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Kinetics of the Oxidation of Sulfite by Hydrogen Peroxide in Acidic Solution

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The kinetics of the oxidation of sulfite by hydrogen peroxide has been investigated by stopped–flow spectrophotometry over the pH range 4–8. The rate law for the oxidation of sulfite in this pH range is $-d[SO_2]_T/dt = k[H^+][H_2O_2][SO_2]_T\{[H^+]/([H^+] + Ka_2)\} + k'[HA][H_2O_2][SO_2]_T\{[H^+]/([H^+] + Ka_2)\}$ where HA represents all possible proton donors in solution. The reaction probably proceeds via a nucleophilic displacement by H_2O_2 on HSO_3^- to form a peroxomonosulfurous acid intermediate which then undergoes a rate-determining rearrangement.

Control of sulfur dioxide produced in the burning of fossil fuels, in chemical manufacturing, and in paper-pulp processing is presently of great concern. With these environmental considerations in mind, we wish to report the preliminary results of a kinetic study of the oxidation of sulfite in acidic solution by hydrogen peroxide.

Sulfur dioxide is readily soluble in water and the resulting equilibrium relationship is normally written as[1]

$$SO_2 + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H^+ + HSO_3^- \qquad (1)$$
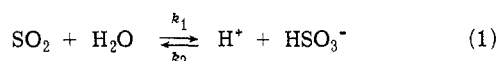
where at 20° and $\mu = 0.1$, $k_1 = 3.4 \times 10^6 \text{ sec}^{-1}$ and $k_2 = 2 \times 10^8 \text{ } M^{-1} \text{ sec}^{-1}$ as determined by ultrasonic absorption. In the present study the reaction between SO_3^{2-} and H_2O_2 was examined in the pH range 8–4. In this range ($pKa_1 = 1.37$, $pKa_2 = 7.0$, $\mu = 0.9$),[2] as the pH decreases, the fraction of total sulfite present as HSO_3^- increases so that at pH 4 the bisulfite ion is the predominant sulfite species in solution. Previous stoichiometric measurements[3–5] have shown that the primary oxidation product is sulfate and only an infinitesimal amount of dithionate is formed.

$$HSO_3^- + H_2O_2 \longrightarrow HSO_4^- + H_2O \qquad (2)$$

If a radical pathway was significantly involved in this oxidation then a considerable amount of dithionate should be formed.

Kinetic data for the reaction were obtained from stopped–flow spectrophotometric measurements at 260 nm with a slit width of 1.0 mm. The reaction was studied under pseudo-first-order conditions with $[H_2O_2] > [SO_3^{2-}]_T \doteq 5 \times 10^{-3}$ to 2×10^{-2} M at 12.0° and $\mu = 1.0$ over the pH range 8–4 using TRIS, TES, phosphate, citrate, pivalate, and acetate buffering systems. Solutions were prepared under nitrogen and EDTA salts were used in all kinetic runs to minimize the effect of trace metal catalysis and the oxidation of sulfite by oxygen.[6] Constant ionic strength was maintained with Na_2SO_4. The reaction rate is first order each in $[SO_2]_T$ and $[H_2O_2]$. Depicted in Figure 1 and listed in Table I are the results of a variation of pH at 12.0° with the sulfite, peroxide, and buffer concentrations held constant. In the pH range 8.3–6.5 the slope of the log k_{obsd} vs. pH plot is roughly −2 whereas in the pH range 6.5–4.5 the slope changes to approximately −1. This pH dependency

indicates that HSO_3^- is the principal reactive sulfite species in solution. Below pH 4.5, with the other conditions held constant the rate of the reaction exceeded the lower limit of detection by the stopped–flow system (i.e., the reaction was completed essentially within the time of mixing ~2 msec). In order to examine the possibility of general acid catalysis as observed by Mader[5] in his kinetic study of the reaction of SO_3^{2-} and H_2O_2 in alkaline solution, a series of kinetic runs was made with the ionic strength, $[H_2O_2]$, $[SO_2]_T$, and pH held constant while the buffer concentration was varied. The results are shown in Figure 2 and listed in Table II for a variation in the phosphate buffer concentration at pH 6.4 $\mu = 1.0$, and 12.0°. The other buffers employed in this study were not tested for possible catalytic behavior.

