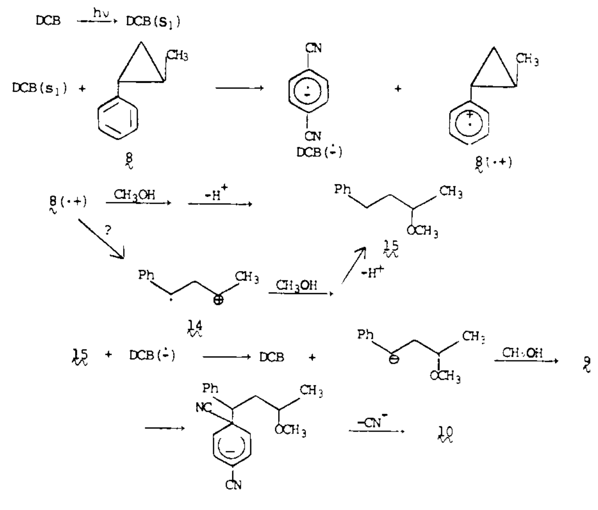
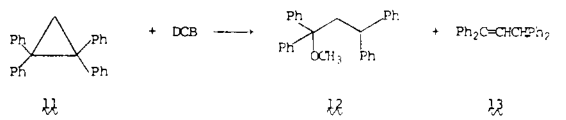
Scheme I



Instead, the major product was 1,1,3,3-tetraphenylpropene (**13**, yield not determined).[7]



Scheme I outlines a reasonable mechanism for reaction of the cyclopropanes, using *trans*-1-methyl-2-phenylcyclopropane (**8**) as an example. Excitation of DCB (under the reaction conditions DCB absorbs nearly all of the incident light) is followed by electron transfer from **8** to give a DCB radical anion-phenylcyclopropane radical cation pair. Attack by methanol on the cyclopropane radical cation $\mathbf{8}^{+\cdot}$ followed by proton loss affords benzylic radical **15**. Reduction of **15** by $\mathrm{DCB}^{-\cdot}$ leads to **9** while coupling of **15** with $\mathrm{DCB}^{-\cdot}$ gives **10**.[8,9]

It is conceivable that methanol does not attack $\mathbf{8}^{+\cdot}$ directly, but instead $\mathbf{8}^{+\cdot}$ is first converted into a ring-opened species such as **14**. The fact that attack occurs at the more substituted carbon of **8** indicates that C-1 does acquire significant positive charge during reaction. However, our finding that only a very small amount of trans-cis isomerization occurs when *trans*-**8** is reacted in the absence of methanol is not readily accommodated by this scheme; for reduction of **14** by $\mathrm{DCB}^{-\cdot}$ to a 1,3 diradical which would close to a mixture of cis and trans cyclopropanes is expected to be a facile process. Most likely the radical cation of **8** undergoing attack by methanol has a significantly weakened yet not broken C-1-C-2 bond; the radical cations of cyclopropanes **1**, **3**, and **8** probably have similarly bonded structures. We are investigating the electron-transfer-mediated addition of other nucleophiles to arylcyclopropanes as well as the reactions of other arylcyclopropane radical cations.

Acknowledgment. We thank the National Science Foundation for support of this research.

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(3) The intermediacy of radical ions in photosensitized reactions has been studied extensively recently by Arnold and by others. See, for example: (a) Albini, A.; Arnold, D. R. *Can. J. Chem.* **1978**, *56*, 2985. (b) Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 535, and references cited in these articles.
(4) Reaction product structures were derived from analysis of their NMR and mass spectra.
(5) In the presence of methanol and DCB after 10 h of irradiation, 85% of **8** was consumed to form 32% **9** and 21% **10**. In the absence of methanol, but under otherwise similar conditions, only 18% of **8** disappeared after 11 h of irradiation. During this time the percentage of cis isomer increased from ~2.9 to 3.9%.
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(7) Ether **12** is essentially stable under the conditions of this experiment.
(8) Cyanide ion formation in the reactions of **5** and **7** is assumed.
(9) Both steric and electronic factors may account for the lack of formation of products analogous to **7** and **10** from the diarylcyclopropanes **1** and **3**.

