

Figure 2. Linear free energy plot. The numbers represent the systems given in Table I.

One learns, therefore, that substituents X induce transfer of electron density between oxygen and copper.

The fact that both X and Y substituent effects can be rationalized on the basis of *positive* values for  $\rho$  is consistent with the interpretation of electron deficiency at the  $d_{z^2}$  orbital of copper facilitating the adduct formation with donor molecules like pyridine.

Spectroscopic studies indicate the contribution of some  $\pi$  bonding to the copper-oxygen interaction, whereas for the copper-nitrogen bond no  $\pi$  bonding can be inferred.<sup>8</sup> The interesting fact that Hammett plots for both the X and Y dependencies result in nearly the same positive value for the reaction constant  $\rho$  leads to the conclusion, therefore, that charge transfer between the donor atoms and the central copper ion occurs via an inductive mechanism only.

Introduction of substituents Y in the 2- and 6-positions of the aniline ring—expected to build up considerable steric hindrance for adduct formation—influences  $K$  only slightly (see Table I). Branching of the alkyl groups R at the  $\alpha$ - and  $\beta$ -carbon atoms decreases  $K$  (for R = *t*-Bu the observed spectral changes are very small and consequently the error for the corresponding  $K$  value is high).

The variation of  $K$  observed upon introduction of substituents in the pyridine molecule is not unexpected (see Table I). Electron-withdrawing (-releasing) groups decrease (increase)  $K$ , and steric hindrance ( $\text{CH}_3$  in the 2-position) makes the addition of the base more difficult. With 2,6-lutidine and quinoline practically no adduct formation does occur, although small spectral changes are observed. The enthalpy and entropy data shown in Table I are negative, as expected for an addition reaction like (1). The addition of pyridine to the various complexes is, however, neither an isoenthalpic nor an isentropic process. The linear free energy plot of  $\Delta H^\circ_{298}$  vs.  $\Delta S^\circ_{298}$  leads to a satisfying linear relationship with a slope of +0.40 (see Figure 2). This would mean that the more exothermic the acid-base reaction is, the less mobile the coordinated pyridine becomes.

In summary, the study of equilibrium 1 leads to the following conclusions, mainly based on Hammett plots: (i) In complexes  $\text{CuL}_2$  substituents X transfer electron density to the copper through oxygen and substituents Y through nitrogen. (ii) This transfer of electron density through oxygen (X) and through nitrogen (Y) is practically of the same size for a given set of substituents; i.e.,  $\rho(\text{O}) \approx \rho(\text{N}) \approx +1$  (see Figure 1). (iii) Adduct formation according to (1) is mainly determined by electronic factors, whereas steric effects play a minor role only.

One has to consider what bearing these thermodynamic arguments have on the kinetic findings mentioned earlier. These stem from an investigation of the isotopic metal<sup>a,b</sup> (in

chloroform and dichloromethane) and ligand exchange<sup>2</sup> (in toluene) of complexes I and II, substituents X and Y and the aliphatic group R (in I) being the parameters. Evaluation of the kinetic data led to the following results: (i) The rate of exchange is strongly governed by the electron density at the donor oxygen.<sup>1a</sup> (ii) Hammett plots (based on rate constants) yield linear relationships for complexes with substituents X in the 5- and 4-positions: the reaction constant  $\rho(\text{O})$  however is *negative*, ranging from  $-1.0$ <sup>1b</sup> to  $-1.5$ .<sup>1a</sup> (iii) Variation of Y in complexes II leads to a rather small reaction constant  $\rho(\text{N}) = -0.35$ .<sup>1b</sup> (iv) Introduction of substituents Y in the 2- and 6-positions of the aniline ring decreases the rate by a factor of up to 400.<sup>1b</sup>

These findings led us to the conclusion that exchange is initiated by the attack of residual water at the Cu-O bond and that the cleavage of this bond is rate determining.<sup>1,2</sup> The results of the present thermodynamic study support this interpretation in the sense that on the basis of the  $\rho$  values derived from  $K$ , any rate-determining attack at the copper can be excluded.

