Formation of the Trihalide Ion Cl_3^- in the Gas Phase

Sir:

In 1928, Hogness and Harkness[1] reported the ion-molecule reactions in iodine and the formation of I_3^-. Since then little experimental evidence for the formation of negative trihalide ions has been reported. Stockdale and Compton[2] described the reaction of SF_6^- with hydrochloric acid leading to the formation of the F_2Cl^- ion and the existence of the Br_3^- ion was established by the three-body attachment reaction of Br^- with bromine.[3] The formation of Cl_3^- has been mentioned,[4] but no further details have been given.

This communication describes the negative ion-molecule reactions in sulfuryl chloride, the formation of Cl_3^-, and its heat of formation, as well as upper limits for heats of formation of the secondary negative ions, calculated from the reactions observed. The measurements were made using a 12-in. 60° sector field magnetic mass spectrometer[5] equipped with a modified ion source, capable of studying ion-molecule reactions up to a source pressure of 100 μ. The full experimental details will be given elsewhere.[6] The sulfuryl chloride was obtained from the Aldrich Chemical Co. and was purified by distillation and degassed on a vacuum line by several freeze-pump-thaw cycles. The hydrochloric acid was obtained from the Matheson Co. and was used without further purification.

Heats of formation used in the calculations are given in Table I. The two dominant secondary ions in SO_2Cl_2 are SO_2Cl^- and Cl_3^- (Figure 1). Both species are formed by the reaction of Cl^- with SO_2Cl_2.

$$Cl^- + SO_2Cl_2 \rightarrow SO_2Cl^- + Cl_2 \quad (1)$$

$$Cl^- + SO_2Cl_2 \rightarrow Cl_3^- + SO_2 \quad (2)$$

A second possibility for the formation of Cl_3^- is the reaction of Cl_2^-, the other primary ion, with SO_2Cl_2:

$$Cl_2^- + SO_2Cl_2 \rightarrow Cl_3^- + SO_2Cl \quad (3)$$

At higher source pressures, the SO_2Cl^- concentration decreases owing to further reactions with sulfuryl chloride, leading to the formation of $SO_2Cl_3^-$, $S_2O_4Cl^-$, and probably $SO_2Cl_2^-$ in a charge exchange reaction:

$$SO_2Cl^- + SO_2Cl_2 \rightarrow SO_2Cl_3^- + SO_2 \quad (4)$$

$$SO_2Cl^- + SO_2Cl_2 \rightarrow S_2O_4Cl^- + Cl_2 \quad (5)$$

$$SO_2Cl^- + SO_2Cl_2 \rightarrow SO_2Cl_2^- + SO_2Cl \quad (6)$$

The formation of HCl_2^- is the result of the reactions of Cl_3^- and SO_2Cl^- with hydrochloric acid, which was present as an impurity. This was easily established by adding HCl to the system (Figure 2). Reactions 1, 4, and 8 have been reported by Sullivan and Beauchamp.[12]

$$Cl_3^- + HCl \rightarrow HCl_2^- + Cl_2 \quad (7)$$

$$SO_2Cl^- + HCl \rightarrow HCl_2^- + SO_2 \quad (8)$$

Heats of Formations. If we assume that Cl^- is formed without excess energy,[13] reaction 2 yields an upper limit of −72.7 kcal mol^{-1} for the heat of formation of Cl_3^-. On the other hand, reaction 7 allows us to estimate a lower limit for that value of −82.8 kcal mol^{-1}. These values are in accordance with the fact that the reaction of Cl^- with phosgene does not lead to the formation of Cl_3^- [14] (i.e., $\Delta H_f(Cl_3^-) > -85$ kcal mol^{-1}).

