 - [\mathrm{H}^+]$$

$$\mu = 2[\mathrm{H}^+] - [\mathrm{H_2SO_4}]_0$$

Representative calculations show that assuming

$$[\mathrm{H}^+] = -\text{ antilog pH}$$

does not significantly affect the final values of log γ.

Phenylhydroxycyclopropenone (1). This compound was prepared by hydrolysis of 2-phenyl-1,1,3-trichlorocyclopropene as described elsewhere.[10] The recrystallized solid was washed with ether to remove traces of ether-soluble impurities, dried, and dissolved in water. Because **1** undergoes slow decomposition in aqueous solution, the stock solution was kept at 0° to prevent decomposition and stored for not more than 2 hr before use. To establish that negligible decomposition had taken place, the spectrum of the stock solution was checked before and after each series of runs; no measurable differences were observed.

For spectral determinations, aliquots of the stock solution were mixed with known volumes of water containing different amounts of sulfuric acid, and the spectrum was immediately determined. Five or six different concentrations of sulfuric acid were used for each run. The pH was measured using a glass electrode with a calibrated Beckman pH meter, and the spectrum was determined in the 240–280-nm region at the slowest possible scan rate. Because of the overlap of the absorption bands for **1** and its anion, D was measured and $(D_{\mathrm{A}} - D)/(D - D_{\mathrm{HA}})$ was calculated at each of the

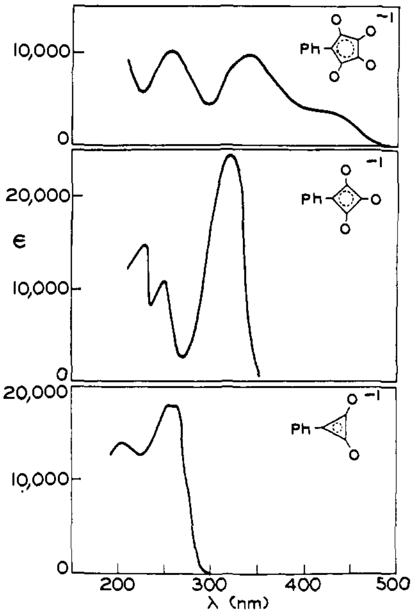

Figure 2. Visible–uv spectra of anions of phenyl-substituted oxocarbons.

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[8] L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, **54**, 2721 (1932).

[9] M. M. Davis and M. Paabo, *J. Res. Nat. Bur. Stand.*, **67**, 241 (1963).

[10] J. S. Chickos, E. Patton, and R. West, *J. Org. Chem.*, in press.

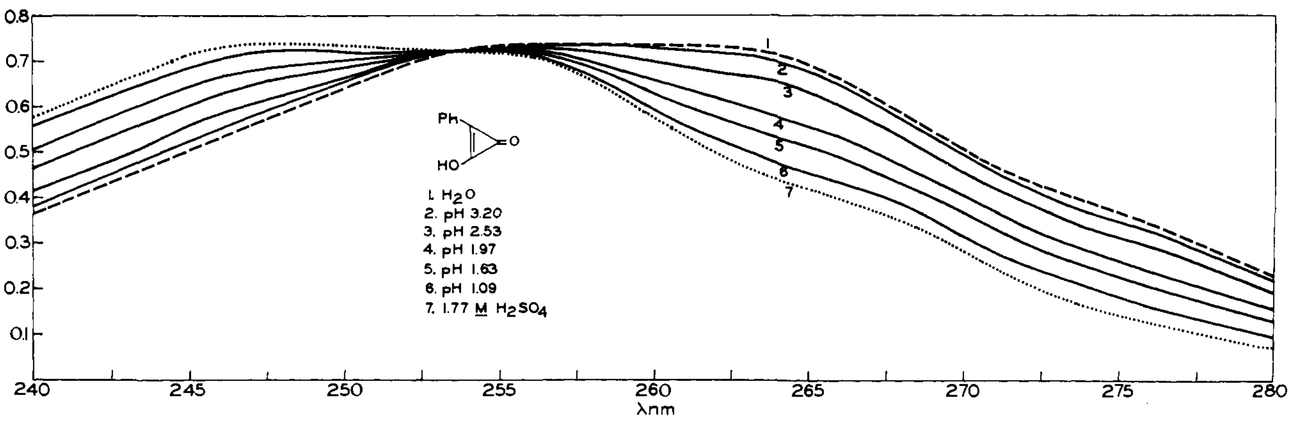

Figure 3. Spectra of phenylhydroxycyclopropenone, 4.1 × 10^{-5} M, as a function of pH.

following different wavelengths: 240, 242.5, 245, 247.5, 262.5, 264, 265, 267.5, 270, 272.5, 275, 277.5 nm. These values were averaged to obtain the best value of $(D_A - D)/(D - D_{HA})$ for each pH. A typical series of spectral curves is shown in Figure 3, and representative pK data from one run are given in Table II.

