the total integrated area of the two EPR signals remains constant.

(20) For an example of valence isomerism between bent and linear coordinated NO in cobalt complexes see Collman, J. P.; Farnham, P.; Dolcetti, G. *J. Am. Chem. Soc.* **1971**, *93*, 1788.

Robert R. Gagné,* D. Michael Ingle
Contribution No. 6104
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125

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Heats of Formation of SO_2Cl^- and $(SO_2)_2Cl^-$

Sir:

Currently, ion-molecule reactions are the objects of intense investigations. Results from these studies have proven to be valuable in expanding the availability of gas-phase thermochemical values such as electron affinities and heats of formation. In particular, data from the study of ion-neutral association reactions provide a foundation for understanding subjects such as ion solvation, atmospheric ion chemistry, nucleation phenomena, and ion-molecule interactions.[1,2]

Recently, Robbiani and Franklin[3] have reported upper limits to the heats of formation of SO_2Cl^- and $(SO_2)_2Cl^-$ based on observations of the ion-molecule reactions

$$Cl^- + SO_2Cl_2 \rightarrow SO_2Cl^- + Cl_2 \tag{1}$$

$$SO_2Cl^- + SO_2Cl_2 \rightarrow S_2O_4Cl^- + Cl_2 \tag{2}$$

From these reactions, they compute $\Delta H_f°(SO_2Cl^-) \leq -136$ kcal/mol and $\Delta H_f(S_2O_4Cl^-) \leq -220$ kcal/mol by postulating that the observed $S_2O_4Cl^-$ is formed by reaction 2. (The authors inadvertently use the upper limit for $\Delta H_f°(SO_2Cl^-)$ as a lower limit to conclude that this value must be *near* −135 kcal/mol.)

In our laboratory, a high pressure mass spectrometric technique has been employed[4] for determining the thermodynamic quantities of gas-phase reactions of the form

$$A^- \cdot B_n + B \rightleftharpoons A^- \cdot B_{n+1} \tag{3}$$

Briefly, ions are formed in a high pressure region, typically 5 to 15 Torr, and focused into a thermally controlled reaction cell. The pressure is sufficiently high such that the ions reside in this cell for a time adequately long for clustering reactions to equilibrate. The ions leak through a small orifice (typically 75-μ diameter) into a high vacuum region where they are mass analyzed and counted. From the ion intensities and known partial pressure of the clustering neutral, the equilibrium constant $K_{n,n+1}$ is determined.

Among the reactions which have been recently studied are the first four addition reactions (n = 0-3) of SO_2 onto Cl^- This work will be presented in greater detail in a future publication. From the enthalpy change $\Delta H°_{n,n+1}$ for the first two of these reactions (−21.8 for n = 0 and −12.3 kcal/mol for n = 1) and from the heat of formation of Cl^- and SO_2, the heats of formation of SO_2Cl^- and $(SO_2)_2Cl^-$ can be computed. These values are listed in Table I.

The heats of formation in the present study are well below the upper limit previously published by Robbiani and Franklin[3] and are, therefore, consistent with their results. The value of $-\Delta H°_{0,1}$ for reaction 3 is 21.8 kcal/mol and is equivalent to $D(SO_2\text{-}Cl^-)$. Robbiani and Franklin[3] concluded that this value was small (~5 kcal/mol) from their erroneous $\Delta H_f°(SO_2\text{-}Cl^-)$. Nonetheless, $D(SO_2\text{-}Cl^-)$ is still somewhat less than $D(Cl\text{-}Cl^-)$ which is 27 kcal/mol. Therefore, their expectation that some of their observed $SO_2Cl_3^-$ is formed by the reaction of SO_2Cl^- with SO_2Cl_2 may still be valid.

Table I. Heats of Formation

M	$\Delta H_f°(M)$, kcal/mol	ref
SO_2	−70.94	5
Cl^-	−58.8	5
SO_2Cl^-	−151.5	this work
$(SO_2)_2Cl^-$	−234.8	this work

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References and Notes

(1) Castleman, A. W., Jr. *NATO Adv. Study Inst., Ser. B: Phys., Kinet. Ion-Mol. React., 1979* **1979**, 295-321.
(2) Castleman, A. W., Jr. *Adv. Colloid Interface Sci.* **1979**, *10*, 73.
(3) Robbiani, R.; Franklin, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 3709.
(4) See, for example: Keesee, R. G.; Lee, N.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 2599. Castleman, A. W., Jr.; Holland, P. M.; Lindsay, D. M.; Peterson, K. I. *Ibid.* **1978**, *100*, 6039. Also see references contained therein.
(5) National Bureau of Standards Technical Note 270-3, 1968. These values were also used by Robbiani and Franklin.

Robert G. Keesee, A. W. Castleman, Jr.*
Department of Chemistry and Chemical Physics Laboratory
CIRES, University of Colorado, Boulder, Colorado 80309

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Formation of Porphyrin Ferryl (FeO^{2+}) Complexes through the Addition of Nitrogen Bases to Peroxo-Bridged Iron(III) Porphyrins

Sir:

The ferryl group $(Fe^{IV}{=}O)^{2+}$, or a protonated form thereof, has been frequently postulated as an intermediate in the mechanism of action of peroxidases, particularly in the identity of compound II of horseradish peroxidase, and in the autoxidation of Fe(II).[2] Complexes of Fe(IV) are rare[3] and no well-characterized, low molecular weight complexes containing the ferryl group are available for detailed study.[4] We recently reported on spectroscopic characterization of the Fe(III) peroxo-bridged complex, $PFeO_2FeP$ (P = a porphyrin dianion), which is formed by the addition of dioxygen to unligated PFe in toluene solution at low temperature.[5] We now report that nitrogeneous bases react with $PFeO_2FeP$ to yield new complexes which appear best described as ferryl complexes.

Addition of *N*-methylimidazole (Me-Im) to $TmTPFeO_2FeTmTP$ (TmTP = dianion of *meso*-tetra-*m*-tolylporphyrin) at −80 °C in toluene solution produces a new complex **1** $(Me\text{-}ImTmTPFeO)_x$, whose unique ^1H NMR and electronic spectra are shown in Figures 1 and 2, respectively. Titration of *N*-methylimidazole into a solution of $TmTPFeO_2FeTmTP$ reveals that 2 mol of base are required to consume all of the peroxide-bridged dimer originally present. Addition of further *N*-methylimidazole results in the growth of peaks characteristic of the free base, thus demonstrating that exchange between free *N*-methylimidazole and the newly formed iron complex is slow. The peaks due to coordinated Me-Im have not been resolved. **1** is indefinitely stable (>1 week) at −80 °C, while above −30 °C it decomposes to TmTPFeOFeTmTP at an appreciable rate.[6] The solution magnetic susceptibility of **1** measured at 360 MHz using the Evans technique[7] is 2.9 ± 0.1 μ_B/iron ion at −52 °C and is invariant down to −90 °C. Moreover the temperature dependence of the porphyrin paramagnetic shifts strictly follows the Curie law[7] over a larger temperature range (−85 to +15 °C) as is shown in the insert of Figure 1. Hence the iron ions exist in well-defined paramagnetic, noninteracting states.

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