eous carbon monoxide (700 Torr) to yield $[Mn(CO)_6]^+$. The latter species is characterized[8] by a single IR band (at 2102 $cm^{-1}$ in $HO_3SCF_3$ solution). Addition of $NCCH_3$ to $[Mn(CO)_5]^+$ immediately produces $[Mn(CO)_5NCCH_3]^+$. This unusual kinetic lability which $[Mn(CO)_5]^+$ exhibits should be contrasted with the behavior of $[Mn(CO)_5NCCH_3]^+$. Even though $NCCH_3$ is a good leaving group, substitution reactions of this complex require times in excess of 30 min to proceed to completion. Furthermore, we find that $[Mn(CO)_5NCCH_3]^+$ does not react with CO in $HO_3SCF_3$ solution (2 h at room temperature). Recently the preparation of $Mn(CO)_5OClO_3$ was described.[9] Although this complex appears to be more reactive than $[Mn(CO)_5NCCH_3]^+$, substitution of $[ClO_4]^-$ with neutral ligands was reported[9] to require several minutes of gentle warming at 30 °C. There is some data in the literature[10] which places the base strength of $[ClO_4]^-$ above that of $[O_3SCF_3]^-$. Apparently, metal-ligand association must be stronger for $L = NCCH_3$ and $[ClO_4]^-$ than for $L = [O_3SCF_3]^-$.

Spectroscopic evidence also supports a weak association or ion-pair formulation. Solutions of $[Mn(CO)_5](O_3SCF_3)$ exhibit a well-resolved electronic absorption band at ~400 nm ($\epsilon_{max}$ ~1400). This absorption cannot be attributed either to metal-to-ligand or to ligand-to-metal charge-transfer transitions. The former are expected to be considerably more intense and would occur at higher energy, as for $[Mn(CO)_6]^+$.[8] We conclude that the latter assignment is also untenable, owing to the high optical electronegativity expected[11] for the potential O donor $[O_3SCF_3]^-$ ligand. By contrast, solutions of $[Mn(CO)_5NCCH_3]^+$ do not absorb appreciably at 400 nm and to longer wavelength. An intense visible absorption band characterizes coordinatively unsaturated metal carbonyl complexes in inert matrices.[12] The $Cr(CO)_5$ species, which is isoelectronic to $[Mn(CO)_5]^+$, exhibits a moderately intense electronic absorption band ($\lambda$ ~490 nm) in Xe and $CH_4$ matrices at 10 K.[13] A low energy is expected for d-d transitions to the orbital which largely occupies the vacant or weakly bound coordination site. Charge effects[11] would place this transition at slightly higher energies in the Mn(I) complex.

Our results show that hydride abstraction from a normally acidic complex may be realized in strong acid media. Ironically, one can put a proton on the carbonyl anion $[Mn(CO)_5]^-$ with an acid, and take it off as hydride with an even stronger acid! While this manuscript was in preparation, an X-ray photoelectron spectroscopic study[15] suggested that the hydrogen in $HMn(CO)_5$ possessed considerable negative charge. The authors noted this, despite the notion[1] that $HMn(CO)_5$ is a weak acid. The reactions presented above underline the dual role of bound hydrogen in the "acidic" metal carbonyl hydrides. We note that hydride abstraction could be regarded as an oxidation of the metal. To some extent, the distinction may be semantic.

We are currently studying the reactions of other Mn and Re hydrido carbonyls in $HO_3SCF_3$ and $HO_3SF/SbF_5$ solutions. This provides an alternative and complimentary approach to the elegant matrix isolation techniques[12,13,16] which have been used to generate coordinatively unsaturated metal complexes. Further knowledge about the solution structures and reactivities of these species should better characterize their role in inorganic[7] and catalytic[17] reaction mechanisms.

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## Energy Deposition in Polyatomic Ions upon High Energy Collision by Angle-Resolved Mass Spectrometry

*Sir:*

Breakdown curves give the product distribution for unimolecular dissociation of an ion as a function of internal energy. As such they are the most fundamental representation of the information in a mass spectrum, but they are difficult to obtain and have been reported for relatively few species.[1,2] We now show that analogous information can be obtained by monitoring the products of collision-induced dissociation of kilovolt energy ions as a function of scattering angle.[3] The technique of angle-resolved mass spectrometry[4] used here also allows approximate selection of the internal energy of ions whose ion/molecule chemistry is to be studied. This provides access to the behavior of ions of variable energy, including highly excited ions.

