half-lives for spontaneous dissociation of Ce(NOTA), Gd(NOTA), and Er(NOTA) at a physiological pH of 7.4 are 7.7, 23.2, and 71.3 h, respectively.

Dissociation of the Ln(NOTA) complexes is catalyzed only by H^+ ions. NH_4^+ ions or other protonated amines that might act as Brønsted acids have no effect upon the rate of dissociation. Spontaneous dissociation of $Ce(DOTA)^-$ was not observed in a similar kinetic study.[11] This likely reflects the differing sizes and rigidities of the tetraaza (DOTA) versus the triaza (NOTA) macrocycles. The coordination cage of NOTA is too small for a Ln^{3+} cation, and as a result, less energy is required for the cation to leave the coordination cage and form the reactive LnL* species.

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Non-Metal Redox Kinetics: Reactions of Iodine and Triiodide with Sulfite and Hydrogen Sulfite and the Hydrolysis of Iodosulfate

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The reactions of I_3^- and I_2 with SO_3H^- and SO_3^{2-} (in the p[H$^+$] range 4.1–6.6) are studied by the pulsed-accelerated-flow technique. Pseudo-first-order rate constants (excess $[SO_3^{2-}]_T$ and $[I^-]$) are measured in the range from 6300 to 74000 s^{-1} (25.0 °C, μ = 0.50). The proposed mechanism is

$$I_3^- + SO_3H^- \xrightarrow{k_1} ISO_3^- + 2I^- + H^+$$

$$I_2 + SO_3H^- \xrightarrow{k_2} ISO_3^- + I^- + H^+$$

$$I_3^- + SO_3^{2-} \xrightarrow{k_3} ISO_3^- + 2I^-$$

$$I_2 + SO_3^{2-} \xrightarrow{k_4} ISO_3^- + I^-$$

where the second-order rate constants (M^{-1} s^{-1}) are $k_1 = 1.5 \times 10^7$, $k_2 = 1.7 \times 10^9$, $k_3 = 2.9 \times 10^8$, and $k_4 = 3.1 \times 10^9$. The iodosulfate that is formed hydrolyzes with a first-order rate constant of 298 s^{-1} at 25.0 °C.

$$ISO_3^- + H_2O \xrightarrow{k_h} I^- + SO_4^{2-} + 2H^+$$

A temperature-dependent stopped-flow study gives $\Delta H^\ddagger$ = 65 kJ mol^{-1} and $\Delta S^\ddagger$ = 21 J mol^{-1} K^{-1} for the hydrolysis reaction. The positive $\Delta S^\ddagger$ value indicates a dissociative mechanism without the addition of H_2O in the transition state for ISO_3^- hydrolysis.

Introduction

The reaction between iodine and sulfite is a component of the Landolt[1] system (a mixture of acidic KIO_3 and Na_2SO_3 that is well-known as a clock reaction). The iodine reaction with sulfite is extremely rapid, but Bünau and Eigen[2] were able to measure the kinetics in acidic solution in the presence of excess iodide. The disappearance of I_3^- was followed by a continuous-flow method with dilute, equimolar reactants. They proposed reactions 1 and 2, where k_1' was 2.2×10^7 M^{-1} s^{-1} and k_2' was 2.3×10^9 M^{-1} s^{-1}

$$I_3^- + HSO_3^- \xrightarrow{k_1'} HSO_3I + 2I^- \tag{1}$$

$$I_2 + HSO_3^- \xrightarrow{k_2'} HSO_3I + I^- \tag{2}$$

(22 °C, ionic strength μ = 1.0). Unfortunately, the abstract of their paper gave an incorrect exponent for k_1' (10^9 rather than the 10^7 value reported in their tables of data) and the incorrect k_1' value was also given in *Chem. Abstr.* **1962**, *57*, 2891f. The proposed HSO_3I intermediate was treated as a steady-state species that hydrolyzed rapidly (eq 3). Inoue and Sudo[3] studied the

$$HSO_3I + H_2O \xrightarrow{k_h} HSO_4^- + I^- + 2H^+ \tag{3}$$

reaction of I_2 and Na_2SO_3 by measurement of the temperature increase due to the heat of reaction under adiabatic conditions in a continuous-flow apparatus. They found that the initial reaction was too fast to be measured and that the rate obtained was due to the first-order hydrolysis of HSO_3I (eq 3). They reported a rate constant (k_h) of 130 s^{-1} at 17 °C for this hydrolysis.

A mixed Landolt chemical oscillator was demonstrated with hexacyanoferrate(II) as an additional reactant.[4] Edblom et al.[5] proposed a set of 13 elementary reactions and rate constants to fix the oscillatory behavior. The rate constant used for eq 4 was

$$I_2 + HSO_3^- + H_2O \rightarrow 2I^- + SO_4^{2-} + 3H^+ \tag{4}$$

1.0×10^6 M^{-1} s^{-1}, which is 3 orders of magnitude lower than the value measured by Bünau and Eigen.[2] Luo and Epstein[6] proposed an alternative feedback pathway for the mixed Landolt reaction and gave a set of 10 elementary reactions to simulate the oscillatory behavior. They used 2.2×10^7 M^{-1} s^{-1} as the value of the rate constant for eq 4 but suggested that most of the iodine was present as I_3^- to justify use of the rate constant for eq 1. Both oscillator studies[5,6] neglected the proposed HSO_3I intermediate.