The question of how substituents Y affect the electron density at the donor oxygen—a neighboring effect through copper or conjugation through an aromatic system—cannot be answered conclusively.

**Acknowledgment.** We thank the "Deutsche Forschungsgemeinschaft" and the "Verband der Chemischen Industrie e.V." for financial support. Salicylaldehyde was kindly provided by Bayer AG.

**Registry No.** 1-py, 66069-96-3; 2-py, 66069-95-2; 3-py, 66069-94-1; 4-py, 66069-93-0; 5-py, 66069-92-9; 6-py, 66069-91-8; 7-py, 66069-90-7; 8-py, 66069-89-4; 9-py, 66069-88-3; 10-py, 66069-87-2; 11-py, 66070-07-3; 12-py, 66070-06-2; 13-py, 66070-05-1; 14-py, 66070-04-0; 15-py, 14837-79-7; 16-py, 66070-03-9; 17-py, 66070-02-8; 18-py, 66070-01-7; 19-py, 66102-26-9; 20-py, 66102-25-8; 21-2-Me(py), 66070-00-6; 22-4-Me(py), 66069-99-6; 23-4-CN(py), 66069-98-5; 24-2,6-Me<sub>2</sub>(py), 66102-27-0; 25-quinoline, 66069-97-4.

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Contribution from the Department of Chemistry, The American University, Washington, D.C. 20016

#### Formation and Decomposition of Thiosulfate in the Ferrous Sulfide-Sulfur Dioxide Reaction<sup>1</sup>

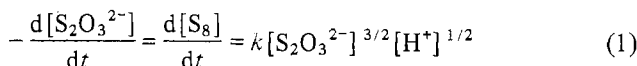
Gary C. Thom,\* Paul F. Waters, and Albert F. Hadermann

Received September 23, 1977

In a recent series of experiments we have confirmed the formation of thiosulfuric acid in the aqueous oxidation of  $\text{FeS}$  by  $\text{SO}_2$  and shown that the acid decomposition of thiosulfate

accounts for the subsequent formation of elemental sulfur in the reaction solution. The FeS-SO<sub>2</sub> reaction and the acid oxidation of naturally occurring sulfide ores (e.g., chalcopyrite, CuFeS<sub>2</sub>) serve as models for several proposed aqueous metal-extraction (hydrometallurgical) processes which eliminate the SO<sub>2</sub> emissions inherent in the smelting of sulfide ores.<sup>2</sup> The primary step in each of these aqueous-based processes is the reaction between a metal sulfide and an oxidant (e.g., SO<sub>2</sub>, O<sub>2</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and FeCl<sub>3</sub>) at a pH < 3 and at temperatures below 120 °C. Although the major reaction products include dissolved metal ions and elemental sulfur (S<sub>8</sub>), the mechanism by which these products form, particularly the mechanism for the formation of S<sub>8</sub>, is poorly understood. This is due to the fact that all previous studies have been concerned with the reaction kinetics as determined by the rate of appearance of dissolved metal ions. To our knowledge, no study has heretofore monitored the formation of "dissolved" sulfur species, e.g., thiosulfate, which are precursors to S<sub>8</sub>.

The key to explaining the mechanism by which S<sub>8</sub> forms lies in recognizing that the acid oxidation of metal sulfides is closely related to the Wackenroder reaction. In the Wackenroder reaction, H<sub>2</sub>S reacts with SO<sub>2</sub> at pH < 3 to form a complex mixture of products which include thiosulfuric acid, the sulfanemonosulfonic and sulfanedisulfonic acids, and S<sub>8</sub>.<sup>3</sup> Although the mechanism of this reaction is not completely understood, a considerable amount of work has been done in identifying the reaction products and the mechanism by which they form. Blasius and Burmeister<sup>4</sup> employed radio-paper chromatography in identifying thiosulfuric acid, H<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and disulfanedisulfonic acid, HO<sub>3</sub>SSSO<sub>3</sub>H, as the major initial products of the Wackenroder reaction. In independent studies, Zaiser and La Mer<sup>5</sup> and Keller<sup>6</sup> have shown that the kinetics of both the acid decomposition of thiosulfate and the formation of elemental sulfur is <sup>3</sup>/<sub>2</sub> order with respect to thiosulfate (eq 1). Thus, the intervening steps in the formation of S<sub>8</sub> from

