LiClO$_4$, k_{salt}/k_0 = 1.2), small substituent effects ($k_{C_6H_5C(Me)OHCO_2H}$:$k_{C_6H_5CHOHCO_2H}$:$k_{p\text{-}CH_3C_6H_4CHOHCO_2H}$ = 0.91:1.0:1.2), and relative insensitivity to solvent polarity (small and parallel rate changes with cosolvents, acetic anhydride, acetonitrile, and benzene) argue against pathways involving rate-determining ionization.[3] Furthermore, none of the observations indicating a free-radical pathway for the decarboxylation of monofunctional carboxylic acids, (1) induction times and sigmoidal rate profile with time, (2) very strong inhibition by oxygen in every case, (3) increased rates with uv illumination, and (4) radical trapping, were observed during mandelic acid cleavage by Pb(OAc)$_4$ in acetic acid solvent. Parallel runs using degassed samples in an oxygen-free atmosphere had virtually identical rates with those exposed to the atmosphere; also, bubbling air through a degassed sample did not change the rate of oxidative cleavage. Decarboxylations of pivalic, phenylacetic, and acetic acids all yielded free radicals which were trapped by acrylonitrile. In contrast, no radicals could be detected during the cleavage of mandelic acid under identical conditions. Similarly, Trahanovsky[5] differentiated between free-radical and non-free-radical mechanisms for glycol cleavage by Ce^{IV} and Pb(OAc)$_4$, respectively, by trapping radicals with acrylamide during the cerium(IV) oxidation. None could be detected during the lead tetraacetate cleavage.

(5) W. S. Trahanovsky, L. H. Young, and M. H. Bierman, *J. Org. Chem.*, **34**, 869 (1969).

(6) R. Criegee, "Oxidations with Lead Tetraacetate", Oxidation in Organic Chemistry, Part A, K. Wiberg, Ed., Academic Press, New York, N.Y., 1965, p 281.

(7) (a) B. Kamenar, *Acta Crystallogr., Sect. A*, **16**, 34 (1963); (b) R. Partch and J. Monthony, *Tetrahedron Lett.*, 4427 (1967).

(8) F. R. Preuss and J. Janshen, *Arch. Pharm.* (*Weinheim*), **295**, 284 (1965).

(9) A. W. Davidson, W. C. Lanning, and M. Zeller, *J. Am. Chem. Soc.*, **64**, 1523 (1942).

(10) R. Criegee, L. Kraft, and B. Rank, *Justus Liebigs Ann. Chem.*, **507**, 159 (1933).

(11) R. E. Partch, *Tetrahedron Lett.*, 3071 (1964).

(12) R. Criegee and E. Buchner, *Ber.*, **73**, 563 (1940).

(13) W. H. Starnes, Jr., *J. Am. Chem. Soc.*, **90**, 1807 (1968).

(14) (a) J. K. Kochi, *J. Am. Chem. Soc.*, **87**, 3609 (1965); (b) J. K. Kochi, *J. Org. Chem.*, **30**, 3265 (1965).

(15) (a) D. Benson, P. J. Proll, L. H. Sutcliffe, and J. Walkley, *Discuss. Faraday Soc.*, **29**, 60 (1960); (b) D. Benson and L. H. Sutcliffe, *Trans. Faraday Soc.*, **55**, 246 (1960); (c) D. Benson and L. H. Sutcliffe, *ibid.*, **55**, 2107 (1959).

(16) R. O. C. Norman, *J. Chem. Soc. B*, 781 (1969).

(17) C. A. Grob, M. Ohta, and A. Weiss, *Angew. Chem.*, **70**, 343 (1958).

(18) Y. Pocker and B. P. Ronald, *J. Am. Chem. Soc.*, **92**, 3385 (1970).

(19) J. A. Riddick and W. B. Bunger, "Organic Solvents, Techniques of Chemistry", Vol. 2, 3rd ed, Wiley-Interscience, New York, N.Y., 1970.

(20) A. I. Vogel, "A Textbook of Practical Organic Chemistry Including Qualitative Analysis", 3rd ed, Wiley, New York, N.Y., 1964, pp. 177.

(21) Reference 20, p 169.

(22) C. P. Smyth and W. S. Walls, *J. Am. Chem. Soc.*, **53**, 527 (1931).

(23) R. O. C. Norman, *J. Chem. Soc. B*, 184 (1968).

(24) Y. Pocker and B. P. Ronald, *J. Org. Chem.*, **35**, 3362 (1970).

(25) Y. Pocker and B. C. Davis, *J. Chem. Soc., Chem. Commun.*, 803 (1974).

(26) J. Buchi, *Pharm. Acta Helv.*, **6**, 1 (1931).

(27) Rate constant for the catalytic portion, $\Delta k = k_{obsd} - k_0$, where k_{obsd} is the experimentally determined second-order rate constant and k_0 is the constant for mandelic acid cleavage in the absence of catalyst; $k_0 = 9.80 \times 10^{-3}\ M^{-1}\ sec^{-1}$.

(28) These rate constants were extrapolated from the data in Table I and Figures 1 and 2, correcting to the solvent dilution found when both addends are present, i.e., [HOAc] = 14.9 *M*.