The reaction of HOCl and SO_3^{2-} to give chlorosulfate (eq 5) proceeds by a very rapid Cl$^+$-transfer process with a rate constant

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of 7.6×10^8 M^{-1} s^{-1} at 25.0 °C.[7] This is followed by the slower

$$HOCl + SO_3^{2-} \rightarrow ClSO_3^- + OH^- \tag{5}$$

$$ClSO_3^- + H_2O \rightarrow Cl^- + SO_4^{2-} + 2H^+ \tag{6}$$

hydrolysis reaction eq 6 (270 s^{-1}, 25.0 °C).[8] Yiin and Margerum showed that the HOCl and SO_3^{2-} reaction system first releases base (eq 5) and then releases acid (eq 6).[8] Chlorosulfuric acid is a well-known strong acid that reacts violently with water in an exothermic process,[9] not unlike the effect when fuming H_2SO_4 is mixed with water. Halosulfuric (or halosulfonic) acids are known for F and Br as well as Cl, so we expect the reaction of iodine with sulfite to occur by I^+ transer to sulfur (nucleophilic attack by SO_3^{2-} on I_2) to give ISO_3^- as the initial product. This is consistent with the proposed[2,3] formation of an intermediate species and with an exothermic hydrolysis reaction.[3]

In other studies of sulfite oxidation by NH_2Cl,[10] by $NHCl_2$,[11] and by NCl_3,[11] where Cl^+ transfer to sulfur is also proposed, we have found SO_3^{2-} to be more than 2 orders of magnitude faster to react than SO_3H^-. Hence, we wished to explore the kinetics of the reactions of I_3^- and I_2 with SO_3^{2-} as well as with SO_3H^-. These reactions are too fast to be measured by conventional continuous-flow spectroscopy (e.g. Bünau and Eigen[2] used reaction times of 1.6–6.2 ms) but can easily be measured by pulsed-accelerated-flow (PAF) spectroscopy where reaction half-lives can be as much as several thousand times smaller.[12-14] In addition, the precision of the PAF measurements is superior to that possible with the instrument used by Bünau and Eigen.[2,15] The PAF measurements permit pseudo-first-order conditions to be used (excess sulfite and excess iodide) so that it is easier to resolve rate constants for parallel paths. We determine four rate constants for the reactions of I_3^- and I_2 with SO_3H^- and SO_3^{2-}. Our results confirm the magnitude of the rate constants for SO_3H^- reported previously[2] and show even larger rate constants for SO_3^{2-} with I_3^- and I_2. Our chemical system is less complex than that of Bünau and Eigen, because their measurements depended on the equilibrium between SO_3H^- and $H_2O{\cdot}SO_2$ to suppress the rate. They also observed reversible formation of the first intermediate, and the rate of hydrolysis of ISO_3^- contributed to their overall rate. We are able to force the initial formation of ISO_3^- to completion to give simple pseudo-first-order reactions.

We use stopped-flow spectroscopy to measure the rate of hydrolysis of ISO_3^- over a temperature range of 2.0 to 25.0 °C. Our results confirm the hydrolysis behavior suggested by Inoue and Sudo.[3] We propose that the intermediate is ISO_3^- (with an I–S bond) rather than HSO_3I (with an I–O bond).

Experimental Section

Reagents. Fresh sulfite solutions were prepared by dissolving weighed amounts of sodium sulfite in aqueous buffer solutions and were standardized by iodometric titration. Anaerobic and metal-free conditions were strictly observed during use to avoid the trace-metal-catalyzed autoxidation of sulfite.[16-20] Stock solutions of I_2/I_3^- were prepared by dissolving solid sublimed iodine in water with small amounts of NaI at pH 5–6. Dilution of the stock I_2/I_3^- solution was performed just prior to use. The solution was standardized spectrophotometrically after adding a large excess of NaI (ϵ_{353} = 26 400 M^{-1} cm^{-1} for I_3^-).[21] Acetate buffer was prepared from a stock acetic acid solution that was standardized by titration with standard NaOH to the phenolphthalein end point. Phosphate buffer was prepared from NaH_2PO_4 and Na_2HPO_4 by weight. Ionic strength was maintained at 0.50 with recrystallized sodium perchlorate.

Table I. Formation and Protonation Constants[a]

equilibrium reacn	K, M^{-1}
$I_2 + I^- \rightleftarrows I_3^-$	721[b]
$SO_3^{2-} + H^+ \rightleftarrows SO_3H^-$	$10^{6.6}$[c]
$CH_3COO^- + H^+ \rightleftarrows CH_3COOH$	$10^{4.48}$[d]
$HPO_4^{2-} + H^+ \rightleftarrows H_2PO_4^-$	$10^{6.46}$[e]

[a] μ = 0.50, 25.0 °C. [b] References 27 and 29–31. [c] Cuta, F.; Beranek, E.; Pisecky, J. *Chem. Listy* **1957**, *51*, 1614–1617. Frydman, M.; Nilsson, G.; Rengemo, T.; Sillen, L. G. *Acta Chem. Scand.* **1958**, *12*, 878–884. [d] Deneux, M.; Meilleur, R.; Benoit, R. L. *Can. J. Chem.* **1968**, *46*, 1383–1388. [e] Mesmer, R. E.; Baes, C. F. *J. Solution Chem.* **1974**, *3*, 307–321.

p[H+] Measurements. An Orion Model 601A Research digital pH meter equipped with a Corning combination electrode was used. The pH measurements were corrected to p[H^+] values at 25.0 °C and μ = 0.50 on the basis of electrode calibration by titration of standard $HClO_4$ with standard NaOH solution.

