2482 J. Phys. Chem. 1986, 90, 2482–2488

Kinetics, Thermodynamics, and Mechanism of the Formation of Benzaldehyde–S(IV) Adducts

Terese M. Olson, Scott D. Boyce, and Michael R. Hoffmann*

Department of Environmental Engineering Science, W. M. Keck Laboratories, California Institute of Technology, Pasadena, California 91125 *(Received: October 11, 1985; In Final Form: January 8, 1986)*

The kinetics and mechanism of the formation of α-hydroxyphenylmethanesulfonate (HPMS) by the addition of bisulfite to benzaldehyde were studied at low pH. A three-term rate law was observed as $d[\mathrm{HPMS}]/dt = \{k_1\alpha_2 + (k_2 + k_3K_H[\mathrm{H}^+])\alpha_1\}[\mathrm{S(IV)}]_t[\mathrm{C_6H_5CHO}]$ where $\alpha_1 = [\mathrm{HSO_3^-}]/[\mathrm{S(IV)}]$, $\alpha_2 = [\mathrm{SO_3^{2-}}]/[\mathrm{S(IV)}]$, and K_H is the proton association constant of benzaldehyde. The rate-limiting steps of each term appeared to be the nucleophilic attack of SO_3^{2-} on the carbonyl carbon of benzaldehyde, the attack of HSO_3^- on the carbonyl carbon, and the attack by HSO_3^- on the protonated carbon of the carbocation, $C_6H_5C^+H(OH)$, respectively. Over the pH range of most natural systems, only the k_1 and k_2 steps contribute to adduct formation while the k_3 term becomes important for pH < 1. At 25 °C and $\mu = 1.0$ M, the intrinsic rate constants were determined to be $k_1 = (2.15 \pm 0.09) \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$, $k_2 = (0.71 \pm 0.03)\ \mathrm{M^{-1}\ s^{-1}}$, $k_3 \cong 2.5 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$. Para-substitution on the benzaldehyde ring resulted in a slight increase in reactivity for p-NO_2– and p-Cl–, and a decrease for p-OH–, p-OCH_3–, and p-CH_3–C_6H_5CHO. The equilibrium association constant, $K = [\mathrm{C_6H_5CH(OH)SO_3^-}]/[\mathrm{HSO_3^-}][\mathrm{C_6H_5CHO}]$, at 25 °C was determined to be $4.8\ (\pm 0.8) \times 10^3$ at $\mu = 0.1$ M and $0.98\ (\pm 0.11) \times 10^3\ \mathrm{M^{-1}}$ at $\mu = 1.0$ M. $\Delta H°$ and $\Delta S°$ were determined to be $-64.6\ \mathrm{kJ\ mol^{-1}}$ and $-146\ \mathrm{J\ mol^{-1}\ deg^{-1}}$, respectively.

Introduction

Benzaldehyde has been found to be present in fogs, clouds, and rain at substantial levels.[1-3] In aqueous solution, benzaldehyde reacts with SO_2 to form α-hydroxyphenylmethanesulfonate (HPMS). Formation of S(IV)–carbonyl adducts such as HPMS leads to the apparent stabilization and enhancement of S(IV) in atmospheric water droplets. Previously, we established that hydroxymethanesulfonate (HMS, the formaldehyde–bisulfite adduct) is often present in fogwater in appreciable concentrations.[4a-c]

The kinetics[5-7] and thermodynamics[5,7-11] of bisulfite addition to benzaldehyde have been studied previously. Stewart and Donnally[5a,b] proposed a three-term rate law for the dissociation of HPMS over the pH range 0–13. In their proposed mechanism, three discrete forms of the diprotic hydroxyphenylmethanesulfonic acid dissociate to give benzaldehyde and SO_3^{2-}, HSO_3^-, or $H_2O{\cdot}SO_2$, respectively. Blackadder and Hinshelwood[6] reported overall dissociation rate constants for the release of HSO_3^- at pH 3 ($1.55 \times 10^{-4}\ \mathrm{s^{-1}}$) and pH 5 ($7.76 \times 10^{-3}\ \mathrm{s^{-1}}$); their values were consistent with those reported by Stewart and Donnally,[5] which were $\sim 1.7 \times 10^{-4}$ and $\sim 1 \times 10^{-2}\ \mathrm{s^{-1}}$ for pH 3 and 5, respectively. Iodometric titration was used as an analytical method by both groups. However, a rate constant of $1.7 \times 10^{-2}\ \mathrm{s^{-1}}$ (13 °C), which appears to be at least an order of magnitude higher than that reported by Stewart and Donnally[5] at pH ~ 4.1 for the dissociation of $HPMS^-$ to HSO_3^- and C_6H_5CHO, was reported by Sousa and Margerum,[7] based on spectroscopic measurements.

Values for the formation constant of the bisulfite–benzaldehyde adduct are compiled in Table I. In some cases, pH was not reported; therefore some of the cited values, which vary by more than an order of magnitude, may be apparent constants. In addition, iodometric titration as used by Kerp,[8] Gubareva,[9] and Stewart and Donnally[5a,b] may have led to errors in that rapid dissociation of the complex most likely occurred during titration. Kokesh and Hall[11] examined this possibility by measuring K_{obsd} vs. pH spectrophotometrically and found that the titration method yielded inaccurate equilibrium constants above pH 8.

TABLE I: Literature Values for the Equilibrium Association Constant of HSO_3^- and Benzaldehyde

$10^{-3}K$, M^{-1}	conditions	method	ref
11.3	20.9 °C, pH 5.21	iodometric titration	5b
4.7	23 °C	UV spectrophotometry	7
10.0	15–17 °C, $\mu \simeq 0.1$ M	iodometric titration	8
0.44	30 °C	iodometric titration	9
1.27	20 °C, pH 4.3	UV spectrophotometry	10
6.4	21 °C, $\mu = 1.0$ M, pH 3.5–5.3	UV spectrophotometry	11
4.8	25 °C, $\mu = 0.1$ M	UV spectrophotometry	this work

In view of the above uncertainties, a thorough investigation of the kinetics, mechanism, and thermodynamics of bisulfite–benzaldehyde was conducted by using spectrophotometric methods. The rate of adduct formation was studied over the pH range 0–4.4, which is typical of acidic fogs, clouds, and haze aerosols.[12,13] The formation constant for HSO_3^- and benzaldehyde was determined as a function of ionic strength and temperature.

Experimental Procedures

Materials. Reagent grade sodium sulfite (Mallinkrodt), sodium bisulfite (Mallinkrodt), hydrochloric acid (Mallinkrodt), sodium hydroxide (Mallinkrodt), chloroacetic acid (MCB), dichloroacetic acid (MCB), glacial acetic acid (Dupont), formic acid (Mallinkrodt), and phosphoric acid (Spectrum) were utilized without further purification. Benzaldehyde (MCB) was redistilled periodically. Stock solutions of para-substituted benzaldehydes (p-Cl, NO_2, OH, CH_3, and CH_3O) were prepared by dissolving analytical grade Aldrich reagents in 60% (v/v) methanol/H_2O. The sodium salt of the benzaldehyde–bisulfite addition compound, which was used in equilibrium constant determinations, was prepared according to Blackadder and Hinshelwood.[6] Elemental analysis of the salt (Galbraith Laboratories) suggested a stoichiometry of $Na{\cdot}C_6H_5CH(OH)SO_3{\cdot}{}^1/_2(H_2O)$. Ionic strength was maintained ($\mu = 1.0$ M) with sodium chloride (Mallinkrodt). All water used

---

(1) Grosjean, D.; Wright, B. *Atmos. Environ.* **1983**, *17*, 2093–96.

(2) Kawamura, K.; Kaplan, I. R. *Environ. Sci. Technol.* **1983**, *17*, 497–501.