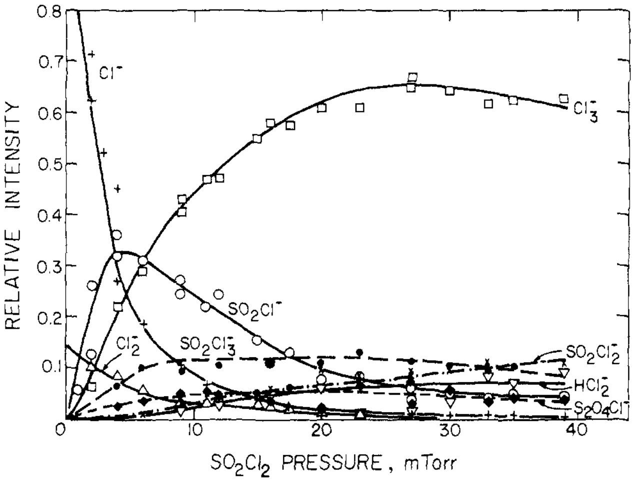

Figure 1. Fractional abundances of the negative ions at 2 eV vs. pressure from SO_2Cl_2.

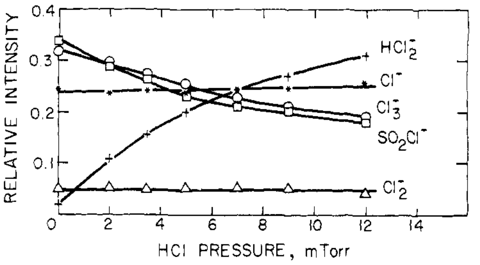

Figure 2. Fractional abundances of primary and secondary ions from SO_2Cl_2 (10 μ) vs. HCl pressure.

Table I. Heats of Formation Employed in This Study

M	ΔH_f(M), kcal/mol	ref
SO_2Cl_2	−84.8 ± 0.5	7
SO_2	−70.9	7
Cl^-	−58.8	8
HCl	−22.1	8
HCl_2^-	−104.9	9
Cl_2^-	−56.7	10
$COCl_2$	−52.6	8
CO	−26.4	8
Cl_3	25.7	11

The upper and lower limits of the heat of formation of SO_2Cl^-, calculated from reactions 1 and 8, are −143.6 and −153.7 kcal mol^{-1}, respectively. The upper limits for the heats of formation of $SO_2Cl_3^-$ and $S_2O_4Cl^-$ are, therefore, −156.4 and −228.4 kcal mol^{-1}.

Electron Affinity. The above deduced upper limit for $\Delta H_f(Cl_3^-)$ in connection with the heat of formation of the neutral molecule led to an electron affinity for Cl_3 of >4.3 eV.

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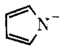
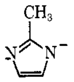
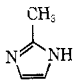
Anion Complexes of Ferrous Porphyrins[1]

Sir:

Although anionic ligands such as carboxylate, phenoxide,[2] imidazolate,[3-7] and mercaptide[8,9] have been considered as proximal iron ligands in hemoproteins, detailed model studies have so far been confined to the ferric and ferrous porphyrin complexes with mercaptide and certain ferric derivatives of other anions.[3,4,6,7] Ferrous porphyrin complexes with hydroxide[10] and alkoxide[11] have been described but the authors were unable to obtain carbon monoxide complexes of the anion heme.[11,12] The interesting suggestion that hydrogen bonding or deprotonation of proximal imidazole might provide a means by which hemoproteins can control heme reactivity[4,5] prompted as to prepare this unknown imidazolate–heme–CO and other anionic complexes.

The reported difficulties in forming both five- and six-coordinated hydroxy heme complexes and in producing anion–heme–CO complexes[10,11] were overcome by careful exclusion of water or other protic solvents from dimethyl sulfoxide (Me_2SO) solvent. Anionic bases were prepared as ~0.01 M solutions by treating the conjugate acid with sodium hydride in the presence of a slight excess of 18-crown-6 ether. In a typical example, dry argon purged Me_2SO (10 mL), in a 1-cm^2 cuvette, was treated with 6 mg of 2-methylimidazole and 2 mg of sodium hydride and the solution heated to make the imidazolate ion. Successive additions of 1 mg of a sodium dithionite-18-crown-6 complex[13] (as reducing agent) and 2 μL of a 3 mM solution of protohemin dimethyl ester (or its *N,N*-dimethyl diamide) produced a 5 μM solution of the heme-2-methylimidazolate complex, entry 13 in Table I. In a similar manner it was possible to prepare heme dialkoxides or, in some cases, five-coordinated heme-anion complexes. Either ferric[7] or ferrous complexes of imidazolate could be prepared if the Me_2SO anion (which could reduce ferric porphyrins) was carefully excluded. Table I lists the absorption maxima of the anion and other complexes. These complexes, and their carbon monoxide derivatives, provide references for comparison with hemoproteins.