(29) J. P. Cordner and K. H. Pausacker, *J. Chem. Soc.*, 102 (1953).

(30) All the evidence so far cited indicates that the oxidative cleavage of mandelic acid by (B)$_n$Pb(OAc)$_4$ occurs via a more or less concerted pathway in which the rate-determining step apparently involves the decomposition of the cyclic intermediate **3**. In Scheme I, we depicted intermediate **3** as being formed from **2** ≡ PhCH(COOH)OPb(OAc)$_3$(B)$_n$; however, none of the above observations would preclude its formation from **2′** ≡ PhCH(OH)COOPb(OAc)$_3$(B)$_n$. Similarly, in the reaction pathway depicted in Scheme II, intermediate **2** ≡ PhCH(COOH)OPb(OAc)$_3$ could be replaced by **2′** ≡ PhCH(OH)COOPb(OAc)$_3$. At the same time, the importance of a free hydroxyl group in the substrate is made apparent by the fact that whereas 1,2-diols, 2-hydroxy acids, 2-hydroxy esters, and benzoin are oxidized by LTA, 2-keto acids, mandelic acetate, and benzil are not.[3]

(31) (a) E. D. Hughes, C. K. Ingold, S. F. Mok, S. Patai, and Y. Pocker, *J. Chem. Soc.*, 1265 (1957); (b) Y. Pocker, *Proc. Chem. Soc., London*, 226 (1959).

(32) (a) I. M. Kolthoff and S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1 (1956); (b) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 10 (1956); (c) I. M. Kolthoff, *Experientia, Suppl.*, V, 33 (1956).

(33) Clearly, it should be recognized that even more complex equilibria may play a significant part in catalysis; e.g., efficiency among acetate salts may also be related to the relative abilities of $(M^+)^n[Pb(OAc)_{4+n}{}^{-n}]$ ion pairs to form Pb(IV)–mandelic acid intermediates. Further, changing Δk/[addend] with greater catalyst concentration could be related not only to the number of addend molecules in the activated complex, but also to the amount of aggregation into even larger species. Norman[16] has isolated a salt from a mixture of NaOAc and LTA in pyridine and acetic acid containing two lead and ten acetate moieties, and Kolthoff and Bruckenstein[32a] have reported that KOAc and pyridine in HOAc begin to form ionic aggregates above 0.04–0.05 *M* addend.

(34) R. C. Paul and B. R. Sreenathan, *Indian J. Chem.*, **4**, 348 (1966).

A Reexamination of the Equilibrium Addition of Bisulfite and Sulfite Ions to Benzaldehyde

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The equilibrium constants for the addition of "bisulfite ion" to benzaldehyde were determined at 21° and μ = 1.0 *M* over the pH range 3.55–12.62. A spectrophotometric method was employed. The pH dependence of these observed constants was used to obtain values for the equilibrium constants for the reaction of benzaldehyde with HSO_3^- and SO_3^{2-}, and for the acidity constant of the benzaldehyde–HSO_3^- adduct. A comparison of our results with the earlier reports of Stewart and Donnally suggests that the titration method used by these workers yielded inaccurate equilibrium constants at pH's >8. The effect of our equilibrium results on the kinetic scheme and parameters for the reaction of benzaldehyde and bisulfite ion is also discussed.

Some time ago Stewart and Donnally[1] reported a study of the equilibria for the reaction of bisulfite ion[2] and benzaldehyde over the pH range 0–13 in which they determined the extent of reaction by titration of unreacted bisulfite ion with iodine. We became interested in reexamining this reaction because in the above study the observed dependence of the equilibrium constant vs. pH led to the claim that at the more basic pH's hydroxide ion was adding to a measurable extent to the carbonyl group of benzaldehyde. Using Stewart and Donnally's value for the equilibrium constant for the addition of hydroxide ion to benzaldehyde, $10^{1.4}\ M^{-1}$,[1c,3] together with an estimate of the pK_a of benzaldehyde hydrate of $10^{-12.7}\ M$,[4] one can calculate that in aqueous solution the ratio of hydrated to unhydrated benzaldehyde should be about 1.0, which is contrary to the known lack of hydration of this compound.[5] Recently, Greenzaid[5] and Zuman[6] have determined that the equilibrium constant for the addition of hydroxide ion to benzaldehyde is in fact only $10^{-0.9}\ M^{-1}$. Thus either Stewart and Donnally's determination of the observed equilibrium constant[1b] for the addition of bisulfite ion to benzaldehyde at high pH is in error, or their interpretation of the observed behavior is in error.

Similarly, the work of Stewart and Donnally[1c] led to a value for the pK_a of PhCH(OH)SO$_3^-$ of 9.5, while Taft[7] and "σ^I"[10] correlations lead to estimates of this pK_a as 11.7

and 13.8, respectively. The discrepancies are rather large to be totally a failure of the methods of estimation. Green and Hine[12] also have noted recently that the pK_a of 9.5 seems low.