Pulsed-Accelerated-Flow Spectrophotometer.[12-14] PAF Model IV[14] was used to obtain data for the reactions of excess sulfite with I_2/I_3^- by following the loss of I_3^- at 353 nm. In this study, the flow was decelerated during the pulse to give a linear velocity profile, and 250 measurements of transmittance were taken as the flow velocity in the observation tube decreased from 12.5 to 3 m/s. The transmittance measurements were converted to the absorbance values, and the analysis of first-order rate constants was based on eq 7 for integrating observation of continuous

$$M_{\text{exptl}} = \frac{A_v - A_\infty}{A_0 - A_\infty} = \frac{v}{bk_{\text{app}}} \tag{7}$$

flow.[13,22,23] M_{exptl} is the defined absorbance ratio, A_v is the absorbance of the reactant mixture at a given instantaneous velocity, A_∞ is the absorbance at infinite time, A_0 is the absorbance at time zero, k_{app} is the apparent rate constant (s^{-1}), b is the path length of the observation tube (0.01025 m), and v is the solution velocity in the observation tube (m/s) at the time A_v is measured. Equation 7 is valid when k_{app} is greater than 4000 s^{-1}, so that $bk_{\text{app}}/v \gg 1$.[13] The apparent rate constant, k_{app}, is related to the first-order rate constant, k_r (s^{-1}), and a mixing rate constant, k_{mix} (s^{-1}), as given in eq 8. The mixing rate constant depends on

$$\frac{1}{k_{\text{app}}} = \frac{1}{k_{\text{mix}}} + \frac{1}{k_r} \tag{8}$$

$$k_{\text{mix}} = k_m v \tag{9}$$

the flow velocity (eq 9), where k_m (m^{-1}) is a proportionality constant and v varies from 12.5 to 3.0 m/s. Substitution of eqs 8 and 9 into eq 7 yields eq 10. Plots of M_{exptl} vs v are linear with a slope of $1/(bk_r)$ and an

$$M_{\text{exptl}} = \frac{A_v - A_\infty}{A_0 - A_\infty} = \frac{1}{bk_m} + \frac{v}{bk_r} \tag{10}$$

intercept of $1/(bk_m)$. Five PAF runs were measured for each set of conditions, and the average k_r values are reported with their standard deviations. At 353 nm typical values of A_0 = 1.07 for $[I_2]_T = 2.0 \times 10^{-5}$ and $[I^-]$ = 0.10 M, while A_∞ is near zero. The p[H^+] values of all the PAF studies are kept ≤7 to prevent interference from the base hydrolysis[24] of I_2 and I_3^-. The rate constants were all measured at 25.0 °C and ionic strength 0.50. The k_r values varied from 6300 to 74 000 s^{-1}, which is a range where eq 10 is valid.[13,14]

Stopped-Flow Spectrophotometer. Data for the rate of ISO_3^- hydrolysis were collected by use of Durrum stopped-flow (1.88-cm cell path)

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Table II. Pseudo-First-Order Rate Constants for the Reaction of Excess SO_3H^- and SO_3^{2-} with I_3^- and I_2[a]

exp no.	$10^4[SO_3^{2-}]_T$, M	$[I^-]$, M	$p[H^+]$	$10^{-4}k_r$, s^{-1}
1	1.40	0.100	4.98	0.628 ± 0.006[b]
2	2.81	0.100	4.98	1.25 ± 0.03[b]
3	4.21	0.100	4.98	1.84 ± 0.07[b]
4	5.62	0.100	4.98	2.59 ± 0.07[b]
5	6.32	0.100	4.98	2.96 ± 0.06[b]
6	1.83	0.075	6.45	2.9 ± 0.2[c]
7	2.75	0.075	6.45	4.6 ± 0.3[c]
8	3.67	0.075	6.45	6.1 ± 0.2[c]
9	1.92	0.100	6.58	3.3 ± 0.1[d]
10	2.56	0.100	6.58	4.5 ± 0.2[d]
11	2.88	0.100	6.58	4.8 ± 0.3[d]
12	3.84	0.100	6.58	7.2 ± 0.2[d]
13	2.47	0.100	4.07	1.01 ± 0.01[b]
14	2.47	0.100	4.23	1.01 ± 0.01[b]
15	2.47	0.100	4.36	0.98 ± 0.01[b]
16	2.47	0.100	4.68	0.85 ± 0.01[b]
17	2.47	0.100	4.92	0.85 ± 0.01[b]
18	1.49	0.035	4.53	1.23 ± 0.03[e]
19	3.22	0.020	4.69	4.4 ± 0.2[b]
20	1.49	0.015	4.53	2.54 ± 0.04[e]
21	2.34	0.012	4.65	4.4 ± 0.2[e]
22	3.22	0.010	4.69	7.4 ± 0.3[b]
23	1.28	0.070	6.63	2.7 ± 0.2[d]
24	1.28	0.040	6.63	2.94 ± 0.09[d]
25	1.28	0.020	6.63	3.9 ± 0.3[d]
26	1.28	0.015	6.63	4.5 ± 0.1[d]
27	1.28	0.010	6.63	5.5 ± 0.2[d]

[a] Conditions: $\mu = 0.50$, 25.0 °C; $[I_2]_T = (0.60\text{–}2.00) \times 10^{-5}$ M; $\lambda_{obsd} = 353$ nm. [b] $[CH_3COOH]_T = 0.100$ M. [c] $[PO_4^{3-}]_T = 0.050$ M. [d] $[PO_4^{3-}]_T = 0.075$ M. [e] $[CH_3COOH]_T = 0.050$ M.

or Hi-Tech stopped-flow (2.0-mm cell path) spectrophotometers interfaced to a Zenith 151 PC with a MetraByte DASH-16 A/D interface card.[25] The observed first-order rate constants (k_{obsd}, s^{-1}) for the ISO_3^- hydrolysis were determined at 300 nm from a least-squares-linear-regression plot of ln $(A_t - A_\infty)$ vs time (eq 11), where A_∞ represents the

$$\ln \frac{A_t - A_\infty}{A_0 - A_\infty} = -k_{obsd}t \qquad (11)$$

final absorbance and A_t is the absorbance at any time. All the k_{obsd} values were corrected for mixing effects (eq 12)[26] to give the corrected

$$k_h = k_{obsd}/(1 - k_{obsd}/k_{mix}) \qquad (12)$$

hydrolysis rate constant (k_h, s^{-1}), where $k_{mix} = 1700$ s^{-1} for the Durrum stopped-flow and $k_{mix} = 1000$ s^{-1} for Hi-Tech stopped-flow spectrophotometers. The ionic strength for the ISO_3^- hydrolysis study was 0.005–0.20. All the kinetics data were analyzed over 4 or more half lives. Each k_h value is the average of at least 5 runs and is reported with its standard deviation.