The results depicted in Figure 2 indicate that the oxidation is definitely subject to general acid catalysis. Mechanistically, this implies that hydrogen ions are transferred from a Brønsted acid (HA) to a substrate in the transition state or that there is an equilibrium protonation of the substrate followed by proton transfer to A⁻. In such cases any acidic molecule or ion can act to transfer the proton to the substrate; therefore, a multiterm rate law should be observed.[7] A two-term rate law which accounts for the observed kinetic behavior in the pH range 8–4 is

$$-d[SO_2]_T/dt = k[H^+][H_2O_2][SO_2]_T \{[H^+]/([H^+] + Ka_2)\} + k'[HA][H_2O_2][SO_2]_T \{[H^+]/([H^+] + Ka_2)\} \qquad (3)$$

where

$$[SO_2]_T = [HSO_3^-] + [SO_3^{2-}] \qquad (4)$$

$$Ka_2 = [SO_3^{2-}][H^+]/[HSO_3^-] \qquad (5)$$

In the pH range greater than 6.5, the sulfite is primarily unprotonated in the ground state; therefore, in going from the ground state to the transition state, two protons are needed which is reflected by the slope of approximately −2 in Figure 1. In pH range less than 6.5, the sulfite in the ground state is mostly protonated; therefore, in going from the ground state to the transition state, only one additional proton is required and this is reflected by a slope which is close to −1 in the lower pH range. k and k' have been calculated to be 5.8×10^1 and 7.2×10^2 $M^{-2} \text{ sec}^{-1}$, respectively, from the data in Table II for the described conditions.

TABLE I: Summary of Kinetic Data for the Oxidation of Sulfite by Hydrogen Peroxide at 12.0° where $[SO_3^{2}]_0$ = 2.0 × 10^{-2} M and $[H_2O_2]_0$ = 1.0 × 10^{-1} M

Buffer	pKa^a	[HA], M	[A⁻], M	pH	k_{obsd}, sec⁻¹	S^b
TRIS	8.3	0.2	0.2	8.25	0.02	
TES	7.5	0.2	0.2	7.45	0.11	
Phosphate	6.8	0.2	0.2	6.52	19.37	1.07
Citrate	5.6	0.2	0.2	5.65	119.98	6.16
Pivalate	5.1	0.2	0.2	5.08	205.01	10.52
Acetate	4.7	0.2	0.2	4.65	381.63	11.91

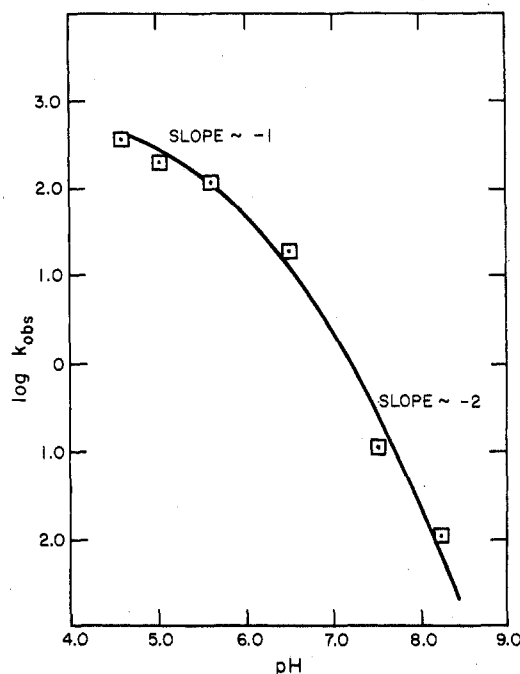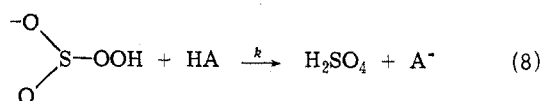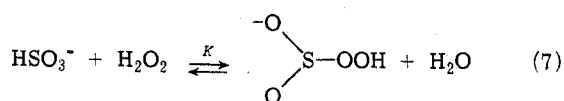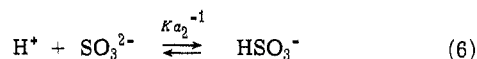^{a} At 20.0°. ^{b} Sample standard deviation where $N \geq 5$.

TABLE II: Summary of Kinetic Data for the Variation of $[H_2PO_4^-]$ at pH 6.40, 12.0°, μ = 1.0, $[SO_3^{-2}]_0$ = 5.0 × 10^{-3} M and $[H_2O_2]_0$ = 2.5 × 10^{-2} M

$[H_2PO_4^-]$, M	k_{obsd}, sec⁻¹	$[H_2PO_4^-]$, M	k_{obsd}, sec⁻¹
0.32	5.78	0.08	2.28
0.16	3.51	0.04	1.75

Figure 1. Plot of log k_{obsd} vs. pH for the oxidation of sulfite by hydrogen peroxide.