Experimental Section

Reagents and Solutions. Benzaldehyde (J. T. Baker "N.F.") was redistilled at atmospheric pressure under nitrogen and stored under nitrogen in small vials at −15°. Samples of benzaldehyde stored in this way showed no signs of oxidation (as evidenced by the formation of crystals of benzoic acid inside or around the cap) for about 3 weeks. A ^1H NMR spectrum of neat freshly distilled benzaldehyde showed that there was at most 0.1% benzoic acid in the sample.

Stock solutions of benzaldehyde about 0.03 or 0.06 M in 95% ethanol as solvent were prepared by syringing 35 or 70 μl of benzaldehyde into a tared 10-ml volumetric flask that contained 1–2 ml of ethanol, reweighing the flask, and diluting to the mark with ethanol. Using solutions prepared by accurately syringing aliquots of these stock solutions into known volumes of cyclohexane, the molar extinction coefficient of benzaldehyde at 242 nm was measured as 14,540 cm^2/mol (lit.[13] 14,500). In 0.10 M phosphate buffer, pH 7.18, $\mu = 1.0\ M$ with KCl, benzaldehyde showed a slight deviation from Beer's law with ϵ^{250} decreasing from 1.387×10^4 at $1.125 \times 10^{-5}\ M$ to 1.335×10^4 at $7.836 \times 10^{-5}\ M$. In a separate experiment, the addition of a fixed volume of benzaldehyde stock solution to aliquots of the various buffers used for the equilibrium experiments (vide infra) showed that ϵ^{250} was independent of pH and the nature of the buffer. If care was taken to exclude O_2, benzaldehyde stock solutions were stable at −15° for up to 1 week, as shown by the fact that the absorbance at 250 nm of samples prepared by mixing a fixed volume of stock solution to a fixed volume of buffer were constant over this length of time.

Stock solutions of sodium sulfite 0.05–0.10 M were prepared from Fisher "Certified A. C. S." anhydrous Na_2SO_3 and degassed distilled water containing 5% (v/v) ethanol[14] and were stored under nitrogen at 4°. Standardization was carried out by addition with stirring of an aliquot of the Na_2SO_3 to an excess of standard I_2–KI solution followed by back titration of the excess I_2 with standard sodium thiosulfate solution.[15] All operations were done under a nitrogen atmosphere. Although this standardization is described in numerous texts, it is not usually mentioned that efficient stirring during the addition of the sulfite solution to the iodine solution is extremely important. Without rapid stirring we obtained erratic results that probably resulted from the fact that the stoichiometry of the reaction between iodine and sulfite is pH dependent and the desired reaction $I_3^- + SO_3^{2-} + H_2O \rightarrow 3I^- + SO_4^{2-} + 2H^+$ is obtained only at acid pH's. Stock solutions of 0.125 M K_2SO_3 ($\mu = 1.0\ M$ withKCl) were prepared from reagent-grade chemicals and standardized as above. These solutions were used at pH 11.90 and 12.62.

Buffer solutions were prepared from Fisher Certified reagents and degassed distilled water. Following any necessary dilutions (*c.f.* Equilibrium Studies) the buffers consisted of pH 3.55, 0.63 M acetic acid–sodium acetate; pH 5.27, 0.60 M acetic acid–sodium acetate; pH 6.78 and 7.46, 0.80 M NaH_2PO_4–Na_2HPO_4; pH 8.14, 9.08, and 10.24, 0.10 M boric acid–sodium borate. At pH 11.11 and above, potassium hydroxide of an appropriate concentration was prepared using a carbonate-free J. T. Baker "Dilut-it" concentrate. All buffers were brought to ionic strength 1.0 M with KCl. Buffer solutions were stored at 4° under nitrogen.

Standard hydrochloric acid solutions were prepared from "Dilut-it" concentrate.

Equilibrium Studies. For equilibrium determinations at or above pH 9.08, 2.0 ml of buffer solution was pipetted into a 25-ml erlenmeyer flask, n ml of sodium sulfite stock solution was added, then $8 - n$ ml of water. The solution was thoroughly mixed and a 1.0-ml aliquot was transferred to a 0.5-cm path length quartz cuvette with a Teflon stopper. At or below pH 8.14, 3.0 ml of buffer was pipetted directly into a 1.0-cm path length quartz cuvette with a Teflon stopper, and 10–70 μl of stock sulfite solution was added from a 100-μl Hamilton syringe. The accuracy and precision of this syringing technique were checked by doing several dilutions of acidic dichromate solutions and monitoring the final dichromate concentration at 257 nm, an absorption maximum. This control showed that delivery of 40-μl aliquots was reproducible within less than 1%, and that with volumes up to 70 μl the accuracy of this dilution was comparable to that achieved using ordinary volumetric techniques. At all pH's flasks and cuvettes were flushed with nitrogen. The cells were placed in the temperature-controlled cell holder of the spectrophotometer and allowed at least 10 min to equilibrate to temperature.[16] The absorbance at 250 nm of the buffer + sulfite solution was measured vs. air, and then an aliquot (constant in a "run" but varying from 2 to 4 μl) of benzaldehyde stock solution was added to the cell and the solution was well mixed. The cell was returned to the spectrophotometer and the absorbance at 250 nm was read after 10 min or after the absorbance became constant. Following equilibration the pH of the reaction solution was remeasured; in all cases the addition of benzaldehyde caused no measureable pH change.