Equilibrium Constants. In order to resolve the four individual rate constants for the reactions of SO_3H^- and SO_3^{2-} with I_3^- and I_2, it is important to use equilibrium constants that have been established at 25.0 °C and $\mu = 0.50$. These are summarized in Table I along with protonation constants of the buffers for these conditions.

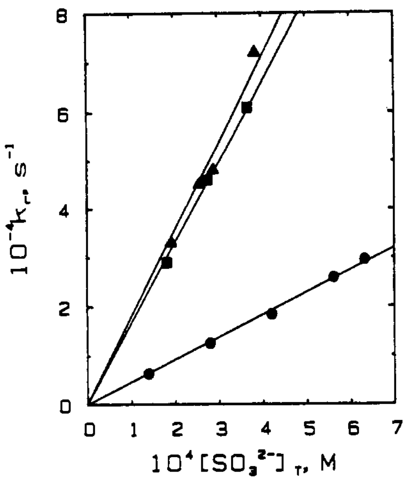

Figure 1. Dependence of the pseudo-first-order rate constant (k_r) on the total sulfite concentration at different $p[H^+]$: (●) $[I^-] = 0.100$ M, $p[H^+] = 4.98$; (■) $[I^-] = 0.075$ M, $p[H^+] = 6.45$; (▲) $[I^-] = 0.100$ M, $p[H^+] = 6.58$.

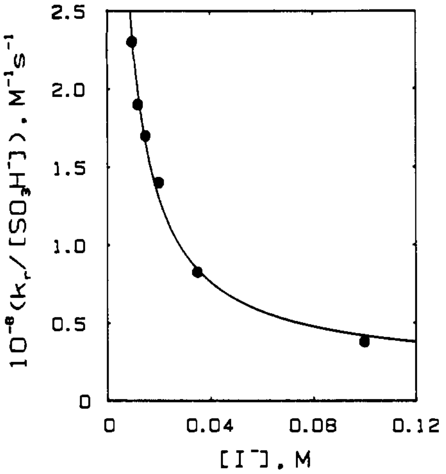

Figure 2. Dependence of k_r value on the I^- concentration. $p[H^+] = 4.07\text{–}4.92$. The curve is evaluated from eq 22, where $k_1 = 1.8$ (±0.6) × 10^7 M^{-1} s^{-1} and $k_2 = 1.80$ (±0.06) × 10^9 M^{-1} s^{-1}.

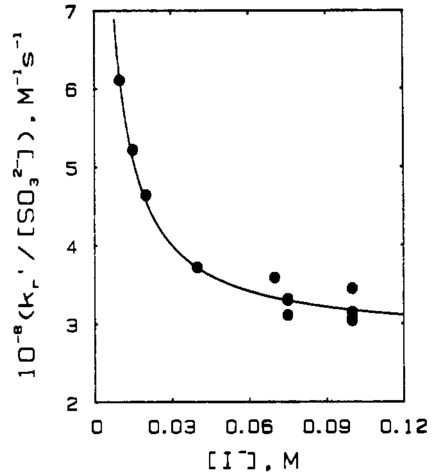

Figure 3. Dependence of the reduced k_r' value (k_r less the SO_3H^- contribution) on the I^- concentration. $p[H^+] = 6.45\text{–}6.63$. The curve is evaluated from eq 23, where $k_3 = 2.8$ (±0.1) × 10^8 M^{-1} s^{-1} and $k_4 = 3.0$ (±0.3) × 10^9 M^{-1} s^{-1}.

Results

PAF Studies. Linear M_{exptl} versus velocity plots are obtained for the reactions of I_2/I_3^- mixtures with a 10-fold or greater excess of total sulfite ($[SO_3^{2-}]_T = [SO_3H^-] + [SO_3^{2-}]$). The resulting pseudo-first-order rate constants, k_r, increase with the concentration of $[SO_3^{2-}]_T$, as seen in Table II for experiment nos. 1–5 at $p[H^+]$ 4.98, experiment nos. 6–8 at $p[H^+]$ 6.45, and experiment nos. 9–12 at $p[H^+]$ 6.58. Figure 1 shows the first-order dependence in $[SO_3^{2-}]_T$, where the larger slope at higher $p[H^+]$ is due to the greater reactivity of SO_3^{2-} compared to SO_3H^-. On the other hand, experiment nos. 13–17 show negligible change in k_r values (average 9400 ± 700 s^{-1}) from $p[H^+]$ 4.07 to 4.92 when $[SO_3^{2-}]_T$ and $[I^-]$ are held constant. This indicates that in this $p[H^+]$ range SO_3H^- is the predominant reactant and that the SO_3^{2-} concentration is too small to contribute significantly to the rate.