Figure 1 compares the breakdown curve of 1-propanol, as calculated by quasi-equilibrium theory (RRKM theory),[1a] with the results of collision-induced dissociation of the 1-propanol molecular ion at various scattering angles. The agreement is excellent, and apparently reflects a correlation between the impact parameter for the collision (which determines the scattering angle) and the internal energy transferred to the ion from the relative kinetic energy of the collision partners. Thus, a larger scattering angle and harder collision corresponds to increased excitation of the ion. Similar agreement is achieved for the alkanes, for the lower alcohols,[5] and for 2-pentanone (Figure 2). Our data also compare well with breakdown curves obtained by a point-by-point experiment using different charge exchange gases.[2]

The scattering data were obtained using a conventional double-focusing mass spectrometer modified by addition of a collision cell at the point of focus between the sectors and by

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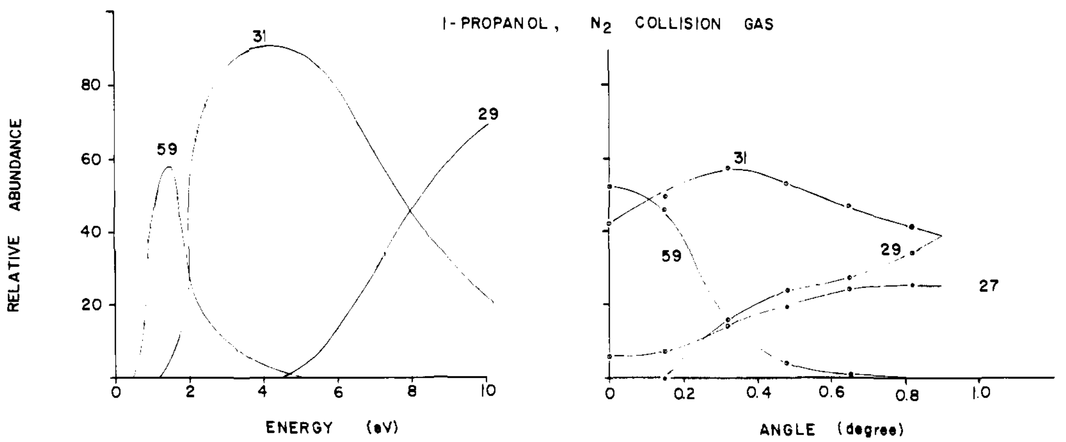

**Figure 1.** Breakdown curves for the 1-propanol molecular ion as calculated by quasi-equilibrium theory[1a] compared with the normalized collision-induced dissociations ($N_2$ collision gas) of this ion plotted as a function of the laboratory scattering angle. At energies below the threshold for dissociation only the molecular ion exists; so comparisons are restricted to higher energies.

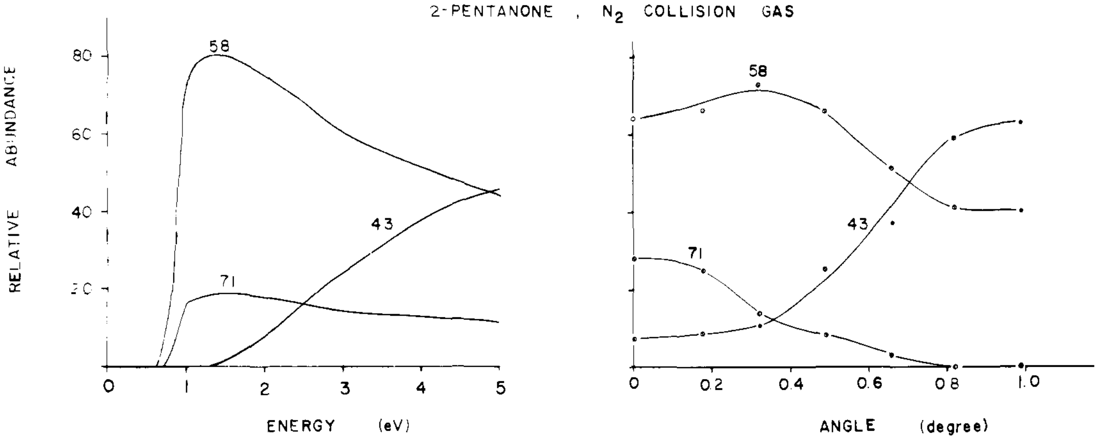

**Figure 2.** Comparison of the calculated breakdown curves for 2-pentanone[1a] with the angle-resolved collision-induced dissociations of this ion using $N_2$ collision gas.

insertion of a set of angle-resolving slits between the cell and the magnetic sector.[3] All data were obtained by momentum analysis of the collision products collected at the indicated laboratory scattering angle with an angular resolution of ±0.1°.