Potentiometric Titrations. Duplicate titrations of 25.0-ml aliquots of 0.1159 M Na_2SO_3 ($\mu = 1.0\ M$ with KCl) with 0.1000 M HCl, duplicate titrations of 20.0-ml aliquots of 0.0772 M Na_2SO_3 ($\mu = 1.0\ M$ with KCl) with 0.1000 M HCl that was 0.90 M in KCl, and a single titration of a 20.0-ml aliquot of 0.0166 M Na_2SO_3 ($\mu = 1.0\ M$ with KCl) with 0.0100 M HCl were performed using a reaction vessel thermostated at 21°. The observed pH–volume HCl points were used to calculate an apparent pK_a according to the equation $pK_a = pH - \log([SO_3^{2-}]/[HSO_3^-]$, where the concentrations of SO_3^{2-} and HSO_3^- are calculated from mass and charge balance assuming $[H^+] = 10^{-pH}$. The pK_a's calculated in this way were 6.59–6.64 for $[SO_3^{2-}]/[HSO_3^-]$ ratios of 0.2–20.

Instrumentation. Absorbance measurements were made on a Pye-Unicam SP1700 visible-uv spectrophotometer that was equipped with a circulating water-type thermostable cell holder connected to a Lauda K4R thermostat that was operated at 21.0 ± 0.3°. Absorbance readings were taken directly from the digital readout, which has a precision of 0.001 absorbance units. At higher absorbances, where meter fluctuations exceeded ±0.001, 20–50 instantaneous readings were averaged to obtain the true absorbance. The linearity of the absorbance readout was checked in two ways. First we showed that the absorbances at 250 nm of acidic potassium dichromate solutions were linear with dichromate concentrations. Secondly, during the determination of K_{obsd} at pH 12.6, we found that if after we measured the absorbance of a solution of sulfite we placed in the sample beam an additional cell containing a dichromate solution, then the increase in absorbance was nearly independent of the absorbance of the sulfite, decreasing from 1.073 at no sulfite to 1.040 when the absorbance due to sulfite was 1.2. In this same interval of sulfite concentrations, the increase in absorbance caused by addition of constant volume aliquots of benzaldehyde stock solution decreased from 1.053–1.083 to 0.934–0.937.

The pH measurements were made with a Radiometer Model 26 pH meter equipped with a Radiometer GK2321C combination pH electrode that was calibrated using Fisher and Radiometer standard buffers.

Results

The equilibrium constant for the formation of benzaldehyde bisulfite at any given pH was obtained by adding a known amount of benzaldehyde to buffers that contained known concentrations of bisulfite ion, which was always in a large molar excess. Under these conditions the assumption that the free aldehyde but not the adduct absorbs leads to eq 1

$$\frac{1}{\Delta A} = \frac{K_{obsd}[\text{bisulfite}]_{total}}{\epsilon_B[\text{benzaldehyde}]_{total}} + \frac{1}{\epsilon_B[\text{benzaldehyde}]_{total}} \tag{1}$$

where ΔA is the increase in absorbance caused by addition of the benzaldehyde, K_{obsd} is the observed equilibrium constant for adduct formation (defined below), ϵ_B is the molar extinction coefficient of benzaldehyde, and the remaining terms are total concentrations. Plots of $1/\Delta A$ vs. $[\text{bisulfite}]_{total}$ were made for a five-to-eight-fold charge in $[\text{bisulfite}]_{total}$ and at two separate toal aldehyde concentrations at most pH's. All such plots were linear (and therefore showed no evidence of bisulfite oxidation during sample preparation or analysis) and gave intercepts on the $1/\Delta A$ axis in agreement with the extinction coefficient of benzaldehyde that was determined independently. Plots of the absorbance (vs. air) of the buffered solutions of bisulfite ion were approximately linear at all pH's studied. Using the apparent extinction coefficient of bisulfite ion at any

Table I
Values of Log K_{obsd} vs. pH at 21° and $\mu = 1.0\ M$

pH	Log K_{obsd}	[Benzaldehyde]$_{total}$ × 10^5	[Bisulfite]$_{total}$ × 10^3	No. of points
0.081	2.300	9.86	2.64	5
3.55	3.796	9.86	2.64	6
3.55	3.806	4.93	2.64	6
5.27	3.803	8.52	2.60	6
5.27	3.871	4.26	2.60	6
6.78	3.721	9.86	2.64	6
6.78	3.704	4.93	2.64	6
7.46	3.082	8.52	2.60	6
7.46	3.003	4.26	2.60	6
8.14	2.549	9.86	2.64	6
8.14	2.581	4.93	2.64	6
9.08	1.549	12.78	79.7	7
9.08	1.509	6.39	79.7	7
10.24	0.541	15.98	91.1	6
10.24	0.539	12.78	91.1	5
10.70	0.236	~16.6	98.2	7
11.11	−0.0567	14.80	69.5	5
11.71	0.0056	12.78	79.7	6
11.90	0.3175	~16.6	99.5[a]	5
12.62	0.1178	~16.6	99.5[a]	12

[a] Prepared from potassium sulfite.