The values of k_r decrease as the iodide concentration increases at constant $[SO_3^{2-}]_T$ and constant $p[H^+]$ (Table II, experiment nos. 18–27), as seen in Figures 2 and 3. This indicates that I_3^-

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Table III. First-Order Rate Constants for Study of ISO_3^- Hydrolysis[a]

temp, K	$10^3[SO_3^{2-}]_T$, M	pH	k_h, s^{-1}
298.0	2.60	7.83	292 ± 2
298.0	2.60	3.64	294 ± 7
298.0	5.10	6.94	297 ± 7
298.0	5.10	3.29	294 ± 8
298.0	0.415	3.10	304 ± 14[b]
298.0	0.415	3.10	307 ± 8[c]
			298 ± 5 (av)
293.0	2.57	7.54	202 ± 18
288.0	2.57	7.54	127 ± 7
283.0	2.57	7.54	73 ± 4
278.0	2.57	7.54	42 ± 1
275.0	2.57	7.54	32 ± 1

[a] Conditions: $\mu = 0.005–0.20$; $\lambda_{obsd} = 300$ nm; temp, ±0.1 K; $[I_2]_T = 2.63 \times 10^{-4}$ M, $[I^-]_i = 1.22 \times 10^{-3}$ M. [b] $[I_2]_T = 2.81 \times 10^{-5}$ M, $[I^-]_i = 0$ M. [c] $[I_2]_T = 2.81 \times 10^{-5}$ M, $[I^-]_i = 0.20$ M.

is less reactive than I_2. Changes in buffers (CH_3COOH/CH_3COO^- or $H_2PO_4^-/HPO_4^{2-}$) or in the buffer concentrations have no effect other than that associated with a change of $p[H^+]$ values. Hence, there is no evidence for general acid or general base catalysis or for rate limitations due to proton-transfer reactions.

Stopped-Flow Studies. Excess sulfite and I_2/I_3^- solutions were mixed in the stopped-flow spectrophotometer, and the reaction was monitored from 260 nm to 360 nm at 10-nm intervals. Little or no signal change with time was observed except at 300 nm. An excellent first-order absorbance decrease was observed at 300 nm whereas no signal was seen at 353 nm (I_3^- absorption peak). The Durrum stopped-flow spectrophotometer used in this study has a 4.1-ms "dead-time" limitation.[26] The initial ISO_3^- absorbance at 300 nm is corrected for the "dead time" by extrapolating the absorbance to time zero. The calculated molar absorptivity of ISO_3^-, based on the assumption of a 100% yield of ISO_3^- upon mixing iodine and sulfite, equals 500 M^{-1} cm^{-1}. The experimental conditions and results are given in Table III. At 25.0 °C, the resolved rate constants, k_h, are essentially the same (292–307 s^{-1}) within experimental error despite the changes in $[SO_3^{2-}]_T$ (0.415–5.10 mM), $[I^-]$ (0–0.20 M), $[I_2]_T$ (0.0281–0.263 mM), ionic strength (0.005–0.20), and pH values (3.10–7.83). The Hi-Tech stopped-flow spectrophotometer was used to study the temperature dependence from 293.0 to 275.0 K. The k_h values decrease by 1 order of magnitude as the temperature decreases from 298.0 to 275.0 K. An Eyring plot of $\ln(k_h/T)$ against $1/T$ gives $\Delta H^{\ddagger} = 65\ (\pm 2)$ kJ mol^{-1} and $\Delta S^{\ddagger} = 21\ (\pm 1)$ J mol^{-1} K^{-1}.

Discussion

Proposed Mechanism. Equations 13–19 give the reaction mechanism, where eqs 13 and 14 are preequilibrium reactions prior to the rate-determining steps in eqs 15–18 that are observed by the PAF methods. The hydrolysis of ISO_3^- in eq 19 is not

$$I_2 + I^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} I_3^- \qquad (13)$$

$$SO_3H^- + B \underset{k_{HB}}{\overset{k_B}{\rightleftharpoons}} SO_3^{2-} + HB^+ \qquad (14)$$

$$I_3^- + SO_3H^- \xrightarrow{k_1} ISO_3^- + 2I^- + H^+ \qquad (15)$$

$$I_2 + SO_3H^- \xrightarrow{k_2} ISO_3^- + I^- + H^+ \qquad (16)$$

$$I_3^- + SO_3^{2-} \xrightarrow{k_3} ISO_3^- + 2I^- \qquad (17)$$

$$I_2 + SO_3^{2-} \xrightarrow{k_4} ISO_3^- + I^- \qquad (18)$$

$$ISO_3^- + H_2O \xrightarrow{k_h} I^- + SO_4^{2-} + 2H^+ \qquad (19)$$

observed in the PAF measurements, which monitor the loss of I_3^- at 353 nm. The absorbance of ISO_3^- at this wavelength is very small, and it does not contribute significantly to the observed signal. In order for eq 13 to be a preequilibrium step, the $k_f[I^-]$ and k_b values must be much larger than the observed first-order rate constants (k_r). This is the case because $k_f = 6.2 \times 10^9$ M^{-1} s^{-1} and $k_b = 8.5 \times 10^6$ s^{-1}, as determined by relaxation methods.[27] In eq 14, B refers to bases (H_2O, OH^-, CH_3COO^-, HPO_4^{2-}) that can accept a proton from SO_3H^-. The presence of moderately high concentrations of buffers (0.05–0.10 M) ensures that the proton-transfer reactions are rapid[28] compared to the I_2/I_3^- reactions with SO_3H^-/SO_3^{2-}. These precautions are necessary because the extremely large rate constants for the I_2 reactions (k_3 and k_4) are of magnitudes similar to those of proton transfer rate constants. The rate expression for the loss of $[I_2]_T$ is given in eq 20, where $[I_2]_T = [I_2] + [I_3^-]$. The general expression for k_r values

$$-d[I_2]_T/dt = k_r[I_2]_T = (k_1[I_3^-] + k_2[I_2])[SO_3H^-] + (k_3[I_3^-] + k_4[I_2])[SO_3^{2-}] \qquad (20)$$

$$k_r = \frac{(k_1K_I[I^-] + k_2)[SO_3H^-] + (k_3K_I[I^-] + k_4)[SO_3^{2-}]}{K_I[I^-] + 1} \qquad (21)$$

from the PAF studies is given by eq 21, where $K_I = [I_3^-]/([I_2][I^-])$. The value of K_I is very temperature dependent,[29,30] but it is independent of ionic strength.[27,30,31] A careful review of the literature gives 721 M^{-1} as the best value at 25.0 °C.[30]