Table II. pK of Phenylhydroxycyclopropenone

pH	Log $[(D_{A^-} - D)/(D - D_{HA})]$	$-$Log γ	pK
1.09	+0.82	0.09	2.00
1.63	+0.31	0.06	2.00
1.97	−0.02	0.05	2.00
2.53	−0.53	0.03	2.03
			2.01 ± 0.03

Values of D_A were taken from the spectrum of **1** in pure water, which was shown to be identical with the spectrum in 0.1 N sodium hydroxide. To obtain D_{HA}, the spectrum of **1** was determined in solutions containing progressively higher concentrations of sulfuric acid, until (at 1.77 M H_2SO_4 or higher) no further change was observed; it was assumed that the anion was then completely protonated and the spectrum in 1.77 M H_2SO_4 was used to calculate D_{HA}. This procedure is preferable to the common method of determining D_{HA} from solutions in highly concentrated acid, because at very high acid concentrations both solvent shifts of the absorption bands and further protonation to give cationic species may take place.

The determined pK value, 2.01 ± 0.03, agrees remarkably well with the previous determination on the same compound, 2.0 ± 0.5.[11] Because of the low accuracy of the earlier value the excellent agreement is probably fortuitous.

Determination of H₋. H_- is defined by the relationship

$$\mathrm{p}K = H_- + \log([\mathrm{HA}]/[\mathrm{A}^-]) \qquad (2)$$

It follows that

$$H_- = -\log[\mathrm{H}^+] + \log[\gamma_{\mathrm{HA}}/(\gamma_{\mathrm{A}^-} - \gamma_{\mathrm{H}^+})] \qquad (3)$$

The value of H_- for solutions of a strong acid is best determined by dissolving in it a chromophoric acid of known pK, and determining log ([HA]/[A⁻]) spectrophotometrically. This measurement can be carried out for several concentrations of the strong acid to determine H_- as a function of concentration. Once this relationship is established, it can be used to determine the value of H_- for solutions of the same strong acid in which a chromophoric acid of unknown pK is dissolved. Log ([HA]/[A⁻]) is measured spectrophotometrically and pK for the unknown acid is found from eq 2.[8]

No satisfactory tables of H_- values exist, so it was necessary to determine H_-. Sulfuric acid was chosen as the strong acid, and picric acid was used as the reference chromophore; according to the recent redetermination by Davis and Paabo,[9] its pK is +0.33.

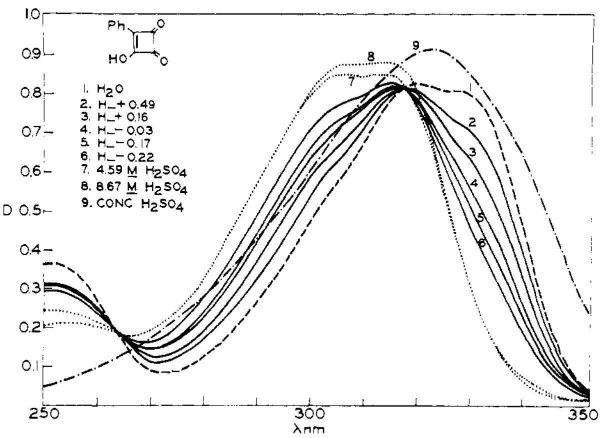

Figure 4. Spectra of phenylhydroxycyclobutenedione, 3.5 × 10^{-5} M, in aqueous sulfuric acid as a function of H_-.

A primary problem in studying an acid of this strength is to obtain a spectrum of the undissociated acid free of solvent shifts. Davis and Paabo circumvented this problem by selecting a wavelength (450 nm) at the tail of an absorption band where they could assume the optical density of the free acid was zero.

Following Davis and Paabo,[9] we dissolved picric acid in solutions of sulfuric acid of various concentrations and determined log [HPic]/[Pic⁻] at 450 nm. Results are shown graphically as a plot of H_- *vs.* H_2SO_4 concentration in Figure 1. The plot is linear at low concentrations, but falls off above $[H_2SO_4] = 1$ M, perhaps because the assumption that D_{HA} (450 nm) = 0 for picric acid is not exact and becomes less accurate at high concentrations, or because the variation of log $(\gamma_{HA}/\gamma_{A^-})$ is not linear in this region. (The function H_0 *vs.* log $[H_2SO_4]$ is also nonlinear in the highly acid region.)