The relationship between scattering angle and internal energy deposited upon collision was sought by comparing cross points in the two sets of data. By choosing points where fragment ion abundances are equal, any effects associated with differences in resolution are minimized. In this way it was found that an approximately linear correlation exists for a given target between crossing points in the breakdown curves and those in the angle-resolved curves. An empirical correlation between internal energy ($\epsilon$, electronvolts) and lab scattering angle ($\theta$, degrees) for nitrogen targets covering the systems studied so far is $\epsilon = 6\theta + 2$. Other targets gave very similar angle-resolved plots but there is a slight target mass dependence in the $\epsilon,\theta$ relationship.

Breakdown curves should show the occurrence of fragmentation from isolated electronic states, if this occurs. Angular resolution data were therefore obtained on two systems, $CS_2$[6] and 2-pentanone,[7] in which such a phenomenon has been proposed. The $CS_2$ data (Figure 3) show that fragmentation to yield $S^{+\cdot}$ and $CS^{+\cdot}$ produces crossings which could occur if noncommunicating states are accessed at the larger scattering angles. If one uses the propane and alcohol data[5] to roughly calibrate the scattering angle in terms of internal energy, as described above, the isolated state proposed[7] in 2-pentanone (6-7 eV) should cause a discontinuity in the angle-resolved curve at 0.7 to 0.8°. This type of behavior was not observed here (Figure 2), although this energy is near the upper limit accessible in this experiment.

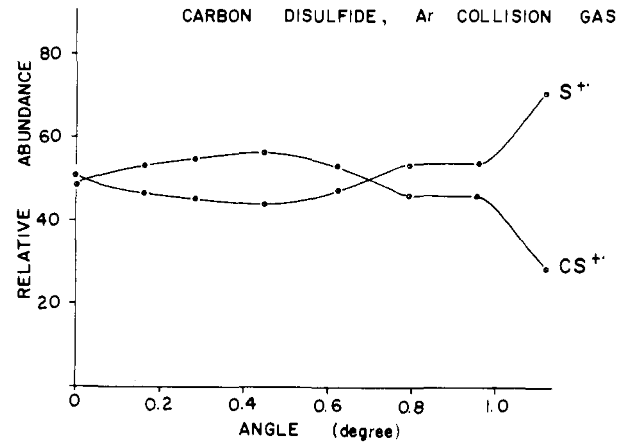

**Figure 3.** Angle-resolved collision-induced dissociation of $CS_2^+$ (Ar collision gas) to give $S^{+\cdot}$ and $CS^{+\cdot}$.

A particular advantage of angular resolution is that at large angles one can study the chemistry of very energetic ions. As an example of this effect, the dissociation of the fragment ion of aniline, $66^+ \rightarrow 39^+$ increased by a factor of five relative to the $65^+ \rightarrow 39^+$ dissociation over the range 0 to 0.5°. This is the expected result if higher energy processes are preferentially induced at larger scattering angles, as the process $66^+ \rightarrow 39^+$ occurs through two steps, $66^+ \rightarrow 65^+ \rightarrow 39^+$. As indicated earlier,[3] angle-resolved measurements also provide data on the relative stability to collision of particular ions. For example, the species just noted, $66^+$ ($C_5H_6^{+}\cdot$) and $65^+$ ($C_5H_5^+$), have different probabilities of surviving hard collisions, the radical cation showing a twofold greater depletion than the even electron ion as the lab scattering angle was increased from 0 to 0.6°.

The growing importance of collision-induced dissociation (collisional activation) as a method of determining ion structures[8] and in the MIKES (MS/MS) methodology for analysis of complex mixtures[9] underlines the value of the type of data obtained here. It is particularly noteworthy that many species of interest in the above studies do not have stable neutral counterparts (e.g., protonated molecules formed in chemical ionization); so charge exchange cannot be used to obtain breakdown curves. Use of this methodology on instruments with the reverse geometry will allow direct comparisons of all the dissociations of individual mass-selected ions over a range of internal energies.

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## X-ray Crystallographic Results on Tantallacyclopentane Complexes Derived from Ethylene and 1,6-Heptadiene: $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ and $Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2$

*Sir:*

Although unsaturated metallacyclopentadiene complexes occur commonly as a result of dimerization of acetylenes on transition metal centers, the corresponding *saturated* metallacyclopentane complexes are relatively uncommon. Indeed, there is a distinct paucity of accurate structural data on (saturated) metallacycloalkane complexes in general.

Structural data on some group 8 derivatives—an iridacyclopentane,[1] a platinacyclopentane,[2] and a platinacyclobutane[3] species—have appeared previously.