Iodide Dependence of SO_3H^- and SO_3^{2-} Reactions. The iodide dependence of SO_3H^- reactions is shown in Figure 2. In the $p[H^+]$ range 4.07–4.92, $[SO_3H^-] \gg [SO_3^{2-}]$ ($pK_a = 6.6$ for SO_3H^-, Table I); thus, the $[SO_3^{2-}]$ terms are eliminated from eq 21 to give eq 22. Data for the iodide dependence study (experiment nos. 13–22

$$k_r = \frac{(k_1K_I[I^-] + k_2)[SO_3H^-]}{K_I[I^-] + 1} \qquad (22)$$

in Table II) are analyzed on the basis of eq 22 by using a nonlinear-least-squares algorithm. The plot of the $k_r/[SO_3H^-]$ values against $[I^-]$ (Figure 2) gives $k_1 = 1.8\ (\pm 0.6) \times 10^7$ M^{-1} s^{-1} and $k_2 = 1.80\ (\pm 0.06) \times 10^9$ M^{-1} s^{-1}.

The iodide dependence study for the SO_3^{2-} reaction is performed in the $p[H^+]$ range from 6.45 to 6.63. The portion that the SO_3^{2-} reactions contribute to the k_r values (experiment nos. 6–12 and 23–27 in Table II) is isolated by subtracting the $(k_1K_I[I^-] + k_2)/(K_I[I^-] + 1)[SO_3H^-]$ term from both sides of eq 21. The reduced k_r' value as a function of $[I^-]$ is given in eq 23. The

$$k_r' = \frac{(k_3K_I[I^-] + k_4)[SO_3^{2-}]}{K_I[I^-] + 1} \qquad (23)$$

nonlinear-least-squares fit of $k_r'/[SO_3^{2-}]$ values against $[I^-]$ is shown in Figure 3 and gives $k_3 = 2.8\ (\pm 0.1) \times 10^8$ M^{-1} s^{-1} and $k_4 = 3.0\ (\pm 0.3) \times 10^9$ M^{-1} s^{-1}.

Refined Values for the Resolved Rate Constants. The initial assumption that the k_3 and k_4 paths do not contribute to the rate below $p[H^+]$ 5 is almost, but not quite, valid. The k_2 path predominates (53–92% of the rate), and the k_3, k_4 paths carry less than 10% of the rate. In the $p[H^+]$ range 6.45–6.63 the k_3 path predominates (27–77% of the rate). A multilinear regression was performed on eq 21, where $[SO_3^{2-}] = K_a[SO_3^{2-}]_T/(K_a + [H^+])$ and $[SO_3H^-] = [H^+][SO_3^{2-}]_T/(K_a + [H^+])$, for all the $[SO_3^{2-}]_T$, $[I^-]$, and $p[H^+]$ values given in Table II. The results for the rate constants (M^{-1} s^{-1}) are $k_1 = 1.5\ (\pm 0.8) \times 10^7$, $k_2 = 1.7\ (\pm 0.1) \times 10^8$, $k_3 = 2.9\ (\pm 0.3) \times 10^8$, and $k_4 = 3.1\ (\pm 0.8) \times 10^9$, where one standard deviation is given. These values are used to calculate the corresponding slopes in Figure 1, and they agree with the experimental results. Table IV reports the rate constants and also gives the values for k_1 and k_2 that were resolved by Bünau and

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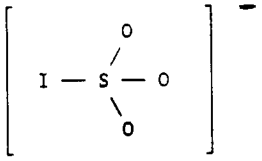
Table IV. Second-Order Rate Constants for the Reaction of SO_3H^- and SO_3^{2-} with I_3^- and I_2[a,b]

reacn	k, M^{-1} s^{-1}	reacn	k, M^{-1} s^{-1}
$SO_3H^- + I_3^- \xrightarrow{k_1}$	1.5 (±0.8) × 10^7	$SO_3^{2-} + I_3^- \xrightarrow{k_3}$	2.9 (±0.3) × 10^8
	2.2 × 10^7[c]	$SO_3^{2-} + I_2 \xrightarrow{k_4}$	3.1 (±0.8) × 10^9
$SO_3H^- + I_2 \xrightarrow{k_2}$	1.7 (±0.1) × 10^9		
	2.3 × 10^9[c]		

[a] 25.0 °C, $\mu = 0.50$; $K_1 = 721$ M^{-1}. [b] The rate constants given for hydrogen sulfite are for $[SO_3H^-]_T$ and neglect different reactivities of the two isomers: SO_3H^- and HSO_3^-.[10,35] The specific rate constants for the SO_3H^- species (with the proton on the oxygen) should be corrected by the factor 5.9/4.9. [c] Reference 2, 22 °C, $\mu = 1.0$, $K_1 = 816$ M^{-1} (the precision is not specified).

Eigen. Their evaluation was excellent despite the limitations of their equipment and is in general agreement with our values.