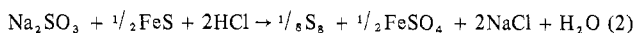


S<sub>2</sub>O<sub>3</sub><sup>2-</sup> must be rapid as indicated by Davis.<sup>7</sup> Finally, on the basis of La Mer's observations, Davis has interpreted the acid decomposition of thiosulfate on a mechanistic basis involving the formation of intermediate sulfanemonosulfonic acids which lead to elemental sulfur. Our experiments indicate that the results of these authors explain not only the mechanism of the Wackenroder reaction but also the kinetics and mechanism of the closely related FeS-SO<sub>2</sub> reaction as well as other reactions involving the acid oxidation of sulfide ores in hydrometallurgy.

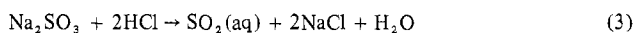
### Experimental Section

The reaction between FeS and SO<sub>2</sub> was conducted in a 500-mL high-pressure Parr reaction bottle which was fitted with a 0-30 psig Monel pressure gauge (Air Products), a 0-100 °C thermometer calibrated to ±0.05 °C, and a sampling port consisting of a rubber septum inserted in a stainless steel tubing fitting.

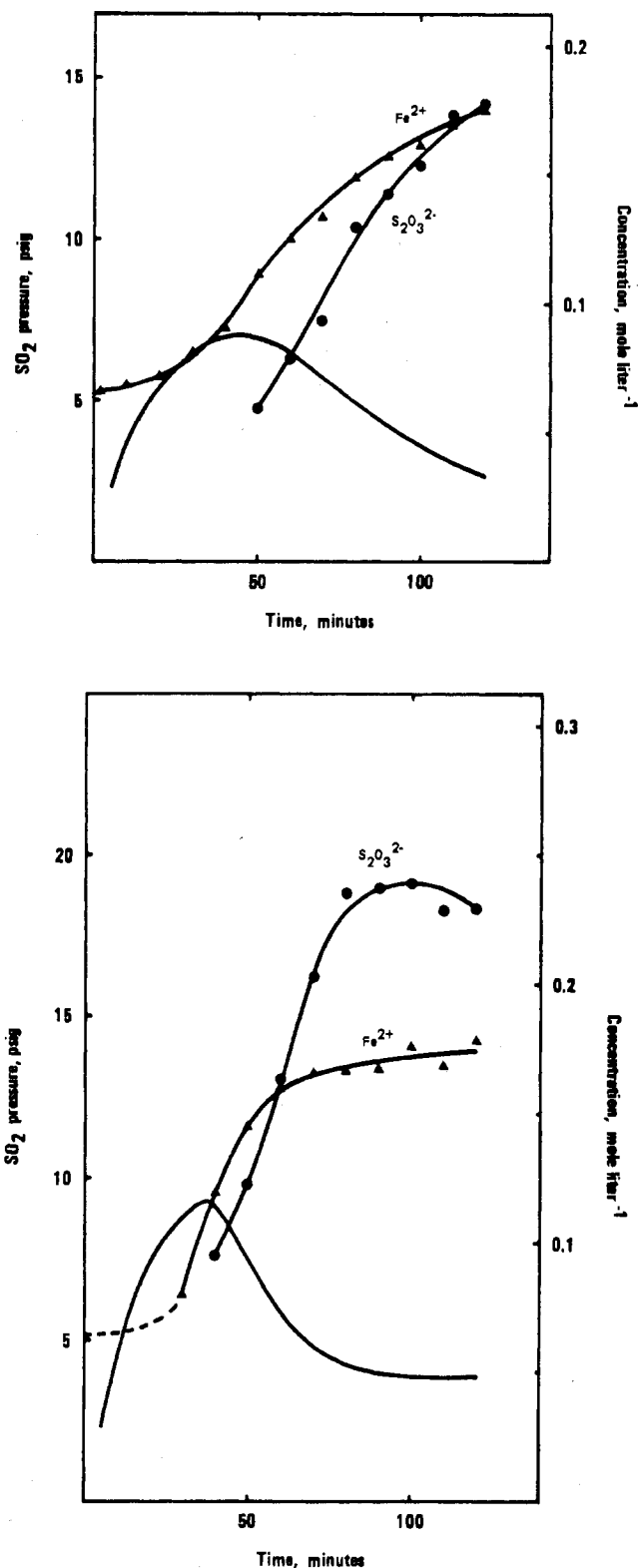
The quantities of reactants used in each experiment were based on a one-tenth stoichiometry of the overall reaction