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Received April 16, 1979

Hydridic Reactivity of $\mathrm{HMn(CO)_5}$ Stabilization of a Nearly Coordinatively Unsaturated Metal Carbonyl Cation in $\mathrm{HO_3SCF_3}$

Sir:

Although it is well known that $\mathrm{HMn(CO)_5}$ ($\mathrm{p}K_\mathrm{a} = 7$) behaves as a weak acid,[1] the hydridic character of the hydrogen attached to the metal is still to be established. If it proved possible to abstract hydride from this compound with a "noncoordinating" acid, then one might prepare solutions of metal carbonyl complexes whose properties approach those expected for a coordinatively unsaturated species.[2]

A recent synthesis[3] of $\mathrm{HMn(CO)_5}$ employed the reaction

$$[\mathrm{Mn(CO)_5}]^- + \mathrm{HO_3SCF_3} \xrightarrow{\mathrm{THF}} [\mathrm{O_3SCF_3}]^- + \mathrm{HMn(CO)_5} \qquad (1)$$

Neat $\mathrm{HO_3SCF_3}$ is a considerably stronger acid medium than is its THF solution and we find that the subsequent reaction[4]

$$\mathrm{HMn(CO)_5} + \mathrm{HO_3SCF_3} \xrightarrow{\mathrm{HO_3SCF_3}} \mathrm{H_2} + [\mathrm{Mn(CO)_5}](\mathrm{O_3SCF_3}) \qquad (2)$$

can occur when $\mathrm{(PPN)[Mn(CO)_5]}$[5] is allowed to react with pure $\mathrm{HO_3SCF_3}$. The stoichiometry of reaction 2 has been confirmed by Toepler pumping of the evolved gas (1.03 ± 0.05 mol of gas/mol of $\mathrm{HMn(CO)_5}$) and its identity as $\mathrm{H_2}$ has been verified by combustion over copper oxide, as well as by mass spectroscopy. Quantitative Fourier transform IR spectroscopy of the gas fails to reveal the presence of CO and sets a limit on CO loss at <5%, if any. The IR spectrum of the deep yellow solution exhibits weak absorptions at 2164 and 2117 $\mathrm{cm^{-1}}$, as well as a strong band at 2083 $\mathrm{cm^{-1}}$, and one of medium intensity at 2042 $\mathrm{cm^{-1}}$. An identical spectrum is obtained when $\mathrm{[Mn(CO)_5py]BF_4}$[6] is dissolved in $\mathrm{HO_3SCF_3}$. In this case the reaction

$$[\mathrm{Mn(CO)_5py}]^+ + \mathrm{HO_3SCF_3} \rightarrow \mathrm{Hpy}^+ + [\mathrm{Mn(CO)_5}]^+[\mathrm{O_3SCF_3}]^- \qquad (3)$$

goes to completion in 1.5 h at room temperature. The IR bands are assigned, respectively, to the $A_1^{(2)}$, B_1, E, and $A_1^{(1)}$ carbon-oxygen stretching modes of $[\mathrm{Mn(CO)_5}]^+$. A C_{4v} or distorted C_{4v} structure seems likely, by analogy to $[\mathrm{Mn(CO)_5NCCH_3}]^+$, which displays $A_1^{(2)}$, E, and $A_1^{(1)}$ frequencies of 2161, 2060, and 2030 $\mathrm{cm^{-1}}$.[6] The weak B_1 stretch was not reported for $[\mathrm{Mn(CO)_5NCCH_3}]^+$.[6] Although $[\mathrm{O_3SCF_3}]^-$ probably occupies the vacant coordination site of $[\mathrm{Mn(CO)_5}]^+$, several experiments show that the association is extremely weak.

Substitution reactions of octahedral Mn(I) carbonyls are generally slow.[7] Trifluoromethanesulfonic acid solutions of $[\mathrm{Mn(CO)_5}]^+$, however, react immediately (<10 s) with gaseous 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 (ϵ_{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 (λ ~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.

Acknowledgments. The author thanks Professors Fred Basolo and Duward Shriver, for helpful comments, and Jay Nitschke, for experimental assistance. This work was supported by the National Science Foundation (CHE78-01615). Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for initial support of this research. W.C.T. thanks the Du Pont Corp. for a Young Faculty Grant.

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Received May 29, 1979

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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