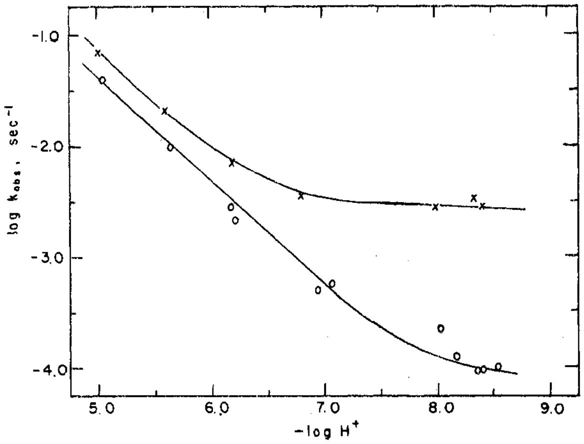

Figure 1. Decomposition rate for $\mathrm{NiH_{-2}glyglyglyCN^{2-}}$ and $\mathrm{NiH_{-2}glyglaCN^{-}}$ at different hydrogen ion concentrations (T = 25.0°, $\mu = 0.10\ F$ ($\mathrm{NaClO_4}$)): ×, $\mathrm{NiH_{-2}glyglyglyCN^{2-}}$; o, $\mathrm{NiH_{-2}glyglaCN^{-}}$.

is the sum of the two terms shown in eq 4. The solid lines

$$k_{\mathrm{obsd}} = k_{\mathrm{d}} + k_{\mathrm{H}}[\mathrm{H^+}] \qquad (4)$$

in Figure 1 are calculated using the rate constants listed in Table II. Two-term rate equations have been observed for other similar systems.[3]

Discussion

The transfer of protons to deprotonated nickel–polypeptide complexes can be general acid or specific hydrogen ion catalyzed.[3,6] A general mechanism (eq 5 and 6) has been

$$\mathrm{MH_{-\mathit{n}}L + HX} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{M(H_{-\mathit{n}}L)H + X} \qquad (5)$$

$$\mathrm{M(H_{-\mathit{n}}L)H} \xrightarrow{k_2} \mathrm{M(H_{-\mathit{n}+1}L)} \qquad (6)$$

proposed to account for the different reactivity patterns.[6]

Two cases are particularly applicable to the kinetics observed in this study. Under conditions where the concentration of the intermediate, $\mathrm{M(H_{-2}L)H}$, is small and $k_2 >> k_{-1}[\mathrm{X}]$, general acid catalysis will be observed. This fits the kinetic data observed for $\mathrm{NiH_{-2}glyglygly^{-}}$ and $\mathrm{CuH_{-2}glyglygly^{-}}$. The other case also has negligible intermediate concentrations; however, $k_2 << k_{-1}[\mathrm{X}]$. This fits the data for $\mathrm{NiH_{-3}glyglyglygly^{2-}}$ and $\mathrm{NiH_{-3}glyglygla^{-}}$ over a wide pH range.

When cyanide ion adds to $\mathrm{NiH_{-2}glyglygly^{-}}$, it probably replaces the bound carboxylate group. Cyanide coordination generates a stronger ligand field which results in increased stability of the intermediate $\mathrm{Ni(H_{-2}glyglyglyCN)H}$ and a change in the relative magnitude of $k_{-1}[\mathrm{X}]$ and k_2. With $k_{-1}[\mathrm{X}] >> k_2$ the system becomes specific hydrogen ion catalyzed and in essence involves preequilibrium followed by Ni–N(amide) bond breakage. This fits the data from pH 5 to pH 9, Figure 1. The rate constant k_{H} from eq 3 is equal to K_1k_2 as defined in eq 5 and 6. Both systems, $\mathrm{NiH_{-2}glyglyglyCN^{2-}}$ and $\mathrm{NiH_{-2}glyglaCN^{-}}$, are interpreted in the same manner. One would predict a loss of hydrogen ion dependence at low pH values. As the hydrogen ion concentration increases, the concentration of the intermediate will become an ever-increasing fraction of nickel total. When complete conversion has occurred, $k_{\mathrm{obsd}} = k_2$. Rapid-mixing techniques are required to verify this prediction.