(3) Lunde, G.; Gether, J.; Gjos, N.; Lunde, M. B. S. *Atmos. Environ.* **1977**, *11*, 1007–14.

(4) (a) Munger, J. W.; Jacob, D. J.; Waldman, J. M.; Hoffmann, M. R. *J. Geophys. Res.* **1983**, *88*, 5109–21. (b) Munger, J. W.; Jacob, D. J.; Hoffmann, M. R. *J. Atmos. Chem.* **1984**, *11*, 335–50. (c) Munger, J. W.; Tiller, C.; Hoffmann, M. R. *Science* **1986**, *231*, 247–249.

(5) (a) Stewart, T. D.; Donnally, L. H. *J. Am. Chem. Soc.* **1932**, *54*, 2333–40. (b) Stewart, T. D.; Donnally, L. H. *Ibid.* **1932**, *54*, 3555–69.

(6) Blackadder, D. A.; Hinshelwood, C. *J. Chem. Soc.* **1958**, 2720–27.

(7) Sousa, J. A.; Margerum, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 3013–16.

(8) Kerp, W. *Chem. Zentralbl.* **1904**, *75/II*, 56–59.

(9) Gubareva, M. A. *J. Gen. Chem.* **1947**, *17*, 2259–64.

(10) Arai, K. *Nippon Kagaku Zasshi* **1962**, *83*, 765–767.

(11) Kokesh, F. C.; Hall, R. E. *J. Org. Chem.* **1975**, *40*, 1632–36.

(12) Jacob, D. J.; Waldman, J. M.; Munger, J. W.; Hoffmann, M. R. *Environ. Sci. Technol.* **1985**, *19*, 730–36.

(13) Waldman, J. M.; Munger, J. W.; Hoffmann, M. R. *Tellus* **1985**, *37B*, 91–108.

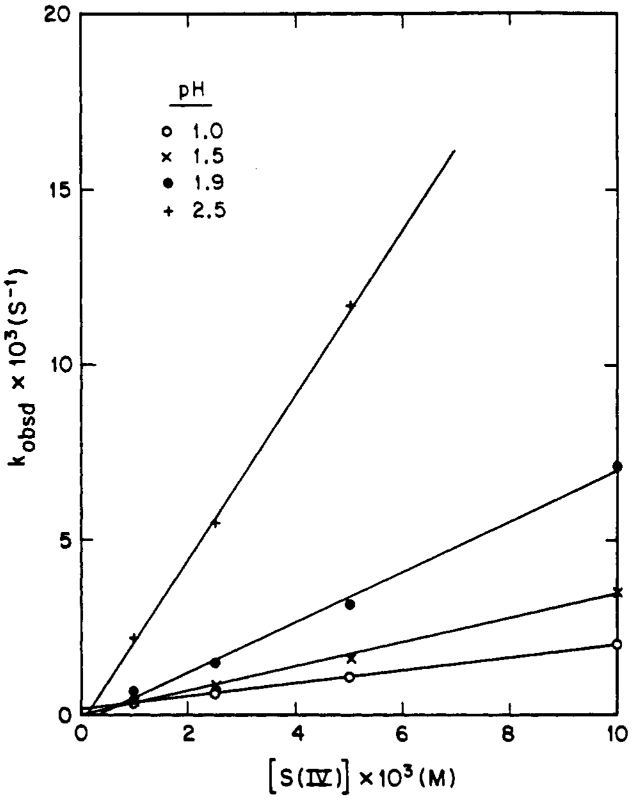

Figure 1. Dependence of the pseudo-first-order rate constant on [S(IV)] over the pH (−log {H$^+$}) range 1.3–4.4. The solid line denotes the linear least-squares fit to the data. Reaction conditions: $[C_6H_5CHO]_t$ = 0.05–0.1 mM, $[S(IV)]_t$ = 0.5–10 mM, T = 25 °C, μ = 1.0 M.

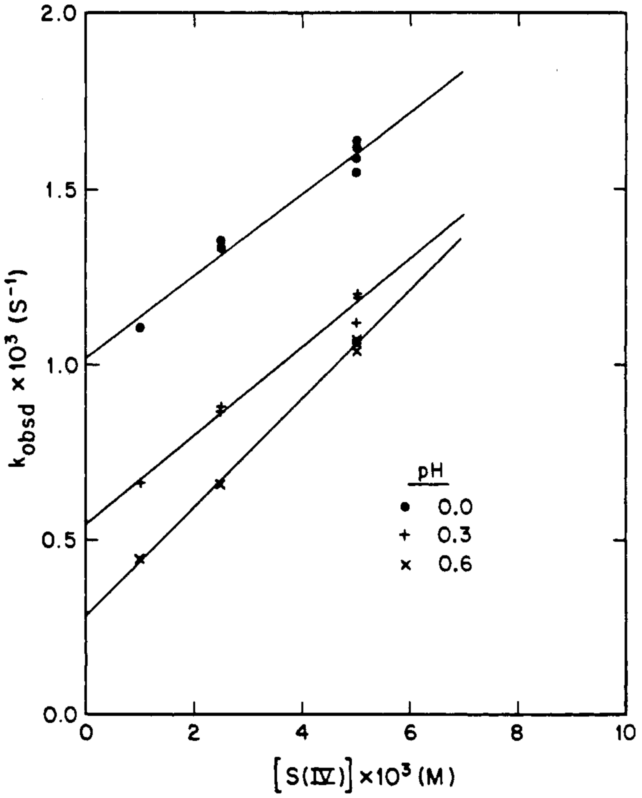

Figure 2. Dependence of pseudo-first-order rate constant on [S(IV)] over the pH range 0–1. Reaction conditions are same as given in Figure 1.

TABLE II: Kinetic Data for the Reaction of S(IV) and Benzaldehyde in Aqueous Solution

pH	10^3[S(IV)], M	$10^4[C_6H_5CHO]$, M	10^3k_{obsd} ($\pm\sigma$),[a] s^{-1}	10^3k_{calcd}, s^{-1}
0.0	5.0	1.0	1.60 ± 0.03	1.87
0.3	5.0	1.0	1.17 + 0.02	1.17
0.6	5.0	1.0	1.06 ± 0.02	0.91
1.0	5.0	1.0	1.08 ± 0.02	1.03
1.3	5.0	1.0	1.29 ± 0.01	1.46
1.51	5.0	1.0	1.63 ± 0.03	1.97
1.87	5.0	1.0	3.16 ± 0.03	3.45
2.12	5.0	1.0	4.69 ± 0.06	5.20
2.55	2.5	1.0	5.38 ± 0.07	5.66
2.84	2.5	1.0	10.1 ± 0.10	10.1
3.10	2.5	1.0	18.0 ± 0.20	17.5
3.42	1.0	1.0	15.5 ± 0.20	14.2
4.43	0.5	0.5	70.0 ± 2.1	70.0

[a] $\sigma = [\{(k_{obsd} - \bar{k}_{obsd})^2/N\}],^{1/2}$ where N = 4.

to prepare the solutions was deionized (18 MΩ cm resistivity; Milli RO-4/Milli Q) and deoxygenated by purging with N_2. Reagent solutions were prepared daily in a glovebox under a N_2 atmosphere. Hydrogen ion activities were measured with a Beckman Altex Model Φ71 pH meter and Radiometer glass electrode.

Methods. Reaction rates were determined by monitoring the disappearance of benzaldehyde with a Hewlett-Packard Model 8450A UV/visible spectrophotometer at 249 nm (λ_{max}). These measurements were made in a 1-cm quartz cell. Temperature was held constant (25 °C unless otherwise stated) with a Haake Model FK-2 water recirculation bath and temperature controller. Between 15 and 200 absorbance measurements were collected for each kinetic analysis and an average of four determinations for each pseudo-first-order rate constant was obtained. Sulfur(IV) concentrations ranged from 0.5 to 10 mM, while total benzaldehyde concentrations in the samples varied from 0.05 to 0.1 mM.