Phenylhydroxycyclobutenedione (2). An analytically pure sample of **2** was kindly provided by J. Chickos. The neutralization equivalent was determined by titration with aqueous base to a phenolphthalein end point; neut. equiv 173.5 (calcd, 174). A weighed sample of the compound was dissolved in water to make a stock solution 3.5 × 10^{-5} M in **2**. Aliquots of the stock solution were mixed with sulfuric acid solutions of known concentration for spectral determinations.

Absorption spectra of **2** as a function of H_- for a typical run are shown in Figure 4. The best results were obtained by assuming that curve 7 was equivalent to D_{HA}. Ratios of $(D_A - D)/(D - D_{HA})$ were measured at the following wavelengths: 245, 274.5, 250, 255, 290, 292.5, 295, 297.5, 300, 302.5, 305, 307.5 nm. These values were averaged to give the best value for each acid concentration. At the highest H_2SO_4 concentrations used, where H_- is no longer linear with acid concentration, a short extrapolation of the linear plot in Figure 1 was used to estimate H_-. The pK values obtained in this region were consistent with those at lower acid concentrations.

Typical results are given in Table III; the pK found is −0.22. Although the reproducibility of the results indicates a precision of

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(11) D. G. Farnum, J. S. Chickos, and P. E. Thurston, *J. Amer. Chem. Soc.*, **88**, 3075 (1966).

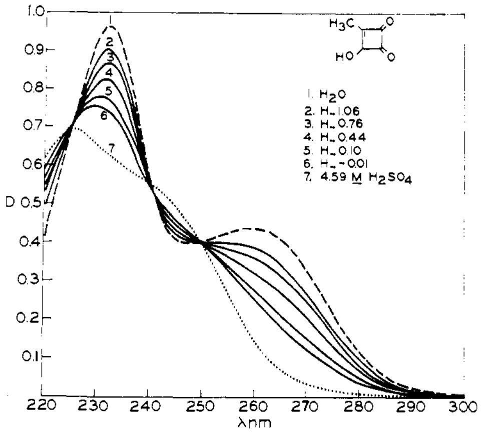

Figure 5. Spectra of methylhydroxycyclobutenedione, 3.6 × 10^{-5} *M*, in aqueous sulfuric acid as a function of H_-.

Table III. p*K* of Phenylhydroxycyclobutenedione

H_-	Log $[(D_{A^-} - D)/(D - D_{HA})]_{av}$	p*K*
−0.17	−0.03	−0.20
−0.03	−0.19	−0.21
+0.16	−0.39	−0.23
+0.49	−0.75	−0.24
		−0.22 ± 0.02

±0.02 p*K* unit, the measured p*K* is estimated to be accurate only to about ±0.1 unit because of uncertainties in H_- and in D_{HA}.

An earlier value of +0.37 has been reported for the p*K* of Smutney, Caserio, and Roberts.[12] Part of the difference between their value and ours is due to their use of an older, less accurate value for p*K* of picric acid, employed as a standard.

Methylhydroxycyclobutenedione (4). Analytically pure material was kindly provided by Chickos;[7] neut. equiv 114 (calcd, 112). The method used was the same as that described for **2** above; a typical family of spectra is shown in Figure 5. A solution in H_2O was used for D_A; a solution in 4.59 *M* H_2SO_4 (curve 7 of Figure 5) was used for D_{HA}. This curve shows very slight solvent shifts so that it does not pass exactly through the isosbestic points of Figure 5. Values of $(D_A - D)/(D - D_{HA})$ were determined at the following wavelengths: 230, 232.5, 257.5, 260, 262.5, 265, 267.5, and 270 nm, and the averages were used to calculate p*K* (Table IV).

Table IV. p*K* of Methylhydroxycyclobutenedione

H_-	Log $[(D_{A^-} - D)/(D - D_{HA})]_{av}$	p*K*
−0.01	0.26	0.25
0.10	0.13	0.23
0.44	−0.17	0.27
0.76	−0.43	0.33
		0.27 ± 0.04

Although the precision of the data is again quite high (±0.04), the accuracy of our value is believed to be ±0.1 p*K* unit, once again because of possible inaccuracies in H_- and D_{HA}. The p*K* of **4** was previously estimated at +0.69 by Chickos;[7] however, this figure was obtained simply by measuring the pH of solutions of **4** of differing concentration, a method which can give only highly approximate p*K* values for acids of this strength.