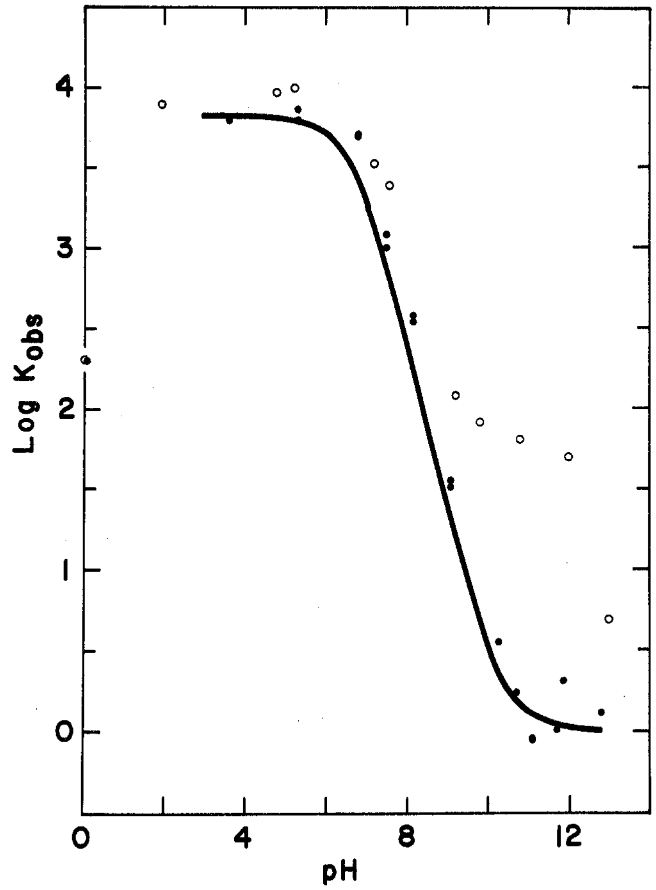


Figure 1. Log K_{obsd} for benzaldehyde bisulfite formation at 21° *vs.* pH: ●, our data; ○, data of Stewart and Donnally.[1b]

pH together with the relative total concentrations of benzaldehyde and bisulfite ion, it can be shown that when benzaldehyde is added to bisulfite solution, the decrease in absorption due to bisulfite caused by the conversion of bisulfite ion to adduct is negligible compared to the increase, ΔA, caused by the benzaldehyde.

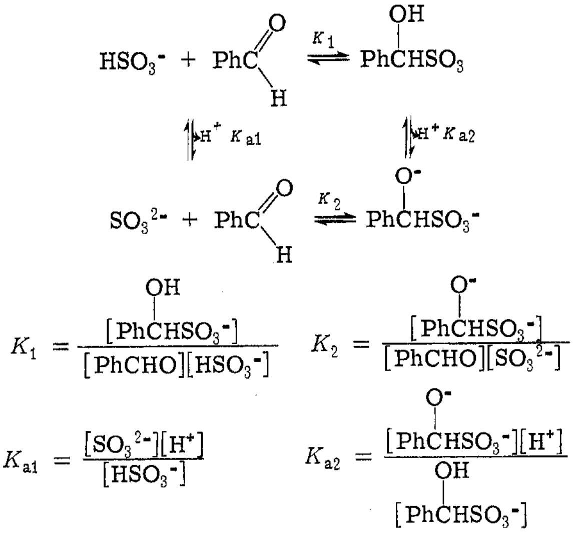
The logarithms of the observed equilibrium constant, K_{obsd} vs. pH are listed in Table I and plotted in Figure 1.

$$K_{obsd} = \frac{[\text{benzaldehyde bisulfite}]_{total}}{[\text{benzaldehyde}]_{total}[\text{bisulfite}]_{total}} \qquad (2)$$

Also shown in Figure 1 are the values of K_{obsd} vs. pH reported by Stewart and Donnally.[1b] Although both sets of determinations were done at 21°, ours were done at constant ionic strength of 1.0 *M*, while those of Stewart and Donnally were at an ionic strength of about 0.1 *M*.

The pH dependence of K_{obsd} can be understood in terms of the pH-independent equilibrium constants for the reactions shown in Scheme I. Except for a single measurement of K_{obsd} at pH 0.08, we studied the reaction of benzaldehyde and bisulfite ion above pH 3.55 only, and, therefore Scheme I does not include the conjugate acids of either HSO_3^- or the adduct of benzaldehyde with HSO_3^-. Of course, only three of the four constants are independent, and $K_2 = K_1K_{a2}/K_{a1}$. In terms of the scheme, the pH-dependent constant K_{obsd} can be expressed

Scheme I



$$K_1 = \frac{[\text{PhCH(OH)SO}_3^-]}{[\text{PhCHO}][\text{HSO}_3^-]} \qquad K_2 = \frac{[\text{PhCH(O}^-)\text{SO}_3^-]}{[\text{PhCHO}][\text{SO}_3^{2-}]}$$

$$K_{a1} = \frac{[\text{SO}_3^{2-}][\text{H}^+]}{[\text{HSO}_3^-]} \qquad K_{a2} = \frac{[\text{PhCH(O}^-)\text{SO}_3^-][\text{H}^+]}{[\text{PhCH(OH)SO}_3^-]}$$

$$K_{obsd} = K_1\frac{1 + K_{a2}/[\text{H}^+]}{1 + K_{a1}/[\text{H}^+]} \qquad (3)$$