The equilibrium constant was determined by dissolving the sodium salt of the addition compound in solution and measuring the absorbance of the equilibrated solution at 250 nm in a 1-cm cell. Published values of the extinction coefficients of the complex (ϵ = 152 L/(mol cm)) and benzaldehyde (ϵ = 1.26 × 10^3 L/(mol cm)) at this wavelength were then used to calculate the equilibrium constant. Our independent determination of ϵ for benzaldehyde did not differ significantly from the literature value; the absorptivity of benzaldehyde varied by less than 1.5% over the temperature range 15–35 °C. The pH of each solution was adjusted to 3.9 ± 0.1 with HCl. Thermodynamic parameters were determined by varying the cell temperature with a Hewlett-Packard Model 89100A temperature controller. The averages of four absorbance measurements at three different concentrations of the addition compound were used to calculate the equilibrium constant. Total sulfonate concentrations ranged from 41.0 to 92.0 μM.

Results

Kinetic Studies. Pseudo-first-order conditions were maintained throughout the kinetic study whereby $[S(IV)]_t \gg [C_6H_5CHO]_t$, with a minimum tenfold excess of S(IV). Plots of ln $\{(A - A_\infty)/(A_0 - A_\infty)\}$ vs. time were linear ($r^2 \geq 0.99$) for better than 90% of the reaction, confirming that the reaction is first-order in benzaldehyde. At constant pH the observed pseudo-first-order rate constant was also a linear function of the total S(IV) concentration, as Figures 1 and 2 illustrate. Above pH 1.0 (see Figure 1), k_{obsd} increased with increasing pH, a phenomenon also characteristic of the formation of hydroxymethanesulfonate[14] and other carbonyl–S(IV) adducts.[15] For pH greater than 2.5, the pH dependence of reaction rate can be made linear by plotting $k_{obsd}/[S(IV)]_t$ vs. the reciprocal of the hydrogen ion activity. A least-squares fit (Figure 3) of data from Table II demonstrates this pH dependence.

Below pH 1.0, however, k_{obsd} increases with decreasing pH (see Figure 2) and the y intercept steadily increases above zero. A similar dissociation rate minimum near pH 1.0 was found by Stewart and Donnally.[5b] Between pH 0.0 and 1.0 there is no

---

[14] Boyce, S.; Hoffmann, M. R. *J. Phys. Chem.* **1984**, *88*, 4740–46.
[15] Jencks, W. P. *Prog. Phys. Org. Chem.* **1964**, *2*, 63–118.

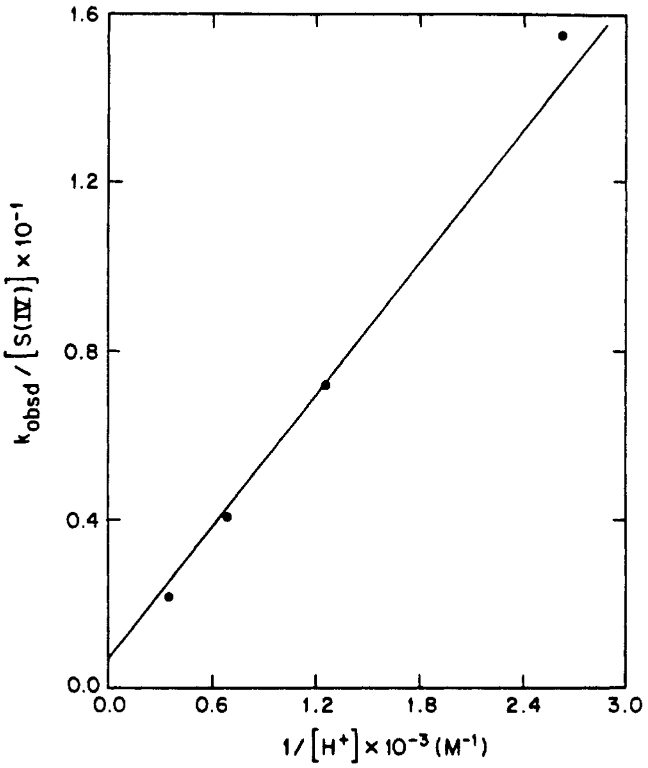

Figure 3. Dependence of $k_{obsd}/[S(IV)]_t$ vs. $1/[H^+]$ for pH ≥ 2.5. Solid line denotes linear least-squares fit to the data taken from Table II.

simple dependence on the hydrogen ion activity. Instead Figure 2 suggests that the slope of k_{obsd} vs. $[S(IV)]_t$ approaches a constant value as the pH approaches zero. The intercepts, when divided by $\{H^+\}$, yield a constant value (1.08 (±0.06) $\times 10^{-3}$ M^{-1} s^{-1}) at very low pH. A decrease of $[C_6H_5CHO]$ at pH $\leq$ 1, that could be attributed to either a slow decarbonylation or a specific acid-catalyzed hydration, in the absence of S(IV), was not observed over 2 h. Sulfur(IV) solutions at pH 0 (without benzaldehyde) were also stable over the same time period.

The possibility of general acid catalysis by the various buffers used herein was examined by measuring the reaction rate over a tenfold range of buffer concentrations. To correct for small variations in the pH of the sample solutions, the observed pseudo-first-order rate constant was normalized as $k_{obsd}\{H^+\}/[S(IV)]_t$. No buffer dependence was found for formate, acetate, chloroacetate, or dichloroacetate. However, the reaction was catalyzed slightly by phosphoric acid. In this case, general acid catalysis may occur in the presence of relatively strong acids. General base catalysis of the dissociation of ketone bisulfite compounds has been demonstrated and the mechanism is said to involve the formation of an encounter complex with the oxocarbonium ion, $>C=O^+H$, bisulfite and buffer, and subsequent removal of a proton from bisulfite.[16] At the phosphate concentration used in these studies (0.1 M), less than a 7–8% change in the pseudo-first-order rate constant was attributed to phosphate catalysis and consequently k_{obsd} values were not corrected.

Based on the preceding kinetic data, the following reaction mechanism is proposed for the pH range of 0–4:

$$H_2O{\cdot}SO_2 \overset{K_{a1}}{\rightleftharpoons} H^+ + HSO_3^- \quad \text{(fast)} \qquad (1)$$

$$HSO_3^- \overset{K_{a2}}{\rightleftharpoons} H^+ + SO_3^{2-} \quad \text{(fast)} \qquad (2)$$

$$C_6H_5CHO + SO_3^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_6H_5CH(O^-)SO_3^- \quad \text{(slow)} \qquad (3)$$

$$C_6H_5CHO + HSO_3^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_6H_5CH(OH)SO_3^- \quad \text{(slow)} \qquad (4)$$

$$C_6H_5CH(OH)SO_3H \overset{K_{a1(HPMS)}}{\rightleftharpoons} C_6H_5CH(OH)SO_3^- + H^+ \quad \text{(fast)} \qquad (5)$$

$$C_6H_5CH(OH)SO_3^- \overset{K_{a2(HPMS)}}{\rightleftharpoons} C_6H_5CH(O^-)SO_3^- + H^+ \quad \text{(fast)} \qquad (6)$$

$$C_6H_5CHO + H^+ \overset{K_H}{\rightleftharpoons} C_6H_5C^+H(OH) \quad \text{(fast)} \qquad (7)$$

$$C_6H_5C^+H(OH) + HSO_3^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C_6H_5CH(OH)SO_3^- + H^+ \quad \text{(slow)} \qquad (8)$$

$$C_6H_5C^+H(OH) + H_2O \underset{k_{-h}}{\overset{k_h}{\rightleftharpoons}} C_6H_5CH(OH)O^+H_2 \quad \text{(slow)} \qquad (9)$$

$$C_6H_5CH(OH)O^+H_2 \rightleftharpoons H^+ + C_6H_5CH(OH)_2 \quad \text{(fast)} \qquad (10)$$

Steps 3 and 4 involve the rate-limiting nucleophilic attack by bisulfite and sulfite on the carbonyl carbon of benzaldehyde to form the sulfonate. A specific acid-catalyzed pathway for bisulfite addition is also proposed in steps 7 and 8 to account for the increased reactivity of S(IV) at low pH. Reaction 7 leads to the rapid formation of a carbocation and the enhanced positive character of its carbon center facilitates the rate-limiting nucleophilic attack of bisulfite in eq 8. Analogous acid-catalyzed pathways have been proposed for the dissociation of acetophenone bisulfites.[16] Specific acid catalysis has not been observed in the formation of formaldehyde–S(IV) adducts,[14] but since formaldehyde is present primarily as the *gem*-diol, $CH_2(OH)_2$, very little of the probable intermediate, $C^+H_2(OH)$, will form.