A 1:2 Na<sub>2</sub>SO<sub>3</sub>:HCl mole ratio was used to ensure the complete conversion of SO<sub>3</sub><sup>2-</sup> to SO<sub>2</sub>(aq) (eq 3). To obtain a suitable reaction



rate, two times the stoichiometric amount of FeS was used. For each experiment, reactants were added to the reaction bottle in the following order: first, 0.10 mol of Na<sub>2</sub>SO<sub>3</sub> (anhydrous, Baker Analyzed) in 100 mL of distilled H<sub>2</sub>O, and then 0.10 mol of FeS (Fisher laboratory grade: 62.9% Fe, 37.1% S), which had been pulverized to give a



**Figure 1.** FeS-SO<sub>2</sub> reaction characterization at 58.3 °C (top) and 71.9 °C (bottom). Note the inverse relationship between the time of appearance of thiosulfate and the reaction temperature; information about the reaction kinetics may be obtained from the various slopes.

200-mesh sieve distribution of 14.6% > 200 and 85.4% < 200. Finally, the reaction was initiated by adding 0.20 mol of HCl to give a total volume of 200 mL. The reaction bottle was then immediately attached to the pressure-temperature-sampling apparatus.

During the course of the reaction, the mixture was heated (ca. 1.0 °C/min) and stirred (720 rpm) using a Fisher Thermixer. Pressure and temperature readings were recorded at 5-min intervals; at 10-min intervals, 100- or 200-μL samples were removed from the reaction

**Table I.** Kinetic Data for the Decomposition of Thiosulfate in a FeS-SO<sub>2</sub> Reaction Product Solution

Time from termination of FeS-SO <sub>2</sub> reactn, h	[S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> ] × 10 <sup>2</sup> mol L <sup>-1</sup>	dc/dt × 10 <sup>4</sup> mol L <sup>-1</sup> h <sup>-1</sup>
19.3	21.9	6.8
51.8	19.7	8.2
76.3	17.7	7.4
100.5	15.9	6.4
164.9	11.8	3.0
191.8	11.0	3.8
218.1	10.0	2.9
263.6	8.7	3.1
289.2	7.9	2.5
317.1	7.2	1.5
505.9	4.3	0.8
554.8	3.9	