Table I. Spectra of Complexes of Protoheme Dimethyl Ester with Anions and Carbon Monoxide in Me_2SO at 25 °C at ~5 μM Concentration[a]

	λ_{max}, nm			
entry	ligand	five coordinated	six coordinated	CO complex
1	Me_2SO		424, 524, 552[b]	414, 532, 562[b]
2	H_2O ($CetMe_3NBr$)[c]	probably four coordinated		414, 532, 562[b]
3	HO^- (dry)	444, 561,[b] 595[d]	433, 532, 562[b]	438, 545
4	HO^- (wet)	444, 405, 561,[b] 595		414, 532, 562[b,c]
5	HO^- (wet)[e]	444, 405, 561, 595		no change with CO
6	HO^- ($CetMe_3NBr$)	444, 561, 595		414, 532, 562[b,c]
7	MeO^-		433, 532, 562[b]	360,[f] 437, 545
8	*t*-BuO^-		427, 532, 560[b]	414,[c] 437, 545
9	PhO^-		434, 530 (sh), 558, 595 (sh)[g]	438, 545
10			430, 530, 560[b]	431, 539,[b] 570
11			429, 529, 559[b]	430, 542,[b] 573 (sh)
12			425, 525, 556[b]	420, 540,[b] 569
13		440, 560,[b] 595		430.5, 545,[b] 575[h] (sh)
14		430, 558		419, 537,[b] 563
15	$CH_3SOCH_2^-$	443, 560, 595		414, 532, 562[b,c]

[a] The solvent was Me_2SO except in entries 2 and 6 where the solvent was 2% aqueous cetyltrimethylammonium bromide ($CetMe_3NBr$). The assignment of the spectra as corresponding to five or six coordination is tentative until definite structure proofs are available. They are reasonably based on the typical visible band extinctions for hexacoordinated hemes and on the fact that in some cases the presumed five-coordinated species are converted to the six-coordinated species upon addition of more base. Where no spectra are listed, we were unable to observe the indicated species. Only with hydroxide ion in dry Me_2SO could we observe both five- and six-coordinated heme. [b] The indicated peak is larger than the other visible bands. [c] Complexes of protoheme DME with CO in Me_2SO, alcohols, and water (in cetyltrimethylammonium bromide ($CetMe_3NBr$) suspension) all have essentially the spectrum indicated here. The 414-nm peak is diagnostic for an oxygen ligand in the sixth position. Where the 414-, 532-, and 562-nm spectrum occurs in the presence of anions, we assume that the anion is displaced giving the neutral base–heme–CO complex. [d] At low concentration (10^{-4} M) of hydroxide the five-coordinated heme is obtained. Further addition of OH^- (~10^{-3} M) produces the hexacoordinated species. Both forms bind carbon monoxide to give HO^-HmCO. [e] Using benzyltrimethylammonium hydroxide to increase the hydroxide concentration to 0.2 M in wet Me_2SO produced only the five-coordinated type spectrum. Addition of 1 atm of carbon monoxide had no effect on this spectrum, a result similar to that of ref 11. [f] A trace of a possible hyperporphyrin band at ~360 nm appeared upon addition of carbon monoxide. This band is under investigation. [g] This spectrum appears to be a mixture of five- and six-coordinated hemes. [h] NMR of this complex confirms the anion–Hm–CO structure: A. Berzinis, unpublished results.

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