The nonzero *y* intercepts of Figure 2 suggest a loss of benzaldehyde by a pathway that does not involve S(IV) in the rate-determining step. Even though we were not able to detect any loss of benzaldehyde at pH 0 in the absence of S(IV), we believe these intercepts are due to the acid-catalyzed hydrolysis of the aldehyde as shown in steps 9 and 10. Between pH 0 and 1 the apparent equilibrium constant for adduct formation is quite small. At pH 0 with the lowest concentration of S(IV) which was used (1 mM), the overall change in absorbance was approximately 5%. By these techniques alone, therefore, it probably was not possible to detect hydrolysis of benzaldehyde in the absence of S(IV).

The predominant sulfonic acid species between pH ~ 1–10 will be $C_6H_5CH(OH)SO_3^-$. Some confusion exists regarding the value of $K_{a1(HPMS)}$, however. Stewart and Donnally's initial estimate, based on titration data, was 3.7×10^{-2} M.[5b] They later found that their proposed mechanism was inconsistent with this value and it was then assumed that the sulfonic acid was a much stronger acid. A new $K_{a1(HPMS)}$ value was estimated as ca. 1×10^3 M by fitting this constant to their kinetic data. Based on a fit of our own titration data which was analyzed with the computer code MINEQL,[17] $pK_{a1(HPMS)}$ is approximately 0.7.

From the above mechanism, the rate of disappearance of benzaldehyde over the pH range 0–4 is written as

$$\nu = -d[C_6H_5CHO]/dt = k_1[SO_3^{2-}][C_6H_5CHO] + k_2[HSO_3^-][C_6H_5CHO] + k_3K_H\{H^+\}[HSO_3^-][C_6H_5CHO] + k_hK_H\{H^+\}[C_6H_5CHO] \qquad (11)$$

while the rate expression for the rate of formation of the sulfonic acid is

$$\nu' = d\sum[HPMS]/dt = (k_1[SO_3^{2-}] + k_2[HSO_3^-] + k_3K_H\{H^+\}[HSO_3^-])[C_6H_5CHO] \qquad (12)$$

Terms that describe the decomposition of HPMS were not included in the theoretical rate expression of eq 11 since the equilibrium for the reaction is displaced far to the right. Equation

---

[16] Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1978**, *100*, 1228–35.

[17] Westall, J. C.; Zachary, J. L.; Morel, F. M. *Technical Note No. 18*, Ralph M. Parsons Laboratory for Water Resources and Environmental Engineering, Massachusetts Institute of Technology, 1976.

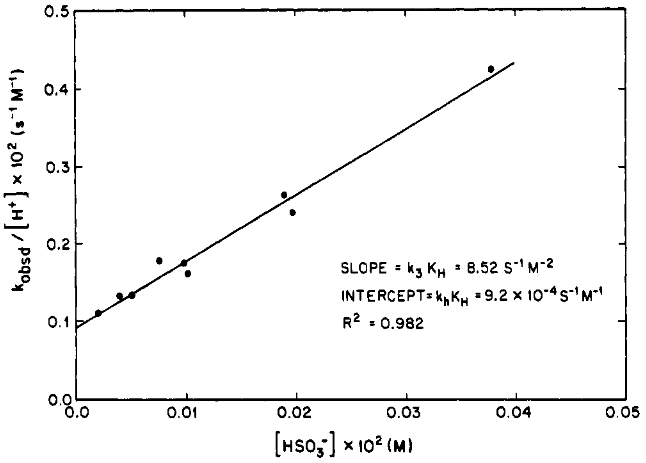

Figure 4. Dependence of $k_{obsd}/[H^+]$ vs. $[HSO_3^-]$ for pH 0–0.6. Solid line represents linear least-squares fit to the data.

11 may be rewritten in terms of total S(IV) and benzaldehyde to yield

$$v = ((k_1\alpha_2 + (k_2 + k_3K_H\{H^+\})\alpha_1)[S(IV)] + k_hK_H\{H^+\}) \times [C_6H_5CHO] \quad (13)$$

where

$$[S(IV)] = [H_2O{\cdot}SO_2] + [HSO_3^-] + [SO_3^{2-}] \quad (14)$$

$$[HSO_3^-] = \alpha_1[S(IV)] \quad (15)$$

$$[SO_3^{2-}] = \alpha_2[S(IV)] \quad (16)$$

$$\alpha_1 = K_{a1}\{H^+\}/D \quad (17)$$

$$\alpha_2 = K_{a1}K_{a2}/D \quad (18)$$

$$D = \{H^+\}^2 + K_{a1}\{H^+\} + K_{a1}K_{a2} \quad (19)$$

The activity scale is retained in the above equations for the hydrogen ion since only H^+ activities were measured and because activity coefficients are difficult to estimate at $\mu = 1.0$ M. If S(IV) is in sufficient excess and pH is held constant, then

$$k_{obsd} = \{k_1\alpha_2 + (k_2 + k_3K_H\{H^+\})\alpha_1\}[S(IV)]_t + k_hK_H\{H^+\} \quad (20)$$

The intrinsic rate constants, k_1 and k_2, and the apparent constant, k_3K_H, were estimated initially from analysis of rate data at low and high pH. In the pH region of 2.5–4.4, $K_{a1}\{H^+\} \gg \{H^+\}^2$ and $K_{a1}K_{a2}$. Furthermore, if $k_3K_H\{H^+\}$ and $k_hK_H\{H^+\}/[S(IV)]_t \ll k_2$, then

$$k_{obsd} = (k_1K_{a2}/\{H^+\} + k_2)[S(IV)]_t \quad (21)$$

and a plot of $k_{obsd}/[S(IV)]_t$ vs. $\{H^+\}^{-1}$ will be linear; the slope and intercept of this plot provides an estimate of k_1 and k_2. This linearity was previously demonstrated in Figure 3. These estimates of k_1 and k_2 were refined by a nonlinear least-squares fitting of the data in Table II (for pH > 1.3) with a routine described by Moore and Pearson.[18] Each data point was weighted in accordance with its statistical variance and values of K_{a1} (1.45×10^{-2} M)[19] and K_{a2} (6.31×10^{-8} M)[20] were held constant. The intrinsic constants, k_1 and k_2, were determined to be $k_1 = 2.15$ (± 0.09) $\times 10^4$ $M^{-1} s^{-1}$ and $k_2 = 0.71$ (± 0.03) $M^{-1} s^{-1}$.