mixture using gastight syringes. Each sample was diluted immediately by a factor of 125–1000. Aliquots from these dilutions were analyzed for Fe<sup>2+</sup> and S<sub>2</sub>O<sub>3</sub><sup>2-</sup>; the [Fe<sup>2+</sup>] was determined by the ferrous phenanthroline method<sup>8</sup> and the [S<sub>2</sub>O<sub>3</sub><sup>2-</sup>] by its absorbance<sup>9</sup> at 215 nm ( $\epsilon$  3.68 × 10<sup>3</sup> L mol<sup>-1</sup> cm<sup>-1</sup>) using a Cary 14 recording spectrophotometer and 1-cm quartz cells. The samples used in the ultraviolet analysis of thiosulfate (500 and 1000 dilutions) had a pH of 3.5–4.0 and contained <3 × 10<sup>-4</sup> M SO<sub>2</sub>. Under these conditions the absorbance due to HSO<sub>3</sub><sup>-</sup> was negligible; this was confirmed by the data of Golding<sup>10</sup> and Ericksen and Lind.<sup>9</sup> Interferences due to the transient sulfanesulfonic acids and colloidal sulfur were assumed to be constant and negligible at the high dilutions used in the thiosulfate analyses.

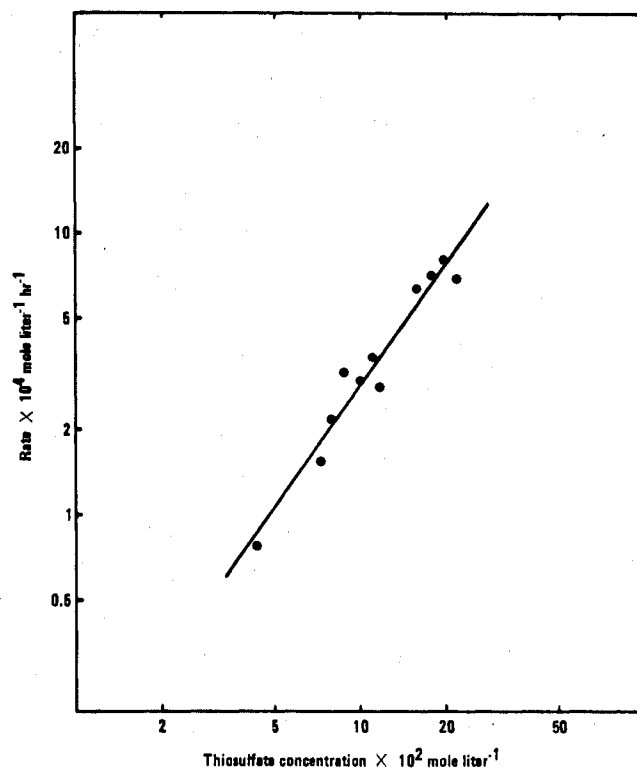
Thus, the progress of each reaction was followed as a function of time, SO<sub>2</sub> pressure, temperature, [Fe<sup>2+</sup>], and [S<sub>2</sub>O<sub>3</sub><sup>2-</sup>]. Upon the completion of the reaction, the remaining SO<sub>2</sub> pressure was released before the reaction bottle was removed from the apparatus, stoppered, and cooled to about 10 °C in an ice bath. This terminated the reaction and allowed the unreacted FeS to settle out. For the kinetic studies on the decomposition of thiosulfate, 25-mL aliquots of the reaction supernatant were maintained at 40 ± 0.05 °C. Using the syringe-dilution method and UV analysis, the thiosulfate concentration in these samples was determined approximately every 24 h for a period of 8–24 days.

## Results and Discussion

The reaction characterization curves for the FeS-SO<sub>2</sub> reaction at two temperatures, 58.3 and 71.9 °C, are shown in Figure 1. These curves are typical of those obtained in all experiments conducted on the FeS-SO<sub>2</sub> reaction. A considerable amount of information about the kinetics of this heterogeneous reaction can be extracted from these curves,<sup>11</sup> but this discussion will be limited to the mechanism for the formation and decomposition of thiosulfate.