Between pH's 3.55 and 5.27 K_{obsd} is pH independent, as would be expected if $K_{a1} \ll [\text{H}^+] \gg K_{a2}$. Using $K_1 = K_{obsd} = 6400\ M^{-1}$ obtained from this pH range, $K_{a1} = 2.40 \times 10^{-7}\ M$ that was obtained by potentiometric titration of $Na_2SO_3^{2-}$ with HCl at 21°, and $\mu = 1.0\ M$ (with KCl), we chose K_{a2} to minimize the sum of the squares of the *fractional* deviations.

$$\Sigma\left(\frac{K_{obsd_i} - K_{calcd_i}}{K_{obsd_i}}\right)^2 = \text{minimum} \qquad (4)$$

$$K_{a2} = \frac{\Sigma(1/(K_{obsd_i}(K_{a1} + [\text{H}^+]_i)))}{K_1\Sigma(1/(K_{obsd_i}(K_{a1} + [\text{H}^+]_i))^2)} - \frac{\Sigma([\text{H}^+]_i/(K_{obsd_i}(K_{a1} + [\text{H}^+]_i))^2)}{K_1\Sigma(1/(K_{obsd_i}(K_{a1} + [\text{H}^+]_i))^2)} \qquad (5)$$

The procedure yielded $K_{a2} = 3.95 \times 10^{-11}\ M$, from which $K_2 = K_1\ K_{a2}/K_{a1} = 1.05\ M^{-1}$. The resultant fit of the data to eq 2 is shown by the calculated line in Figure 1, and has an average fractional deviation of 0.1. The fit can be significantly improved if K_{a1} is treated as a variable; the fit is then optimized with $K_{a1} = 1.48 \times 10^{-7}\ M$ and the sum of the fraction deviations is cut by a factor of 2. We then obtain $K_{a2} = 2.11 \times 10^{-11}\ M$ and $K_2 = 9.12 \times 10^{-1}\ M^{-1}$.

Discussion

At pH's below 8, the observed equilibrium constants for formation of benzaldehyde bisulfite determined here by a spectrophotometric method substantially agree with those determined by Stewart and Donnally by a titration method, and the small deviations between the two sets of data are probably due to differences in the ionic strength. However, above pH 8 the values of K_{obsd} obtained in this study are 3–100 times smaller than those obtained earlier. In order to discuss the differences in the equilibrium constants determined by the two methods, it is useful to summarize the titration procedure.

Stewart and Donnally's method consisted of allowing benzaldehyde and bisulfite ion to equilibrate in a solution that also contained HCl, a buffer, or NaOH to maintain pH. The reaction mixture was then rapidly added to a stirred "quenching solution" containing sufficient HCl so that the final pH was about 2 and an excess (with respect to bisulfite ion) of iodine. Free bisulfite ion but not benzaldehyde bisulfite is oxidized by iodine, and at pH 2 the dissociation of the adduct is slow. The excess iodine was then quickly back-titrated with thiosulfate solution, and a small empirical correction was applied for the amount of dissociation of the adduct during the time of the back titration. This solution was then neutralized with bicarbonate and titrated with iodine. Because the dissociation of benzaldehyde bisulfite is rapid at neutral pH (and in spite of the fact that the equilibrium formation of adduct is favored at neutral pH) this titration determined the amount of bisulfite ion that had been present as adduct. There is, therefore, sufficient information to calculate the value of the equilibrium constant.

The method requires, of course, that the amount of benzaldehyde bisulfite is unaffected by the quenching process. For the quenching of basic solutions where lowering the pH would initially make the equilibrium constant for adduct formation more favorable, the reaction of iodine with bisulfite ion must be fast relative to the reaction of benzaldehyde with bisulfite ion, and the decrease of the pH to 2 must be rapid so that as bisulfite is removed by iodine oxidation adduct does not dissociate. Only the slow removal of bisulfite ion would give equilibrium constants that are too large.

To test the efficiency of the quenching process, Stewart and Donnally performed a control experiment in which 200 ml of a solution containing 0.05 mol of sodium hydroxide and 0.0015 mol of sodium sulfite was added to 300 ml of a rapidly stirred solution containing 0.10 mol of hydrochloric acid, 0.0015 mol of benzaldehyde, and 0.004 mol of iodine. Back-titration with thiosulfate showed that 5×10^{-6} mol of adduct had been formed during the quenching, which was reported to be within experimental error of zero. This amount of adduct formed in an equilibration mixture of 0.003 *M* benzaldehyde and bisulfite ion would correspond to an equilibrium constant for adduct formation of $10^{-0.26}$ M^{-1}. Based on this control the titration method seems to be suited to obtain equilibrium constants as small as those obtained by the spectrophotometric method.