For pH ≤ 1.0, $\{H^+\}^2 \gg K_{a1}\{H^+\}$ and $K_{a1}K_{a2}$; and if $k_3K_HK_{a1} \gg k_2K_{a1}/\{H^+\}$ and $k_1K_{a1}K_{a2}/\{H^+\}^2$, k_{obsd} becomes

$$k_{obsd} = k_3K_H\{H^+\}[S(IV)]_t + k_hK_H\{H^+\} \quad (22)$$

Initial estimates of k_3K_H and k_hK_H were obtained from the slope ($k_3K_H \cong 8.52$ $M^{-1} s^{-1}$) and intercept/$\{H^+\}$ ($k_hK_H \cong 9.2 \times 10^{-4}$ $M^{-1} s^{-1}$) of Figure 4. These two constants were then refined by using eq 20, the initial estimates of k_1 and k_2, and the data from Table II (pH 0–1.3). The refined values of k_3K_H and k_hK_H are 2.5 (± 1.5) $M^{-1} s^{-1}$ and 1.54 (± 0.47) $\times 10^{-3}$ $M^{-1} s^{-1}$, respectively. From our estimate of k_3K_H and a reported value of $K_H \sim 10^{-7}$,[21] the intrinsic constant k_3 is $\sim 2.5 \times 10^7$ $s^{-1} M^{-1}$. The source of error in the value k_3K_H is unknown. A possible source of error is in the uncertainties of the molar absorptivities of $C_6H_5CH(OH)SO_3H$ and $C_6H_5CH(OH)SO_3^-$ at 249 nm.

TABLE III: Rate Constants[a] and Activation Parameters[b] for Bisulfite and Sulfite Ion Addition Reactions with Benzaldehyde and Para-Substituted Benzaldehydes

X	$10^{-4}k_1$, $M^{-1} s^{-1}$	k_2, $M^{-1} s^{-1}$	$\Delta H_1^‡$, kJ mol^{-1}	$\Delta S_1^‡$ J $mol^{-1} deg^{-1}$	$\Delta H_2^‡$, kJ mol^{-1}	$\Delta S_2^‡$, J $mol^{-1} deg^{-1}$
OCH_3	0.777	N/A[d]	41.5	−50.2	N/A	N/A
CH_3	1.56	0.68	43.0	−39.5	42.0	−126
H	2.15	0.71	36.0	−58.1	36.6	−142
Cl	5.53	1.05	37.4	−47.9	32.7	−154
OH[c]	0.582	N/A	30.4	−89.9	N/A	N/A
NO_2[c]	5.66	5.31	37.4	−12.8	29.0	−153

[a] Rate constants k_1 and k_2 correspond to the following reactions at 25 °C and $\mu = 1.0$ M:

$$X{-}C_6H_5CHO + SO_3^{2-} \xrightarrow{k_1} X{-}C_6H_5CH(O^-)SO_3^-$$

$$X{-}C_6H_5CHO + HSO_3^- \xrightarrow{k_2} X{-}C_6H_5CH(OH)SO_3^-$$

where X refers to the para-substituted functional group. [b] Activation parameters based on reaction rate temperature dependence over the range 15–40 °C unless otherwise stated. [c] Activation parameters based on temperature dependence between 15–33 °C. [d] N/A = not applicable; measured activation parameters indicate a change in mechanism.

Since the above rate constants have been determined for the mixed concentration/activity scales used in eq 13, literature values of K_{a1} and K_{a2} (at $\mu = 0$) were corrected to $\mu = 1.0$ M in computing the intrinsic rate constants. Activity coefficients, $\gamma_{SO_3^{2-}}$ and $\gamma_{HSO_3^-}$, were computed by using the Davies approximation for conditions of $\mu = 0.5$ M, as recommended by Butler.[22] The corrected acidity constants were ${}^cK_{a1} = K_{a1}\gamma_{H_2O{\cdot}SO_2}/\gamma_{HSO_3^-} = 0.021$ M and ${}^cK_{a2} = K_{a2}\gamma_{HSO_3^-}/\gamma_{SO_3^{2-}} = 2.43 \times 10^{-7}$ M. A sensitivity analysis to test the effect of using the Davies approximation for conditions outside its limits of applicability indicated that the maximum introduced errors for k_1 and k_2 would be 12% and 8%, respectively.

The temperature dependence of k_2 and k_1 over the range 15–40 °C was determined at pH 1.3 (Figure 5a) and at pH 2.5 (Figure 5b), respectively. From these experiments, $\Delta H_1^‡ = 36.0$, $\Delta H_2^‡ = 36.6$ kJ/mol, $\Delta S_1^‡ = -58.1$, and $\Delta S_2^‡ = -142$ J/mol/°C at $\mu = 1.0$ M.

Substituent effects for para-substituted benzaldehydes were determined for k_2 at pH 1.3 and k_1 at pH 2.5; results are presented in Table III. For each substituted benzaldehyde, plots of k_{obsd} vs. $[S(IV)]_t$ were linear. The magnitude of k_1 increased in the order $-OH < -OCH_3 < -CH_3 < -H < -Cl < -NO_2$, while for k_2, the order was $-CH_3 < -H < -Cl < -NO_2$. A change in the mechanism of HSO_3^- addition was suspected for p-OH– and p-OCH_3–C_6H_5CHO (vide infra). Activation parameters are summarized in Table III.

Formation Constant. Over the pH region of 3–5, the predominant S(IV) species are $C_6H_5CH(OH)SO_3^-$ and HSO_3^-. Stewart and Donnally showed that

$$K_{app} = \frac{(\Sigma HPMS)}{(\Sigma H_2SO_3)(\Sigma C_6H_5CHO)} \quad (23)$$

was pH-independent over the same pH range, and therefore K can be approximated by

$${}^cK = \frac{[C_6H_5CH(OH)SO_3^-]}{[HSO_3^-][C_6H_5CHO]} \quad (24)$$

---

(18) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism, A Study of Homogeneous Chemical Reactions*, 3rd ed.; Wiley-Intersience: New York, 1981; pp 69–70.

(19) Deveze, D.; Rumpf, P. *C. R. Acad. Sci. Paris* **1964**, *258*, 6135–38.

(20) Hayon, E.; Treinin, A.; Wilf, J. *J. Am. Chem. Soc.* **1972**, *94*, 47–57.

(21) Yates, K.; Stewart, R. *Can. J. Chem.* **1959**, *37*, 664–7.

(22) Butler, J. *Ionic Equilibrium, A Mathematical Approach*; Addison-Wesley: Reading, MA, 1964; pp 431–39.