Figure 2. A plot of k_{obsd} as a function of $[H_2PO_4^-]$ at 12.0°, μ = 1.0, and pH 6.4.

A mechanism, which is consistent with the present kinetic results, can be written as follows

$$H^+ + SO_3^{2-} \underset{}{\overset{Ka_2^{-1}}{\rightleftarrows}} HSO_3^- \tag{6}$$

$$HSO_3^- + H_2O_2 \overset{K}{\rightleftarrows} \begin{smallmatrix}-O\\ \\O\end{smallmatrix}S-OOH + H_2O \tag{7}$$

$$\begin{smallmatrix}-O\\ \\O\end{smallmatrix}S-OOH + HA \overset{k}{\longrightarrow} H_2SO_4 + A^- \tag{8}$$

where

$$HA = H_3O^+ \text{ or } H_2PO_4^-$$
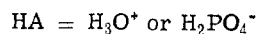
According to this mechanism, the reaction probably occurs via a nucleophilic displacement by H_2O_2 on HSO_3^- to form a peroxomonosulfurous acid intermediate which then undergoes a rate-determining rearrangement. Equation 7 is analogous to the reaction of hydrogen peroxide and sulfuric acid to give peroxomonosulfuric acid.[8]
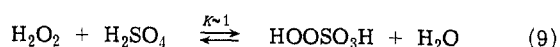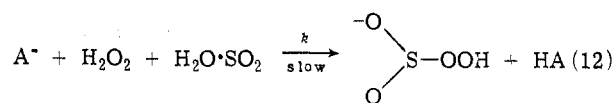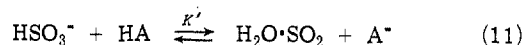
$$H_2O_2 + H_2SO_4 \overset{K \sim 1}{\rightleftarrows} HOOSO_3H + H_2O \tag{9}$$

Alternatively a mechanism in which there would be an equilibrium protonation of the bisulfite followed by a proton transfer to A⁻ can also be written as follows

$$H^+ + SO_3 \underset{}{\overset{Ka_2^{-1}}{\rightleftarrows}} HSO_3^- \tag{10}$$

$$HSO_3^- + HA \overset{K'}{\rightleftarrows} H_2O \cdot SO_2 + A^- \tag{11}$$

$$A^- + H_2O_2 + H_2O \cdot SO_2 \overset{k}{\underset{slow}{\longrightarrow}} \begin{smallmatrix}-O\\ \\O\end{smallmatrix}S-OOH + HA \tag{12}$$

$$\begin{smallmatrix}-O\\ \\O\end{smallmatrix}S-OOH \underset{rapid}{\longrightarrow} HSO_4^- \tag{13}$$
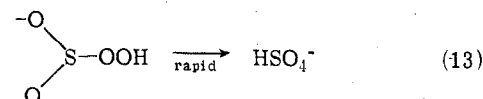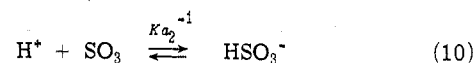
In this scheme, the termolecular step, in which A⁻, H_2O_2, and $H_2O \cdot SO_2$ react to form peroxomonosulfurous acid, would be rate determining. Both of these mechanisms are consistent with the results of an isotopic labeling study of the reaction between SO_3^{2-} and H_2O_2 at pH 5 by Halperin and Taube[9] in which the product sulfate was found to have two ^{18}O atoms which were present initially in the doubly labeled peroxide even though the stoichiometry requires the net addition of only one oxygen atom. Their results were rationalized in terms of a peroxomonosulfurous acid intermediate which rearranges to form the doubly labeled sulfate. Presently, there is no evidence for participation of the

pyrosulfite ion[2] in the reaction scheme, especially

$$2HSO_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S_2O_5^{2-} + H_2O$$

$$k_1 = 7.0 \times 10^2 \, M^{-1} \, sec^{-1}$$

$$k_{-1} = 1.0 \times 10^4 \, sec^{-1}$$

(14)
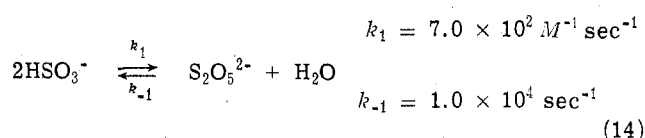
in light of the observed first-order dependence on the total sulfite concentration. Our results do not necessarily preclude a radical mechanism but when combined with the results of Halperin and Taube they seem to favor a polar mechanism. Recently, radical intermediates have been detected by ESR in the reaction of SO_2 and H_2O_2.[10] Contribution of a free-radical pathway in the overall reaction seems unlikely but it definitely cannot be excluded.