We believe, however, that our spectrophotometrically determined values for the equilibrium constant are to be preferred at high pH's. Green and Hine[12] determined the equilibrium constant for the addition of bisulfite ion to isobutyraldehyde using both the spectrophotometric and titration methods, and report that above pH 10 the titration method gives values larger than those by the spectrophotometric method. They attribute these differences to the failure of the quenching procedure even when they used 5 *N* HCl at 0°. We do not understand the precise reasons for the failure of the quenching procedure, but it may be related to the apparent pH dependence of the stoichiometry of the oxidation of bisulfite ion by iodine. Since Stewart and Donnally performed control experiments for a sodium hydroxide solution, which they used to measure the equilibrium constant at pH 13, but did not perform controls with any of the buffered solutions used at lower pH's, it seems possible that the decrease in K_{obsd} that they observed at pH 13 and attributed to an addition of hydroxide ion to benzaldehyde may be only an experimental artifact arising from the fact that the quenching procedure is even less efficient with buffered solutions than it is with a sodium hydroxide solution. We have no current plans to investigate the quenching procedure.

In deriving eq 1, which gives a satisfactory fit to our experimental data, we assumed that the benzaldehyde–bisulfite adduct does not absorb at 250 nm. Jencks[18] made a similar assumption in studying the addition of bisulfite ion to *p*-chlorobenzaldehyde. Sousa and Margerum[19] have claimed that from the spectra of concentrated solutions of benzaldehyde and sulfite ion, in which almost all of the aldehyde was converted to adduct, they have obtained the absorption spectrum of the adduct. However, they do not seem to have considered the possibility that the spectrum obtained was that of an impurity of the aldehyde.

The value of $K_1 = 6.4 \times 10^3\ M$ observed here is similar to $K_{obsd} = 6.25 \times 10^3\ M$ at pH 4.0, 25° in 1.5 *M* acetic acid buffer reported by Geneste, Lamaty, and Rogue,[20] who used a titration technique.

The only other reports of the study of the equilibrium for the reaction of bisulfite ion and benzaldehyde are those of Gubareva,[21] who used a titration like that of Stewart and Donnally, and Sousa and Margerum,[19] who used a spectrophotometric method like that described here. However, in both of these studies the pH of the solutions—indeed, the fact that the solutions were buffered—is not reported, so that a comprison of the reported equilibrium constants with our results is difficult.

Although we have not studied the kinetics of the reaction of benzaldehyde and bisulfite ion, our equilibrium results necessitate some minor changes in the kinetic scheme and parameters reported by Stewart and Donnally.[1c] First of all, our equilibrium study detects no drop of the equilibrium constant for benzaldehyde bisulfite formation near pH 12 like that reported earlier. Therefore, pH's of 8–12.6, where the ratio SO_3^{2-}/HSO_3^- is large, the rate of adduct formation should be independent of pH and need not decrease at the upper pH's of this range as predicted previously. According to Greenzaid[5] and Zuman,[6] at pH 12.6 1% of the aldehyde exists as the hydroxide ion adduct. Therefore, as the pH is raised above 12.6 a decrease in rate will become apparent as benzaldehyde is converted to an adduct that is probably unreactive toward SO_3^{2-}.

Also, because Stewart and Donnally's evaluation of the rate constant for the decomposition of the benzaldehyde–SO_3^{2-} adduct requires the value of K_{a2}. Using $K_{a2} = 3.95 \times 10^{-11}\ M$, we calculate that the rate constant for the first-order decomposition of this species is 3.23×10^3 sec^{-1} rather than 1.80×10^2 sec^{-1}. Thus the rate of addition and loss of SO_3^{2-} from benzaldehyde is as fast as that from isobutyraldehyde,[12] and one would expect comparable problems with the quenching method.

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Registry No.—Benzaldehyde, 100-52-7; bisulfite, 15181-46-1; sulfite, 14265-45-3; sulfurous acid, 7782-99-2; benzaldehyde bisulfite monosodium salt, 4657-72-9.

References and Notes

(1) (a) T. D. Stewart and L. H. Donnally, *J. Am. Chem. Soc.*, **54,** 2333 (1932); (b) *ibid.*, **54,** 3555 (1932); (c) *ibid.*, **54,** 3559 (1932).

(2) Throughout this paper the term "bisulfite ion" will be used to refer to the mixture of SO_3^{2-}, HSO_3^-, H_2SO_3, and dissolved SO_2 regardless of the pH of the solution. Similarly, the adduct will be called benzaldehyde bisulfite.

(3) Reference 1c actually reports that "K_c" = $([PhCH(OH)O^-][H_3O^+])/XPhCHO] = 10^{-12.7}$ *M* at 21°. Therefore, the equilibrium constant for the addition of hydroxide is $[PhCH(OH)O^-]/([PhCHO][OH^-]) = K_c/K_w = 10^{1.4}$ M^{-1} at 21°.

(4) From a Taft correlation of alcohol acidities in aqueous solution at 25°: F. C. Kokesh, Ph.D. Dissertation, The Ohio State University, 1969. pK_a^{chem} $(R_1R_2CHOH) = -1.47 (\sigma^*_{R_1} + \sigma^*_{R_2}) + 16.59$, where $\sigma^*_{OH} = 1.28$.