Table II lists the rate for the mixed cyanide complexes and other similar complexes. The stabilization imparted by cyanide coordination is sizable as reflected by the decrease in the respective rate constants. Cyanide is more effective than the addition of another gly residue in decreasing the rate. It is somewhat surprising that k_{d} for $\mathrm{NiH_{-2}glyglyglyCN^{2-}}$ is not smaller.

An alternate mechanism to the one presented here is the dissociation of $\mathrm{CN^-}$ followed by subsequent reaction with hydrogen ion or dissociation to form products. With this mechanism the rate reduction is due to the fact that a small fraction of the nickel is present as reactant. There are three points that can be made to discount this mechanism. (1) The reactions obey pseudo-first-order kinetics. During the course of reaction cyanide concentration is changing; thus if it is factor in the rate equation, one probably would not observe first-order dependence. (2) Considering the triglycine system, the same percentage decrease should be observed in k_{H} and k_{d} as one goes from $\mathrm{NiH_{-2}glyglygly^{-}}$ to $\mathrm{NiH_{-2}glyglyglyCN^{2-}}$ since both will be dependent upon the fraction of nickel present as the mixed triglycine–cyanide complex. The decrease in k_{H} is a factor of 29 and in k_{d} is a factor of 18.5. These are probably different within experimental error. (3) Triethylenetetramine (trien) reacts with $\mathrm{NiH_{-2}glyglyglyCN^{2-}}$ through a two-path mechanism.[13] One of these paths is trien independent and has a rate constant of 2.3×10^{-3} sec^{-1}, very similar in magnitude to k_{d} for the triglycine–cyanide system. These three points taken by themselves are not sufficient to reject the predissociation mechanism; however, together they provide good evidence that the cyanide mixed complexes are the reactive species.

Registry No. $\mathrm{NiH_{-2}glyglaCN^{-}}$, 53290-91-8; $\mathrm{NiH_{-2}glyglyglyCN^{2-}}$, 51194-58-2.

References and Notes

(1) R. B. Martin, M. Chamberlin, and J. T. Edsall, *J. Am. Chem. Soc.*, **82**, 495 (1960).
(2) M. K. Kim and A. E. Martell, *J. Am. Chem. Soc.*, **89**, 5138 (1967).
(3) E. J. Billo and D. W. Margerum, *J. Am. Chem. Soc.*, **92**, 6811 (1970).
(4) G. K. Pagenkopf and D. W. Margerum, *J. Am. Chem. Soc.*, **90**, 501 (1968).
(5) G. K. Pagenkopf and D. W. Margerum, *J. Am. Chem. Soc.*, **90**, 6963 (1968).
(6) E. B. Paniago and D. W. Margerum, *J. Am. Chem. Soc.*, **94**, 6704 (1972).
(7) H. Hauer, G. R. Dukes, and D. W. Margerum, *J. Am. Chem. Soc.*, **95**, 3515 (1973).
(8) V. T. Brice and G. K. Pagenkopf, *J. Chem. Soc., Chem. Commun.*, 75 (1974).
(9) C. F. V. Mason, P. I. Chamberlain, and R. G. Wilkins, *Inorg. Chem.*, **10**, 2345 (1971).
(10) G. K. Pagenkopf, *J. Am. Chem. Soc.*, **94**, 4359 (1972).
(11) G. K. Pagenkopf, *Inorg. Chem.*, **13**, 1591 (1974).
(12) R. G. Bates, "Determination of pH", Wiley, New York, N.Y., 1964, p 89.
(13) W. A. Marchese, M.S. Thesis, Montana State University, Bozeman, Mont., Aug 1974.