Iodosulfate. We have written the formula of the first reaction product as ISO_3^- (structure I), rather than HSO_3I because we

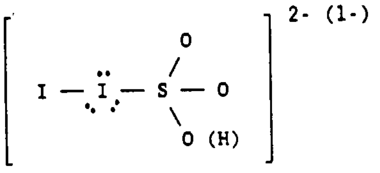


I

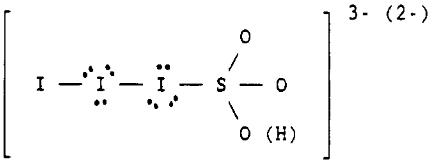
believe that an I–S bond is formed rather than an I–O bond and because we expect ISO_3H to be a strong acid that is fully ionized in water as is the case with FSO_3H and $ClSO_3H$. Bünau and Eigen[2] stated that it remains to be seen whether an I–O bond or an I–S bond is formed, but they emphasized the covalent nature of the product. The crystal structure of $(FSO_3^-)K^+$ has been determined,[32] and the ion is assigned C_{3v} symmetry with a S–F bond distance of 1.58 Å. Chlorosulfuric acid ($ClSO_3H$) is a well-known strong acid. Bromosulfuric acid ($BrSO_3H$) is more difficult to prepare but has been synthesized by the reaction of HBr and SO_3 in liquid sulfur dioxide at −35 °C.[33] Attempts to prepare ISO_3H by the same technique were not successful.[34] However, ISO_3^- has been postulated from studies of I_2 in SO_3.[35]

The hard–soft acid–base principles[36,37] indicate that I–S bonding is more likely than I–O bonding. Although SO_3^{2-} is reported to add a proton preferentially at oxygen rather than sulfur (with a SO_3H^-/HSO_3^- ratio of 4.9),[38] I^+ should prefer to react at sulfur. While H^+ is a very hard acid, I^+ is a very soft acid that prefers a soft base.[39] A similar preference for sulfur bonding is demonstrated for CH_3Hg^+ with SO_3^{2-} compared to PO_4H^{2-}. The protonation stability constants are essentially the same for SO_3^{2-} and PO_4H^{2-}, but the CH_3Hg^+ stability constant is 3.08 log units greater for SO_3^{2-} due to Hg–S bonding.[40] Recent tabulations of absolute hardness (η, eV) give values for Cl^+, Br^+, and I^+ of 5.42, 5.0, and 4.34. The corresponding softness ($\sigma = 1/\eta$) shows I^+ to be a very soft Lewis acid.[41] Hence, it should have a strong preference to bond to sulfur rather than to oxygen in SO_3^{2-}.

Comparison of Reaction Paths. Sulfite is a stronger nucleophile than hydrogen sulfite, and I_2 is a stronger electrophile than I_3^-. This is reflected in the relative values of the rate constants where $k_2 > k_1$, $k_4 > k_3$, $k_3 > k_1$, and $k_4 > k_2$. In the proposed transition state for the reactions of SO_3H^- and SO_3^{2-} with I_2, the valence shell of one iodine expands to five electron pairs (three nonbonding pairs and two bonding pairs) to give structure II, which is similar to the linear structures found for I_3^- and ICl_2^-. Structure II could also be a reactive intermediate that loses I^- in the transition state to give ISO_3^-. However, the observed kinetics do not require that it be an intermediate rather than a transition state. The proposed transition state for the sulfite reactions with I_3^- requires an expanded valence shell for adjacent iodines, as seen in structure III.



II



III

It is obviously less favorable to form III than II and this is reflected in the k_2/k_1 ratio of 130. Charge repulsion between I_3^- and SO_3H^- will have a small effect, but the high ionic strength used in these studies tends to minimize this factor. The k_4/k_3 ratio is only 11 despite the greater charge repulsion between I_3^- and SO_3^{2-}. The smaller ratio for k_4/k_3 compared to k_2/k_1 probably is due to a limiting factor for k_4, because this rate constant is close to the diffusion-limited value. Although the rate constant for I_2(aq) + I^-(aq) in eq 13 is 6.2 × 10^9 M^{-1} s^{-1}, the ionic strength was only 0.02 M[27] and no bond cleavage is required as is the case for the break up of $I_2SO_3^{2-}$ to give I^- and ISO_3^-. The relative ratios for $k_3/k_1 = 19$ compared to $k_4/k_2 = 1.8$ again suggest that k_4 has reached a limiting value and does not fully reflect the greater reactivity of SO_3^{2-} compared to SO_3H^-. The magnitude of the rate constants for I^+ transfer from I_2 to SO_3^{2-} or to SO_3H^- is impressive as the values approach the diffusion limit and exceed some proton-transfer rate constants.

Hydrolysis of Iodosulfate. Bünau and Eigen reported that the decay of the first product formed from the I_2/I_3^- and $SO_3H^-/SO_2{\cdot}H_2O$ reactions was competitive with the reverse of its formation reaction.[2] We adjusted the PAF conditions to avoid this complication. On the other hand, we were able to observe directly the hydrolysis of ISO_3^- in stopped-flow studies. The average k_h value (eq 19) at 25.0 °C is 298 ± 5 s^{-1}. The rate constant and the absorbance change are independent of the I^- concentration. If an $I_2SO_3^{2-}$ species exists as an intermediate in equilibrium with ISO_3^- and I^-, its concentration must be negligible even when $[I^-]$ = 0.20 M.

The temperature dependence of our stopped-flow studies gives a value of 147 ± 10 s^{-1} at 17.0 °C (μ = 0.005–0.20), in good agreement with the value of 130 s^{-1} at 17 °C (μ = 0.08–0.40) measured from the heat of the reaction by Inoue and Sudo.[3] Our temperature dependence corresponds to an E_a value of 16 kcal mol^{-1}, which also is in good agreement with Inoue and Sudo's value of 17 kcal mol^{-1}.

The value of k_h for ISO_3^- (298 s^{-1}) is close to the value of 270 s^{-1} found for the corresponding hydrolysis rate constant of $ClSO_3^-$.[8] These values are 9 orders of magnitude greater than the FSO_3^- hydrolysis rate constant.[42] It is interesting that both FSO_3H and $ClSO_3H$ react violently with water but that their hydrolysis rates are greatly different.[9,43] It was long assumed that both FSO_3H and $ClSO_3H$ hydrolyze instantly, but this is not the case. Much of the heat released on the addition of these anhydrous acids to water is from the heat of solution. However, the $ClSO_3^-$ ion does have a sufficiently large heat of hydrolysis to enable the rate to be followed by a flow thermal method. Srivastava et al.[44] did not

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realize that they were measuring the hydrolysis of $ClSO_3^-$ (eq 6) rather than the reaction between HOCl and SO_3^{2-} (eq 5).[7] Inoue and Sudo were able to use the heat of hydrolysis of ISO_3^- to measure this rate constant by a flow thermal method.