References and Notes

(1) M. Eigen, K. Kustin, and G. Maass, *Z. Phys. Chem. (Frankfurt am Main)*, **30**, 130 (1961).
(2) R. H. Betts and R. H. Voss, *Can. J. Chem.*, **48**, 2035 (1970).
(3) H. W. Albu and H. D. Graf von Schweinitz, *Berichte*, **65**, 729 (1935).
(4) W. C. E. Higginson and J. W. Marshall, *J. Chem. Soc.*, 447 (1957).
(5) P. M. Mader, *J. Am. Chem. Soc.*, **80**, 2634 (1958).
(6) K. Meyer and L. Roth, *Z. Wiss. Photogr.*, **49**, 10 (1958).
(7) J. O. Edwards, "Inorganic Reaction Mechanisms", Benjamin, New York, N.Y., 1965, p 17.
(8) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, N.Y., 1972, p 450.
(9) J. Halperin and H. Taube, *J. Am. Chem. Soc.*, **74**, 380 (1952).
(10) B. D. Flockhart, K. J. Ivin, R. C. Pink, and B. D. Sharma, *J. Chem. Soc. D*, 339 (1971).

Matrix Effects on the Charge Resonance Energy of the Dimer Cations. Low-Temperature Radiolysis of Glassy Aromatic Solutions[1]

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Near-infrared absorption bands due to several aromatic hydrocarbons in irradiated organic glasses have been assigned to the charge resonance band of the corresponding dimer cations. The observed drastic changes of these bands with the matrix characteristics are found to correspond to the changes in the structure of the dimer cation: a hard matrix (e.g., methylcyclohexane) strongly distorts the dimer cation, thereby reducing the charge resonance energy, unless steric effects are involved (difference between benzene and *tert*-butylbenzene). On softening the matrix there is a continuous relaxation process with a simultaneous increase in the charge resonance energy, until the conformation of the free dimer cation is reached. It is concluded that benzene and *tert*-butylbenzene do form quite loose complexes, suffering large matrix effects, that the naphthalene dimer cation is a very tight complex with no matrix effects, and that bromobenzene is intermediate. Earlier published band assignments by Ekstrom for systems with benzene are reconsidered in the context of this matrix effects. For a 3MP glass with benzene and CCl_3Br the benzene dimer cation decays isothermally (77 K) into a new transient, absorbing at 740 nm. The corresponding changes in the absorptions cannot be related to a matrix effect. The new 740-nm band was tentatively assigned to a complex between the benzene cation and CCl_3Br. The decay of the bromobenzene dimer cation in 3MP leads to the formation of a new absorption at 570 nm. This is assigned to the (Br·BrPh) charge transfer complex.

Introduction

In the low-temperature radiolysis of organic glasses and polycrystalline samples it is often puzzling that the position of many absorption bands depends rather critically on the matrix involved, the way the matrix was formed, the type of other solutes added, and on the temperature. This is particularly true for systems with aromatic hydrocarbons and with halogenated compounds. This paper discusses the behavior of the absorption bands of aromatic cations, related to the matrix involved.

It is well known that irradiation of aromatic compounds in hydrocarbon glasses, particularly in the presence of an electron scavenger, do yield aromatic cations. Such cations were studied at 77 K by Hamill and coworkers[3] in polycrystalline CCl_4,[4,5] in butyl chloride glasses,[6] and glasses of 3-methylpentane (3MP).[7] Similar information was given by Ekstrom[8] for a 3MP matrix at 77 K, by Willard and Ekstrom[9] for a methylcyclohexane (MCH) matrix at 20 K, and by Louvrier and Hamill[10] in alkane matrices at 77 K. The most detailed information stems from investigations by Badger and Brocklehurst in isopentane–butyl chloride glasses (IP:BuCl = 1:1) at 77K.[11-13] These authors detected cationic absorptions for many aromatic compounds: e.g., for benzene a charge-resonance band of the dimer cation $(C_6H_6)_2^+$ at 935 nm, an absorption band of the complexed monomer cation $(C_6H_6)_c^+$ at 470 nm and a band for the noncomplexed (free) cation $C_6H_6^+$ at 555 nm.[11] The