(5) P. Greenzaid, *J. Org. Chem.*, **38,** 3164 (1973).

(6) W. J. Bover and P. Zuman, *J. Chem. Soc., Perkin Trans. 1*, 786 (1973); *J. Am. Chem. Soc.*, **95,** 2531 (1973).

(7) The correlation is that noted in ref 4. The necessary value of $\sigma^*_{SO_3^-}$ was estimated as $(2.8)^2 \times \sigma^*_{CH_2CH_2SO_3^-}$, where the latter constant was obtained from Hall's[8] Taft correlation of the pK_a's of primary ammonium ions, and King's[9] value for the pK_a (at 25°) of $H_3N^+CH_2CH_2SO_3^- = 9.061$.

(8) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79,** 5441 (1957).

(9) E. J. King, *J. Am. Chem. Soc.*, **15,** 2204 (1953).

(10) From a σ^I correlation of alcohol acidities in aqueous solution at 25°: F. C. Kokesh, Ph.D. Dissertation, The Ohio State University, 1969. pK_a^{chem} $(R_1R_2CHOH) = -7.19 (\sigma_{R_1}{}^I + \sigma_{R_2}{}^I) + 15.42$, where $\sigma^I_{SO_3^-} = 0.13$.[11]

(11) M. Charton, *J. Org. Chem.*, **29,** 1222 (1964).

(12) L. R. Green and J. Hine, *J. Org. Chem.*, **39,** 3896 (1974).

(13) W. F. Forbes and J. J. J. Myron, *Can. J. Chem.*, **39,** 2452 (1961).

(14) I. M. Kolthoff and R. Belcher, "Volumetric Analysis", Vol. 3, Interscience, New York, N.Y., 1957, pp 383–384.

(15) L. C. Schroeter, "Sulfur Dioxide", Pergamon Press, Elmsford, N.Y., 1966, p 169.

(16) At the higher pH's, the absorbance of sulfite solutions is extremely temperature dependent,[17] so that benzaldehyde was not added until the absorbance reading was constant, as shown by a strip-chart recorder.

(17) D. P. Ames and J. E. Willard, *J. Am. Chem. Soc.*, **75,** 3267 (1953).

(18) E. G. Sander and W. P. Jencks, *J. Am. Chem. Soc.*, **90,** 6154 (1968).

(19) J. A. Sousa and J. D. Margerum, *J. Am. Chem. Soc.*, **82,** 3013 (1960).

(20) P. Geneste, G. Lamaty, and J. Rogue, *Recl. Trav. Chim. Pay-Bas*, **91,** 188 (1972).

(21) M. A. Gubareva, *J. Gen. Chem. USSR*, **17,** 2259 (1947); *Chem. Abstr.*, **42,** 4820*a* (1948).

Notes

Relative Reactivities in the Addition of Dichlorocarbene to Methylenecycloalkanes

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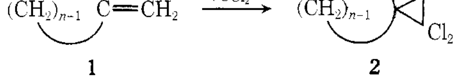
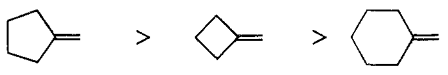
In spite of the multitude of olefins which have been subjected to attack by dichlorocarbene,[2] data have been lacking for the relative rates of addition of these species to simple methylenecycloalkanes. We now report these values for olefins **1** (n = 4–6) under a variety of conditions as summarized in Table I. The products were the dichlorospiroalkanes **2,** which were isolated and characterized (see Experimental Section). Rate constant ratios were determined by VPC procedures described previously.[3] As anticipated, the data of Table I do not show large variations with changes in the mode of generation of the carbene, the solvent, or the temperature.[4,5]



1 **2**

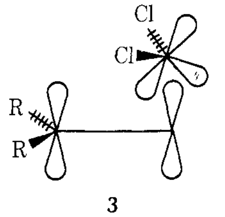
a, $n = 4$
b, $n = 5$
c, $n = 6$

Using data at 25° for the generation of $:CCl_2$ from ethyl trichloroacetate and sodium methoxide in pentane, one obtains the following relative reactivities among olefins **1a–c.**



1b	**1a**	**1c**
2.44 + 0.02	1.53 + 0.1	1.00

Theoretical studies suggest that the transition state for the addition of $:CCl_2$ to an unsymmetrical olefin should resemble **3** and should represent a relatively early stage of the bond formation process.[6] The p orbital of the divalent carbon is in the same plane occupied by the π bond of the methylenecycloalkane. If one recognizes that the preferred direction of attack of $:CCl_2$ on **1c** is equatorial,[7] the already small dihedral angle between the exocyclic carbon–carbon bond and the α-equatorial hydrogens in **1c**[8] should decrease slightly so as to produce an increase in torsional strain as this olefin approaches the transition state. Similar changes in torsional strain for **1a** and **1b** should be small and ought to favor the transition state from **1a** relative to that from **1b.**



3

Changes in bond angle strain on going from ground state to transition state should involve those normally anticipated for the formation of a three-membered ring for **1c** but are more difficult to access for **1a** and **1b** because of the