Phenylhydroxycyclopentenetrione (3). A sample of **3** was kindly provided by Dr. T. Yamazaki.[13] The p*K* of phenylcroconic acid was determined using the same procedure as that employed for phenylhydroxycyclopropenone except that the variation of log $[(D_{A^-} - D)/(D - D_{HA})]$ with pH was only measured at one wavelength, 390 nm. The optical density at this wavelength changed substantially with pH, as illustrated in Figure 6. The p*K* found was 1.64 ± 0.09, in good agreement with the value of 1.75 determined by Yamazaki.[13] Data are listed in Table V.

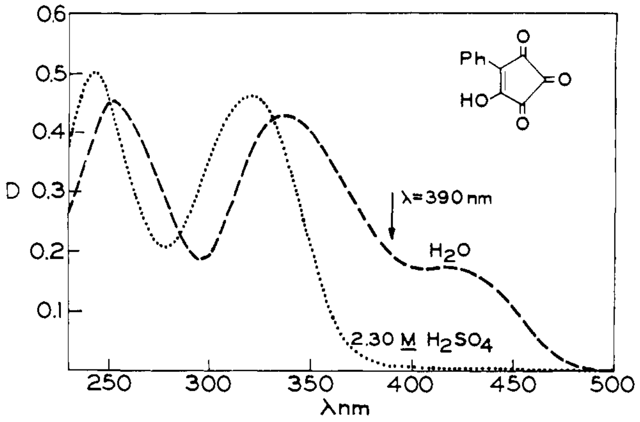

Figure 6. Spectrum of phenylhydroxycyclopentenetrione, 4.5 × 10^{-5} *M*, in water and in 2.30 *M* H_2SO_4. Measurements of *D* were carried out at 390 nm.

Table V. Representative Data. pK_a of Phenylhydroxycyclopentenetrione

pH	Log $[(D_A - D)/(D - D_{HA})]$	−Log γ_{A^-}	p*K*
1.18	+0.37	0.08	1.63
1.44	+0.14	0.07	1.65
1.82	−0.20	0.05	1.67
2.06	−0.60	0.05	1.51
2.36	−0.63	0.03	1.76
			1.64 ± 0.09

Discussion

It is of interest first to examine the p*K*'s of the unsubstituted monocyclic oxocarbons. For these compounds full aromatic delocalization can occur only in the dianions, so the pK_2 values should reflect this stabilization. The second dissociation constants of squaric acid and croconic acid lie between 1.5 and 3.5 (Table I). The diesters of dihydroxymaleic acid are suitable reference compounds; they show pK_2 values between 12 and 12.5.[14] Thus cyclodelocalization in the oxocarbon dianions is associated with a decrease of about 10 p*K* units in base strength, or a corresponding increase in acid strength of the parent oxocarbons.

In a careful conductrimetric study, Schwartz and Howard[15] have shown that the low value of pK_1 for squaric acid is due to an unusually low entropy change, rather than to an unusually large negative $-\Delta H°$ value, for the first dissociation. The low entropy change could be attributed either to (1) an unusual degree of ordering of the solvent by free squaric acid, or to (2) an unusually low degree of solvent ordering by the monoanion, perhaps reflecting its partial electron delocalization. These results raise an interesting question: how

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[12] E. J. Smutney, M. C. Caserio, and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 1793 (1960).

[13] T. Yamazaki, T. Oohama, T. Doiuchi, and T. Takizawa, *Chem. Pharm. Bull.*, 20, 238 (1972)

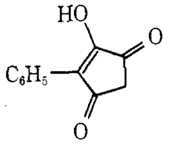
[14] W. D. Kumler and T. C. Daniels, *J. Amer. Chem. Soc.*, **57**, 1929 (1935).

[15] L. M. Schwartz and L. O. Howard, *J. Phys. Chem.*, **74**, 4374 (1970); **75**, 1798 (1971).

much of the stabilization of the oxocarbon dianions is due to energetic and how much to entropy effects? Unfortunately, for the crucial second step of ionization, no data at different temperatures are available for any of the oxocarbons.

Turning now to substituted oxocarbons, the addition of a substitutent group which breaks the symmetry should partially localize charge and hence reduce stabilization of the oxocarbon anions, relative to reference species. Enols of 1,3-diketones, which can be taken as reference compounds, usually have pK = 4.5–5.5. The substituted oxocarbons **1** and **3** have pK values near 2 (Table I); the modest increase in acidity of 3 pK units can perhaps be associated with cyclodelocalization in anions of these species. A still better reference compound for **3** is **5**, for which Yamazaki reports pK = 3.55,[13] or about 2 pK units greater than for **3**.