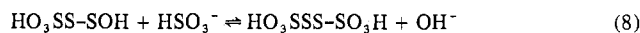
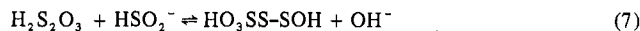
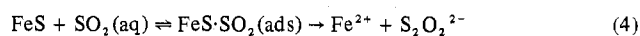
It will be noted that although ferrous ion appears in the reaction solution immediately, the appearance of thiosulfate does not occur until considerably later, at a time which decreases with increasing reaction temperature. This observation was made in all experiments and is indicative of the existence of an unstable intermediate(s) prior to the formation of thiosulfate. This fact is consistent with the mechanism of the closely related Wackenroder reaction as proposed by Blasius,<sup>4</sup> Schmidt,<sup>12</sup> and Steinle,<sup>13</sup> who show the formation of the unstable sulfoxylic acid, H<sub>2</sub>SO<sub>2</sub>, and/or thiosulfurous acid, H<sub>2</sub>S<sub>2</sub>O<sub>2</sub>. Thus, in formulating a mechanism for the FeS-SO<sub>2</sub> reaction, we have used a combination of the mechanisms proposed by these authors.

We propose that the first step in the reaction between dissolved SO<sub>2</sub> and FeS is the adsorption of SO<sub>2</sub> on the surface of the FeS. The subsequent reaction results in the dissolution of the FeS with the formation of ferrous ion and the thiosulfurous acid intermediate.<sup>14</sup> This intermediate then reacts

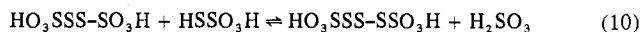
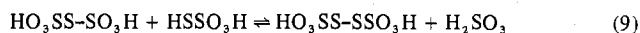


**Figure 2.** Decomposition of thiosulfate in the FeS/Na<sub>2</sub>SO<sub>3</sub>/HCl reaction product supernatant; reaction order with respect to thiosulfate is 1.42;  $r^2 = 0.94$ .

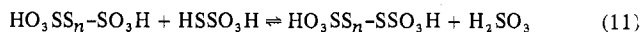
with HSO<sub>3</sub><sup>-</sup> to form thiosulfate which may then react with the sulfoxylate anion to form disulfanedisulfonic acid



Higher sulfanedisulfonic acids are formed by a mechanism given by Foss<sup>15</sup> which involves the nucleophilic displacement of a sulfite group by thiosulfuric acid



and in general

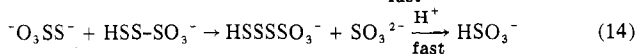
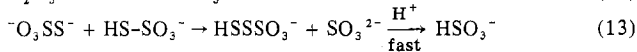


Since these equilibria are shifted to the right as the thiosulfuric acid concentration increases, these species do not appear until later in the reaction.

The rate of formation of elemental sulfur, S<sub>8</sub>, in the FeS-SO<sub>2</sub> reaction product solutions was determined by monitoring the rate of disappearance of thiosulfate (eq 1) after the FeS-SO<sub>2</sub> reaction was terminated. Kinetic data were initially displayed in linear plots of time  $t$  (h) vs. molar thiosulfate concentration  $c$ . Subsequently, the reaction order with respect to thiosulfate was obtained from the slope of a log-log plot of the rates,  $v = dc/dt$ , at various times vs. the corresponding concentration,  $c$ . Kinetic data from a typical experiment are given in Table I. When these data are plotted (Figure 2), a reaction order of 1.42 is obtained; the reaction orders in two other experiments were 1.46 and 1.57 with  $r^2 = 0.68$  and 0.76, respectively.