Our ΔH^* value for the hydrolysis of ISO_3^- is 65 kJ mol^{-1}, which is larger than the value of 49 kJ mol^{-1} found for the hydrolysis of $ClSO_3^-$.[8] On the other hand the ΔS^* value is +21 J mol^{-1} K^{-1} for the ISO_3^- hydrolysis compared to −32 J mol^{-1} K^{-1} for $ClSO_3^-$.[8] The positive ΔS^* value for ISO_3^- indicates that it does not take up a water molecule in attaining the transition state as was proposed for the reaction of $ClSO_3^-$. Instead, the reaction of ISO_3^- appears to be of a more dissociative nature followed by aquation. Steric hindrance may prevent the coordination of H_2O to sulfur in ISO_3^-.

Conclusions

The PAF technique permits the very fast reactions between I_2/I_3^- and SO_3H^-/SO_3^{2-} to be resolved in terms of four rate constants. The rate constant for the reaction between I_2 and SO_3^{2-} (3.1×10^9 M^{-1} s^{-1}) is even larger than the value for HOCl and SO_3^{2-} (7.6×10^8 M^{-1} s^{-1}).[7] In the latter case kinetic evidence exists for a reactive intermediate, $HOClSO_3^{2-}$, and the rate constant for the formation of this intermediate is 5.0×10^9 M^{-1} s^{-1}. We do not have direct kinetic evidence for $I_2SO_3^{2-}$ as a reactive intermediate, but it may exist. In both the HOCl and the I_2 reactions there is evidence for XSO_3^- intermediates that we propose have X–S bonds and hydrolyze with similar rate constants.

In the mixed Landolt chemical oscillator system,[5,6] the pH fluctuates from 3 to 8 and the I^- concentration also fluctuates. Hence, the assignment of a single rate constant for the reactions of I_2/I_3^- with SO_3H^-/SO_3^{2-} does not appear to be appropriate. The observed rate constants could change by 1–2 orders of magnitude as the pH changes. Even if the I^- concentration reaches 0.01 M in these reactions, the I_2 path will predominate over the I_3^- path and the observed second-order rate constants will be greater than 10^9 M^{-1} s^{-1} at high pH. Furthermore, the initial product is ISO_3^- and its rate of hydrolysis may affect the regeneration of I^-. The simulated oscillations appear to fit satisfactorily,[6] but as more accurate kinetic information becomes available, it should be possible to refine the description of the oscillatory behavior.

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Diphosphine-Bridged Heterobimetallic Hydride and Carbonyl Complexes of Rhodium and Iridium. Structure of $[RhIr(CO)_3(Ph_2PCH_2PPh_2)_2]$, a Complex Containing an Ir(−I)→Rh(I) Dative Bond

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The reaction of $[RhIrCl_2(CO)_2(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) with $NaBH_4$ under CO gives $[RhIr(CO)_3(dppm)_2]$ (**1**), while under H_2 the product is $[RhIr(H)(CO)_2(\mu\text{-}H)(dppm)_2]$ (**2**). The former is convertible to the latter via reaction with H_2, while the reverse process proceeds under CO atmosphere. Addition of 1 equiv of $HBF_4 \cdot OEt_2$ to **1** yields $[RhIr(CO)_3(\mu\text{-}H)(dppm)_2][BF_4]$ (**3**) and addition of a second equivalent leads to $[RhIr(CO)_3(\mu\text{-}H)_2(dppm)_2][BF_4]_2$ (**4**); both protonations are reversible. Protonation of **2** produces $[RhIr(H)(CO)_2(\mu\text{-}H)_2(dppm)_2][BF_4]$ (**5**). Like their neutral precursors, the protonated tricarbonyl and trihydride complexes may be interconverted via the appropriate hydrogenation or carbonylation processes. An X-ray structural determination of $[RhIr(CO)_3(dppm)_3]$ shows it to have a non-A-frame structure, with one of the two carbonyls attached to Ir oriented toward Rh in what might be considered a weakly semibridging manner; furthermore, the phosphine groups on Ir have a cis arrangement with a P–Ir–P angle of 104.95 (7)°. The rhodium center is square planar as expected for a Rh(I) formulation, while the geometry about iridium is a distorted tetrahedron (if the Rh–Ir bond is omitted) suggesting an Ir(−I) formulation. As such the $Ir(CO)_2P_2^-$ moiety can be considered as a pseudohalide, bound via a dative Ir→Rh bond. This compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 20.296$ (4) Å, $b = 12.190$ (7) Å, $c = 19.064$ (7) Å, $\beta = 95.11$ (2)°, and $Z = 4$. The structure was refined to $R = 0.047$ and $R_w = 0.053$ on the basis of 5208 unique observed reflections and 559 parameters varied.

Introduction

Hydride and carbonyl complexes of the group 8 metals have been implicated as intermediates in several catalytic processes, notably hydroformylation,[1] olefin hydrogenation,[2] and the water gas shift reaction.[3] However, to date most studies have concentrated on mononuclear complexes. As part of an ongoing effort to determine the effects of adjacent metal centers upon catalytic processes, we have been investigating the chemistry of binuclear diphosphine-bridged complexes of rhodium[4-7] and iridium.[8-14] In a previous paper, we described a series of diiridium complexes that, aside from the diphosphine bridges, contained only hydride and carbonyl ligands.[12] A more limited series of analogous dirhodium species has also been described.[15,16] As an extension of our studies in this area, we set out to prepare and study similar heterobimetallic Rh/Ir complexes. In addition, previous work

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