The four-membered ring compounds **2** and **4** show still higher acid strength. This finding is paralleled by the fact that enols of 1,3-diketones in four-membered rings generally show enhanced acidity. For example, cyclobutane-1,3-dione shows pK = 3.0 compared to 5.25 for 1,3-cyclohexanedione. Smutney, Caserio, and Roberts[12] have discussed the high acid strength of **2**; they suggest that 1,3-transannular bonding as in resonance structure **6** may be responsible, and support this suggestion with qualitative MO calculations.[12] However, Johns and Kriegler[16] have pointed out that favorable dipolar interaction between the CO groups can account for most of the increased acid strength of four-ring 1,3-dicarbonyl compounds. Entropic effects of the sort found by Schwartz and Howard may also be important.[15] Whatever the source of the enhanced acidity of four-membered ring compounds of this type, it is apparently reflected in the acid strength of **2** and **4**, where it combines with electron delocalization to make these compounds very strong acids indeed.[17]



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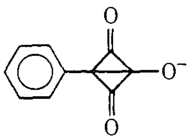

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It is interesting that the enhanced acidity of four-ring dicarbonyl compounds is not found for squaric acid itself, which is actually somewhat weaker in its second dissociation constant than the five-membered ring croconic acid. The stability of squarate dianion may be reduced by 1,3-transannular electron repulsion interactions between carbon atoms, as suggested also by detailed vibrational analysis of the dianion.[3]

Acknowledgment. This work was partially supported by a grant from the National Science Foundation.

(16) R. B. Johns and A. B. Kriegler, *Aust. J. Chem.*, **17**, 765 (1964).

(17) Dissociation constants of two substituted phenylhydroxycyclobutenediones have been measured by W. Broser and M. Seekamp [*Tetrahedron Lett.*, **51**, 6337 (1966)]. They report pK = 1.85 for *p*-methoxyphenylhydroxycyclobutenedione and pK = 2.05 for *p*-hydroxyphenylhydroxycyclobutenedione; their values are repeated in a recent review.[18] These data were obtained potentiometrically on 10^{-2} solutions in 50% aqueous acetone. It is likely that this method gives inaccurate results at this concentration and that Broser and Seekamp's results are in error.

(18) W. Reid and A. H. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **11**, 997 (1972).

N-*tert*-Butylanilino Radicals. II. Dimerization of *N*,3,5-Tri-*tert*-butylanilino Radicals

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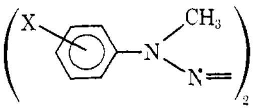
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received July 28, 1973*

Abstract: Thermodynamic parameters for the reaction $(\mathrm{ArN}\text{-}t\text{-}\mathrm{Bu})_2 \rightleftarrows 2(\mathrm{ArN}\text{-}t\text{-}\mathrm{Bu})$, $K = k_1$ (forward reaction)/k_2 (reverse reaction), have been evaluated to be $K = \exp(-31{,}200/RT)\exp(73/R)$, and $k_2 = kt/h \exp(+2200/RT) \exp(-65/R)$ by measuring the concentration of ArN-*t*-Bu using esr. The implications of these unusual $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the mechanism of the reaction are discussed, and it is concluded that their unusual sizes are dictated by the severe conformational restraints on the reaction.

In a previous paper on *N*-*tert*-butylanilino radicals,[1] it was found that both electron-withdrawing and -releasing substituents at the para position of the benzene ring decrease the nitrogen esr splitting constant (a(N)), demonstrating that these radicals are members of Walter's "class S,"[2] in which both types of substituents affect properties such as a(N) in the same direction. This was of particular interest with regard to the effect of substituent upon the rate of decomposition of 1,4-dimethyl-2-tetrazenes (**1**). Since **1** (4-OCH_3) decomposed 200 times as fast as **1** (4-CO_2Et), and other substituents followed the Hammett equation reasonably



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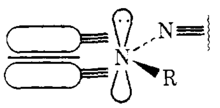

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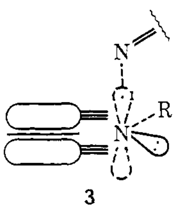

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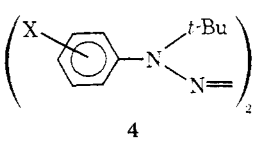

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(1) S. F. Nelsen, R. T. Landis, L. H. Kiehle, and T. H. Leung, *J. Amer. Chem. Soc.*, **94**, 1610 (1972).

(2) (a) R. I. Walter, *ibid.*, **88**, 1923 (1966). (b) For a review of Hammett behavior of esr splittings, see E. G. Janzen, *Accounts Chem. Res.*, **2**, 279 (1969).