These results show that the decomposition of thiosulfate in the reaction product solutions indeed approaches the  $3/2$  order kinetics of eq 1. Although the reaction order with respect to H<sup>+</sup> was not determined, on the basis of the results for thio-

sulfate we propose that the formation of  $S_8$  in the  $FeS-SO_2$  reaction system follows the mechanism derived by Davis.<sup>7</sup> This mechanism has recently been shown by Meyer and co-workers<sup>16</sup> to be consistent with the charge distribution in the intermediate sulfanemonosulfonic acids:



and so forth, until ring closure produces  $S_8$



On the basis of the similarity between the acid oxidation of  $FeS$  by  $SO_2$  and the acid oxidation of sulfide ores by  $O_2$ ,  $Fe_2(SO_4)_3$ , or  $FeCl_3$ , we propose that the formation and decomposition of thiosulfate accounts for the formation of elemental sulfur in these other reactions. Thus, the mechanism we have described would account for the elemental sulfur formed in hydrometallurgical processes which dissolve naturally occurring sulfide ores in the presence of an oxidant such as  $Fe_2(SO_4)_3$ .<sup>2</sup> Furthermore, the mechanism would also account for the formation of elemental sulfur in a process now being developed for the removal of pyritic sulfur from coal by leaching with acid  $FeCl_3$ .<sup>17</sup>

Registry No.  $FeS$ , 1317-37-9;  $SO_2$ , 7446-09-5;  $S_2O_3^{2-}$ , 14383-50-7.

## References and Notes

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# Additions and Corrections

1976, Volume 15

**J. K. Kouba and S. S. Wreford\***: Distortions in Seven-Coordinate Complexes. Extension of the Dihedral Angle Method to Inequivalent Ligand Systems.

Page 1465. The  $\delta'$  in Table I for  $MoBr_2(CO)_2(Ph_2AsCH_2AsPh_2)_2$  should read 25.1, 21.7, 1.7. This compound is best described as a distorted monocapped octahedron on this basis. The  $\delta'$  for the  $C_{3v}$  reference should read 16.2, 16.2, 16.2.—S. S. Wreford

1977, Volume 16

**M. Santos\* and P. F. González-Díaz**: A Model for B Carbonate Apatite.

Page 2132. The proportion for  $PO_4$  ions in formula 6 must be  $6 - 7x/4$  instead of  $6 - 5x/4$ . The origin of the error is purely operational. The conclusions and arguments of the paper remain unchanged.—M. Santos

**T. W. Leung, M. J. Hintz, L. T. Chan, A. D. Sherry, and D. M. Blake\***: Calorimetric Study of the Lewis Acid Properties of Coordinatively Unsaturated Organoiridium(III) Species.

Page 2611. The Acknowledgment for this paper should read: We thank the Robert A. Welch Foundation and donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of the work at The University of Texas at Arlington. Matching funds for the purchase of the calorimeter and  $IrCl_3 \cdot 3H_2O$  were provided by The University of Texas at Arlington Organized Research Fund. An NSF URPP fellowship (Grant SMI 76-03024) and PRF undergraduate fellowship for M. J. Hintz are gratefully acknowledged.—D. M. Blake

1978, Volume 17

**Jan Kuyper**: Dimethyl Compounds of Platinum(II). 2. Reactions Involving Carbon-, Silicon-, and Germanium-Halogen Bonds.

Page 78. In Table I the headings Calcd and Found for columns listed under % others should be transposed.

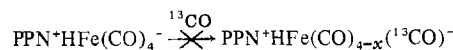
Page 80. The formula in line 3 of paragraph (II) should read  $[PtMe_2Cl(bpy)(SiR_nCl_{3-n})]$ .

Present address of author: Koninklyke Shell Laboratory, Shell Research BV, Badhuisweg 3, Amsterdam, The Netherlands.—Jan Kuyper

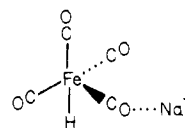
**M. Y. Darensbourg,\* D. J. Darensbourg,\* and H. L. C. Barros**: Solution Structure and Reactivity of Hydridoiron Tetracarbonyl Anion,  $[HFe(CO)_4]^-$ .

Page 299. Figure 4: (---)  $[PPN][HFe(CO)_4]$ , (—)  $[PPN][HFe(CO)_4]$  in the presence of  $NaBPh_4$ .

Page 300. Scheme I:



Page 300. The structure should look like



—M. Y. Darensbourg