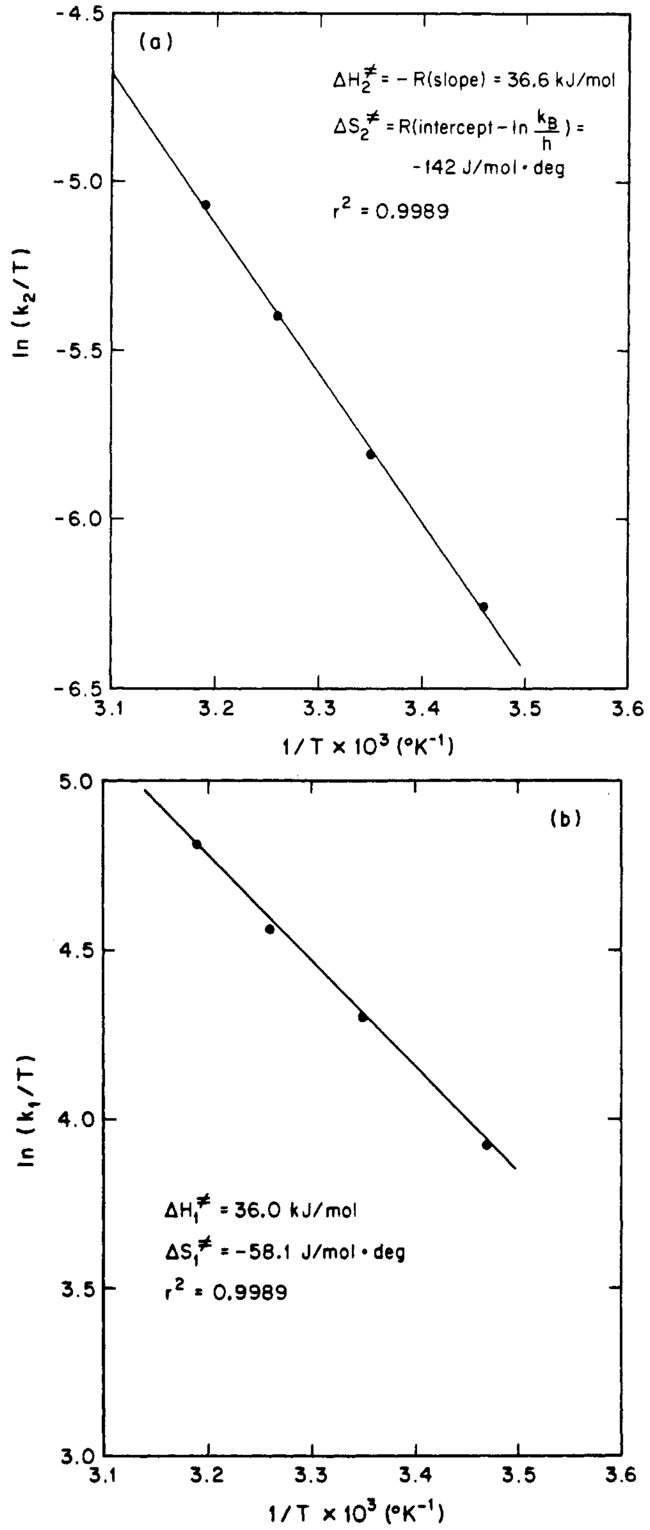

Figure 5. Temperature dependencies of (a) the intrinsic rate constant, k_2, for the nucleophilic addition of bisulfite ion to benzaldehyde, and (b) the intrinsic rate constant, k_1, for the addition of sulfite ion to benzaldehyde. Solid lines denote least-squares fit to the data. Reaction conditions: μ = 1.0 M, T = 25 °C; (a) [S(IV)] = 5.0 mM, [C_6H_5CHO] = 0.1 mM, pH 1.3, and (b) [S(IV)] = 1.0 mM, [C_6H_5CHO] = 0.1 mM, pH 3.41.

TABLE IV: Thermodynamic Data for the Reaction[a] **$C_6H_5CHO + HSO_3^- \rightleftharpoons C_6H_5CH(OH)SO_3^-$**

T, °C	μ, M	10^{-3} K_{eq} ($\pm\sigma$), M^{-1}
15	0.1	11.6 ± 0.6
20	0.1	7.6 + 0.7
25	0.1	4.81 + 0.8
30	0.1	3.21 + 0.8
35	0.1	1.99 + 0.7
25	1.0	0.98 ± 0.11

[a] Determinations were made at pH 3.9 ± 0.1 with [$NaC_6H_5CH(OH)SO_3$]$_t$ = 41.0–92.0 μM.

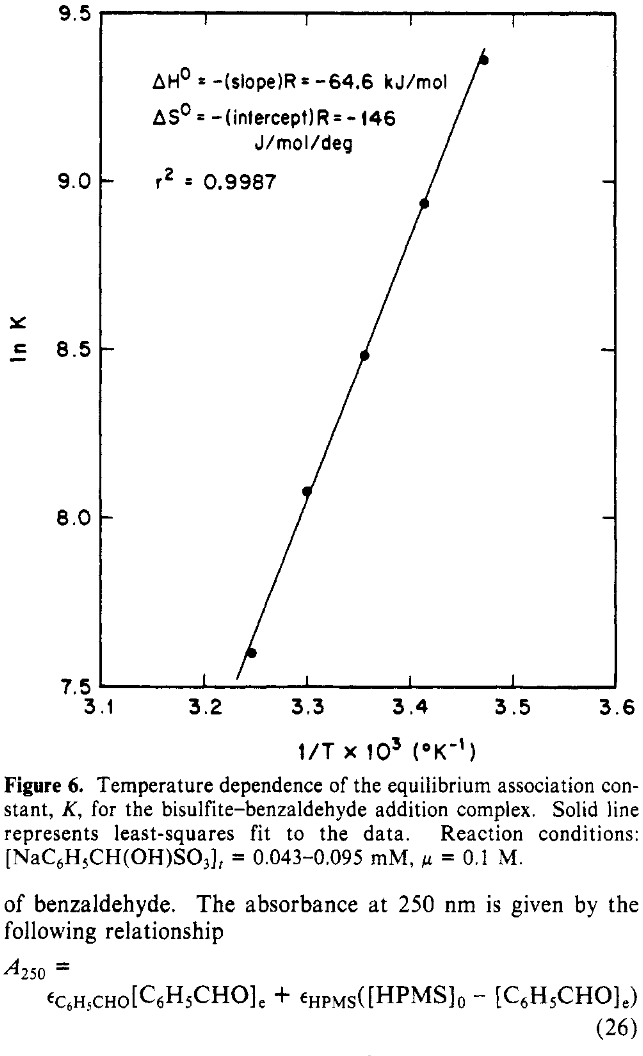

Figure 6. Temperature dependence of the equilibrium association constant, K, for the bisulfite–benzaldehyde addition complex. Solid line represents least-squares fit to the data. Reaction conditions: [$NaC_6H_5CH(OH)SO_3$]$_t$ = 0.043–0.095 mM, μ = 0.1 M.

at pH 4. Dissolution of the sodium sulfonate salt results in [HSO_3^-] = [C_6H_5CHO] at equilibrium; and consequently eq 24 can be reduced to

$$^{c}K = \frac{[\mathrm{HPMS}]_0 - [\mathrm{C_6H_5CHO}]_e}{[\mathrm{C_6H_5CHO}]_e^2} \quad (25)$$

where [HPMS]$_0$ is the initial concentration of the dissolved sulfonate salt and [C_6H_5CHO]$_e$ is the equilibrium concentration of benzaldehyde. The absorbance at 250 nm is given by the following relationship

$$A_{250} = \epsilon_{\mathrm{C_6H_5CHO}}[\mathrm{C_6H_5CHO}]_e + \epsilon_{\mathrm{HPMS}}([\mathrm{HPMS}]_0 - [\mathrm{C_6H_5CHO}]_e) \quad (26)$$

since ϵ of $H_2O{\cdot}SO_2$, HSO_3^-, and SO_3^{2-} at pH ~ 4.0 is negligible. At equilibrium, [C_6H_5CHO]$_e$ was calculated from eq 26 and substituted into eq 25 to yield the values of ^{c}K reported in Table IV. At μ = 0.1 M (25 °C), ^{c}K was determined to 4810 (±770) M^{-1}, which is in close agreement with Sousa and Margerum's[7] value of K = 4700 M^{-1} (dilute solution conditions, 23 °C). Values of $\Delta H°$ and $\Delta S°$ were calculated to be −64.6 kJ/mol and −146 J/mol/deg, respectively (Figure 6). If the activity coefficients of the ionic species are determined by the Davies equation, and $\gamma_{\mathrm{C_6H_5CHO}} \cong 1$, then the formation constant

$$^{c}K = {}^{a}K\left[\frac{\gamma_{\mathrm{HSO_3^-}}\gamma_{\mathrm{C_6H_5CHO}}}{\gamma_{\mathrm{HPMS^-}}}\right] \quad (27)$$

should be relative insensitive to ionic strength. However, when μ was increased to 1 M, ^{c}K decreased to 980 (±110) M^{-1}. This suggests that $\gamma_{\mathrm{C_6H_5CHO}}$ is considerably less than one.