Schrock and co-workers have reported[4] that $Ta(\eta^5\text{-}C_5H_5)({=}CHCMe_3)Cl_2$ reacts with ethylene to give the tantallocyclopentane complex $Ta(\eta^5\text{-}C_5H_5)(C_4H_8)Cl_2$. While this particular species is rather unstable, recent work has led to the obtention of related species of greater stability, including $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ (see eq 1)[5] and $Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2$ (derived from 1,6-heptadiene[6]—see eq 2).

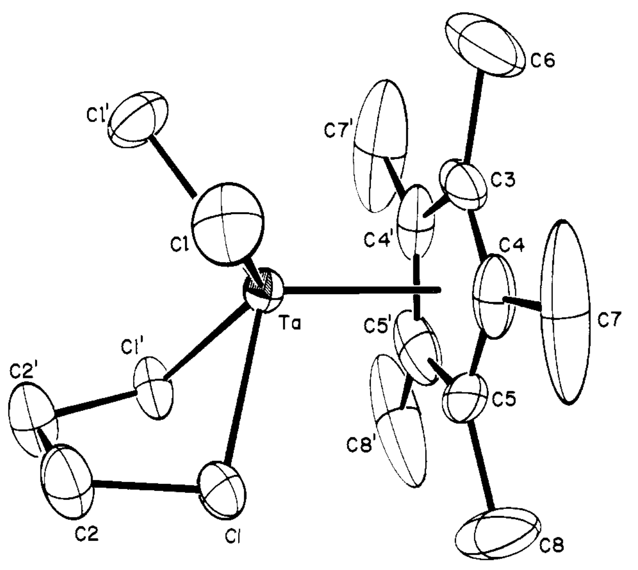

**Figure 1.** Stereochemistry of the $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ molecule, showing the "opened envelope" configuration of the tantallacyclopentane ring. The molecule has crystallographic $C_s$ symmetry. (Hydrogen atoms were not located.)

$$\begin{tikzcd}
\mathrm{Ta(C_5Me_5)(CH_2CMe_3)C\ell_2} \arrow[r, "\frac{1}{2}\mathrm{ZnEt_2}"] & \mathrm{Ta(C_5Me_5)(CH_2CMe_3)(C_2H_5)C\ell_2} \arrow[d, "-\mathrm{CMe_4}"] & \\
\mathrm{Ta(C_5Me_5)(C_4H_8)C\ell_2} & \mathrm{Ta(C_5Me_5)(C_2H_4)C\ell_2} \arrow[l, "\mathrm{C_2H_4}"'] & \text{(Equation 1)} \\
\mathrm{Ta(C_5Me_5)(MeCH{=}CH_2)C\ell_2} & + \quad \mathrm{CH_2{=}CH(CH_2)_3CH{=}CH_2} \arrow[d, "-\mathrm{MeCH{=}CH_2}"] & \\
 & \mathrm{Ta(C_5Me_5)(C_7H_{12})C\ell_2} & \text{(Equation 2)}
\end{tikzcd}$$

Single-crystal X-ray diffraction studies on the tantallacyclopentane derivatives $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ and $Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2$ have now been undertaken; our results are as follows.

The complex $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ crystallizes in the centrosymmetric orthorhombic space group *Pnam* with $a$ = 10.0736 (18) Å, $b$ = 11.2834 (20) Å, $c$ = 13.5239 (24) Å, $V$ = 1537.2 (5) Å$^3$, $\rho$(calcd) = 1.91 g cm$^{-3}$ for mol wt 443.19 and $Z$ = 4. Diffraction data were collected via a coupled $2\theta$ (counter)-$\theta$ (crystal) scan technique using a Syntex P2$_1$ diffractometer and were corrected for absorption. All nonhydrogen atoms were located and refined, the final discrepancy indices being $R_F$ = 5.7% and $R_{wF}$ = 3.9% for all 1850 independent reflections (*none rejected*) with $4° < 2\theta < 55°$ (Mo K$\alpha$ radiation). The molecular geometry is shown in Figure 1. The molecule lies on a crystallographic mirror plane which contains atom C(3), C(6) and Ta; there is substantial librational motion of the $\eta^5\text{-}C_5Me_5$ ligand which prevents the determination of the hydrogen atoms' positions. The tantallacyclopentane ring has an unusual "opened envelope" conformation, the angle between the strictly planar C(1)-Ta-C(1′) and C(1)-C(2)-C(2′)-C(1′) systems being 116.26°. [Note that this conformation is in strict contrast to the puckered $\delta$ or $\lambda$ conformation found in other saturated systems (e.g.,

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