Discussion

The intrinsic rate constants, k_1 and k_2, obtained for the steps leading to the production of HPMS are in fair agreement with

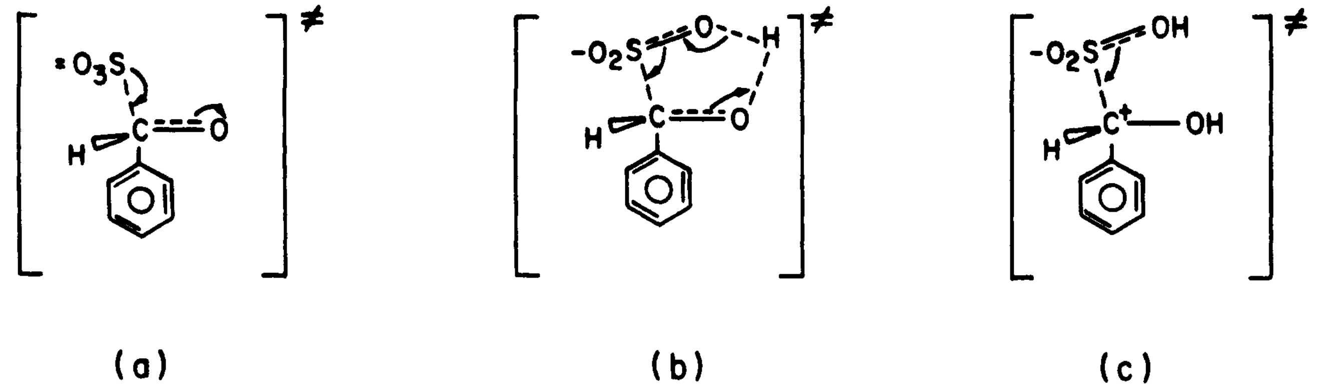

Figure 7. Possible structures for the activated complexes formed by the nucleophilic addition of (a) SO_3^{2-} and (b) HSO_3^- to benzaldehyde, and (c) HSO_3^- to $C_6H_5C^+H(OH)$.

TABLE V: Comparison of Intrinsic Rate Constants with Literature Values for the Formation of S(IV)-Benzaldehyde Addition Compounds

reaction	rate constant, $M^{-1}\ s^{-1}$	source/ref
C_6H_5CHO + SO_3^{2-} (k_1)	1.25×10^4 (21 °C)	5b
	2.15×10^4 (μ = 1 M, 25 °C)	this work
C_6H_5CHO + HSO_3^- (k_2)	0.43 (21 °C)	5b
	245 (13 °C)	7
	0.71 (μ = 1 M, 25 °C)	this work
C_6H_5CHO + $H_2O{\cdot}SO_2$ (k')	0.097 (21 °C)	5b
$C_6H_5C^+H(OH)$ + HSO_3^- (k_3)	2.5×10^7 (μ = 1 M, 25 °C)	this work

the corresponding constants determined by Stewart and Donnally[5b] (see Table V). Our higher values of k_1 and k_2 may be due to the higher temperature used in our study. Based on our $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, however, the 4 °C difference is too small to account for the entire difference in the rate constants. The effect of the higher ionic strength used in our experiments on k_1 and k_2 is not known and activity corrections would be difficult to apply since ionic strength was apparently not held constant in their study. The larger disagreement in k_1 suggests that a portion of the difference may be due to kinetic limitations of their iodometric method at neutral and high pH.

An alternative reaction mechanism for the formation of HPMS in which eq 8 is replaced with the following rate-limiting reaction

$$H_2O{\cdot}SO_2 + C_6H_5CHO \underset{k_{-3}'}{\overset{k_3'}{\rightleftharpoons}} C_6H_5CH(OH)SO_3H \quad (28)$$

as Stewart and Donnally have proposed,[5b] leads to the kinetically equivalent rate law

$$d[\Sigma HPMS]/dt = (k_1\alpha_2 + k_2\alpha_1 + k_3'\alpha_0)[S(IV)]_t[C_6H_5CHO] \quad (29)$$

where $\alpha_0 = [H_2O{\cdot}SO_2]/[S(IV)]$. (The third term in the sum can also be expressed in the form $k'\{H^+\}\alpha_1$.) Their mechanistic interpretation of the kinetics at very low pH appears improbable particularly because the species, $H_2O{\cdot}SO_2$, has not been observed to react with other aldehydes such as HCHO.[14] Since the difference between our mechanism and Stewart and Donnally's is evident only at extremely low pH, the discrepancy is of negligible importance in virtually all natural systems of interest.

Sulfite ion is predicted to be the strongest nucleophile among the S(IV) species for a wide variety of reactions with organic and inorganic substrates.[23-25] The observed order of increasing reactivity among the species, $SO_3^{2-} \gg HSO_3^- \gg H_2O{\cdot}SO_2$, was also demonstrated in our previous study of the formation of hydroxymethanesulfonate.[14] The ratio, k_1/k_2, was $\sim 3 \times 10^4$ for the formation of HPMS and HMS. Rate constants for the reaction of SO_3^{2-} and HSO_3^- with formaldehyde were 2.48×10^7 and 790 $M^{-1}\ s^{-1}$, respectively, and are roughly 3 orders of magnitude greater than the corresponding constants for benzaldehyde. The greater reactivity of formaldehyde is probably due to (1) the greater ordering required to form the benzaldehyde-S(IV) activated complexes and (2), the increased steric hindrance to the formation of the transition-state complex by the phenyl group. Clearly the $\Delta S^{\ddagger}$ values for both the benzaldehyde-sulfite and -bisulfite adducts were more negative than those for the corresponding formaldehyde adducts ($\Delta S_1^{\ddagger} = -40.2$ J mol^{-1} K^{-1} and $\Delta S_2^{\ddagger} = -121.3$ J mol^{-1} K^{-1} for HMS).

From our estimate of the rate constant for the addition of HSO_3^- and the carbocation, $C_6H_5C^+H(OH)$, the latter is at least 7 orders of magnitude more reactive than the unprotonated benzaldehyde. A possible activated complex for the addition of HSO_3^- to the carbonyl group is the cyclic structure shown in Figure 7b. Bisulfite addition to the electron deficient carbon atom of the carbocation most likely occurs without this structural constraint. Instead, the activated state (Figure 7c) is postulated to resemble the complex formed by benzaldehyde and SO_3^{2-} (Figure 7a).

Substituent effects resulted in less than an order of magnitude change in the rate constants, k_2 and k_3, relative to benzaldehyde. Blackadder and Hinshelwood have also demonstrated that para-substituent effects on the dissociation rate are slight.[6] Substantial differences in $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ for the *p*-OH and *p*-OCH_3 substituents suggest that there may be a change in mechanism.[26] These substituents may induce substitution of HSO_3^- directly on the phenyl ring. The *p*-NO_2 group exhibited the greatest reactivity, followed by the *p*-Cl group. The combined effect of electron withdrawal from the carbonyl center and a favorable dipole moment will result in enhanced nucleophilic addition.[27] The decreased reactivity of *p*-CH_3, *p*-OH, and *p*-OCH_3 in the k_1 step may be attributed to increased electron density on the carbonyl carbon due to inductive effects.

Substitution of a phenyl group for the proton of HCHO should lead to a less stable bisulfite-aldehyde adduct due to steric hindrance. Comparison of the HMS and HPMS equilibrium constants supports this notion. Deister et al.[28] have reported that the association constant for HSO_3^- and HCHO (25 °C) is 3.78×10^6 M^{-1}; this is nearly a factor of 10^3 larger than the value for K_{HPMS}.

Conclusions for Atmospheric Systems. Based on the above kinetic and thermodynamic results, certain conclusions can be drawn regarding the importance of these reactions in atmospheric water droplets. A rough estimate of the maximum concentration

---

(23) Schroeter, L. C. *Sulfur Dioxide, Applications in Foods, Beverages, and Pharmaceuticals*; Pergamon: New York, 1966, pp 105-67.

(24) Edwards, J. O. *Inorganic Reaction Mechanisms*; Benjamin: New York, 1965; pp 51-71.

(25) Hoffmann, M. R.; Edwards, J. O. *Inorg. Chem.* **1977**, *16*, 3333-8.

(26) Geissman, T. A. *Principles of Organic Chemistry*, 3rd ed.; W. H. Freeman: San Francisco, 1968; pp 547-59.

(27) Brown, R. F. *Organic Chemistry*; Wadsworth: Belmont, CA, 1975; pp 445-51.

(28) Deister, U.; Neeb, R.; Helas, G.; Warneck, P. *J. Phys. Chem.*, in press.

of aqueous HPMS which might be formed in a polluted open atmosphere was calculated by assuming a concentration of 0.2 μM free benzaldehyde, a SO_2 partial pressure, P_{SO_2}, of 20 ppb, and a pH of 4.0. A P_{SO_2}- of 20 ppb is common in some urban areas. The benzaldehyde concentration was chosen from the highest values cited for Los Angeles rainwater by Kawamura and Kaplan,[2] although it is not clear whether their analytical method measures free or total benzaldehyde. Our estimate would overpredict potential HPMS concentrations if complexed benzaldehyde was also detected by their analysis. A free aqueous benzaldehyde concentration calculated on the basis of a gas-phase–liquid equilibrium assumption leads to comparable concentrations. Solving the following equations for [HPMS]

$$[HSO_3^-] = \frac{P_{SO_2}H_{SO_2}K_{a1}}{\{H^+\}} \qquad (30)$$

$$[HPMS] = K_{HPMS}[C_6H_5CHO]_{free}[HSO_3^-] \qquad (31)$$

where H_{SO_2} (1.26 M atm^{-1} at 25 °C) is the Henry's law constant for SO_2, yields [HPMS] = 5.8 nM. This calculation indicates that only a small fraction of the benzaldehyde and S(IV) would be present as the adduct. The contribution of benzaldehyde to the speciation of S(IV) in atmospheric water droplets will be less important than that due to formaldehyde since benzaldehyde is less abundant and its adduct is less stable. Further research on other carbonyl–S(IV) systems is under way.

Acknowledgment. We gratefully acknowledge the Electric Power Research Institute (RP1630-47) and the Environmental Protection Agency (R811496-01-1) for providing financial support for this research. We also thank Drs. Detlef W. Bahnemann, Eric A. Betterton, and the reviewers for their helpful insight.

Registry No. *p*-$MeOC_6H_4CHO$, 123-11-5; *p*-MeC_6H_4CHO, 104-87-0; PhCHO, 100-52-7; *p*-ClC_6H_4CHO, 104-88-1; *p*-HOC_6H_4CHO, 123-08-0; *p*-$NO_2C_6H_4CHO$, 555-16-8; sodium bisulfite, 7631-90-5; sodium sulfite, 7757-83-7.

The Absolute Kinetics of Several Reactions of Substituted Diphenylcarbenes[1a]

L. M. Hadel,*[1b] V. M. Maloney,[1b] M. S. Platz,*[1b,2] W. G. McGimpsey,[1c] and J. C. Scaiano*[1c]

The Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, and Division of Chemistry, National Research Council, Ottawa, Ontario, Canada K1A 0R6 *(Received: October 16, 1984; In Final Form: December 6, 1985)*

4,4′-Dibromo-, 4-bromo-, 4,4′-dichloro-, 4-chloro-, 4-methyl-, 4,4′-dimethyl-, 4-phenyl-, 4-carbomethoxyl-, 4-cyano-, 4-cyano-4′-methyl-, and 4,4′-dimethyldiphenyldiazomethane were studied by laser flash photolysis. Excitation of the diazo compounds at 308 nm produced the corresponding diarylcarbenes. The kinetics of the reaction of the substituted carbenes with alkanes and methanol were examined. Hydrogen abstraction rates are largely insensitive to ring substitution, while the methanol reaction is accelerated considerably by *p*-methyl substitution and retarded by a para electron-withdrawing substituent.

Physical organic chemists have traditionally used substituent effects to probe the mechanism of a reaction. This is certainly true in the area of carbene chemistry where numerous workers have employed relative rate measurements in this regard.[3] Reports of substituent effects on the absolute kinetics of carbenes are rare. Closs and Rabinow reported on the kinetics of dimerization of diphenyl-, 4,4′-dibromodiphenyl-, and 4,4′-dimethyldiphenylcarbene;[4] they also measured the absolute rate constants for reaction of all three carbenes with 1,3-butadiene. The rate constant was found to be invariant with substituent being (6 ± 2) × 10^5 M^{-1} s^{-1} for all three carbenes. Closs has also studied the hydrogen atom abstraction reactions of four halo derivatives of diphenylcarbene with toluene by CIDNP. Turro and Moss have systematically varied the substituent pattern of phenyl halocarbenes and measured their reactivity toward olefins.[5] Miller and Shechter have studied the kinetics of thermal decomposition of substituted diphenyldiazomethanes.[6] Substitutent effects on the EPR and emission spectra of various diphenylcarbenes have been reported by Trozzolo and Gibbons and by Ware.[7] In this work we report the absolute kinetics of reactions of various diphenylcarbene derivatives with cyclohexane and with methanol.

TABLE I: Absorption Maxima for Substituted Diphenylcarbenes and Their Corresponding Benzhydryl Radicals

R	R′	λ_{max}, nm carbene	λ_{max}, nm radical	τ_G, μs
H	H	314	334 (335)[c]	1.5[a]
H	Br	321 (316)[d]	340	2.1[a]
Br	Br	330 (335)[c]	350 (350)[c]	1.6[a]
H	Cl	321 (311)[d]	338	2.0[a]
Cl	Cl	322	345	2.1[a]
CH_3	CH_3	323	340	1.2[a]
CH_3	CN	300	355–370	3.8[a] 5.9[b]
H	CN	295	350–380	5.4[a] 7.2[b]
H	CO_2CH_3	295	370	5.0[b]
H	Ph	350	380	7.8[a]

[a] Cyclohexane. [b] Isooctane. [c] Closs, ref 4. [d] Trozzolo, ref 7.

Experimental Section

In a typical experiment a deaerated solution of 5 × 10^{-5} M diazo compound was subjected to laser flash photolysis (308 nm, ≃4

---

(1) (a) Issued as NRCC No. 25528. (b) Ohio State University. (c) National Research Council of Canada.

(2) Camille and Henry Dreyfuss Teacher Scholar and Fellow of the Alfred P. Sloan Foundation.

(3) See Moss, R. A. *Carbenes*, Vol. I, Moss, R. A., Jones, Jr., M., Ed.; Wiley: New York, 1973.

(4) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.

(5) (a) Turro, N. J.; Butcher, Jr., J. A.; Moss, R. A.; Guo, W.; Munjal, R.; Fedorynski, M. *J. Am. Chem. Soc.* **1980**, *102*, 7576. (b) Turro, N. J.; Lehr, G. F.; Butcher, Jr., J. A.; Moss, R. A.; Guo, W. *J. Am. Chem. Soc.* **1982**, *104*, 1754. (c) Moss, R. A.; Perez, L. A.; Turro, N. J.; Gould, I. R.; Flacker, N. P. *Tetrahedron Lett.* **1983**, *24*, 685. (d) Cox, D. P.; Gould, I. R.; Hacker, N. P.; Moss, R. A.; Turro, N. J. *Tetrahedron Lett.* **1983** *24*, 5313.

(6) Miller, R. J.; Shechter, H. *J. Am. Chem.* Soc. **1978**, *100*, 7920.

(7) (a) Trozzolo, A. M.; Gibbons, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 239. (b) Ono, Y.; Ware, W. R. *J. Phys. Chem.* **1983**, *87*, 4426.