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On the Base Strengths of (ω-Methoxyalkyl)trichloro- and (ω-Methoxyalkyl)trimethylsilanes

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Infrared base strength measurements have been used to determine the proton affinity of such donor atoms as oxygen,[1-7] nitrogen,[7-12] and sulfur[7] which are bound directly to group 4 metal atoms. These results are among the studies which have indicated that the properties of some organosilicon compounds are affected in a manner which is not evident in the carbon analogs.[13] One such effect may be an interaction between the vacant 3d orbitals of silicon and a lone pair of electrons on a directly bonded donor atom;[13] hyperconjugation (σ–π

Table I. Proton Chemical Shifts[a] for $CH_3O(CH_2)_nSiR_3$ (R = Cl, CH_3) Compounds

	n	$(CH_3)_3Si$-	$-CH_2O-$	CH_3O-
CH_3OSiCl_3	0			3.64
$CH_3OCH_2SiCl_3$	1		3.55[b]	3.39[b]
$CH_3O(CH_2)_2SiCl_3$	2		3.57	3.23
$CH_3O(CH_2)_3SiCl_3$	3		3.37	3.26
$CH_3OSi(CH_3)_3$	0	−0.06[c]		3.25
$CH_3OCH_2Si(CH_3)_3$	1	−0.41	2.59	2.84
$CH_3O(CH_2)_2Si(CH_3)_3$	2	−0.30	3.12	2.91
$CH_3O(CH_2)_3Si(CH_3)_3$	3	−0.37	2.92	2.86

[a] δ = ppm downfield from external TMS; neat liquids; ±0.01 ppm. [b] Also given as δ 3.57 (CH_2O) and δ 3.45 (CH_3O); measured as pure liquid vs. internal TMS; ref 20. [c] H. A. Brune, *Tetrahedron,* 24, 79 (1968), reported +0.06 ppm.

conjugation) has also been suggested as contributing to the atypical properties reported for these organosilicon species.[14]

Similar interactions have also been postulated to occur when the potential donor and receptor are separated from each other by one or more methylene groups.[1,15,16] Since the concept of an intramolecular nonbonded interaction was first postulated by Brook and coworkers,[17] there has been much discussion regarding the existence of such an interaction. The crystal structure[18] of $Ph_2Si(OCH_2CH_2)_2NH$ provides rather convincing evidence that such long-range donor–silicon interactions do occur.

In a recent study of the $CH_3O(CH_2)_nSiH_3$ (n = 1–6) compounds, it was found that the basicity of the lower members of the series was markedly reduced, but approached the basicity of the carbon analogs as n approached 6.[1] In the present investigation, the analogous $CH_3O(CH_2)_nSiR_3$ (R = Cl, CH_3) compounds were studied in order to determine the effects on the basicity of the compounds when the substituent is other than hydrogen.

Experimental Section

Mass spectra were recorded on a Du Pont Model 21-492 double focusing mass spectrometer operating at 70 eV and 50 μA. ^{1}H NMR spectra were recorded on a Varian Associates A-60D spectrometer. Infrared absorption spectra were obtained on a Digilab Model 14 Fourier Transform Spectrometer. Vapor-phase ir were recorded using a 10-cm gas cell with KBr windows. Measurements of ir shifts between free and hydrogen-bonded N–H frequencies ($\Delta\nu$) were obtained using standard liquid cells (1-mm path length) fitted with NaCl windows. The reference and sample cells contained a 0.8 to 0.2 M solution of the appropriate ether in CCl_4 solvent, and the sample cell also contained 0.02 M pyrrole.

Literature methods were used for the preparation of CH_3OSiCl_3,[19] $CH_3OCH_2SiCl_3$,[20] $CH_3O(CH_2)_3SiCl_3$,[21] $CH_3OSi(CH_3)_3$,[22] $CH_3OCH_2Si(CH_3)_3$,[23] $CH_3O(CH_2)_2Si(CH_3)_3$,[24] and $CH_3O(CH_2)_3Si(CH_3)_3$.[25]

$CH_3O(CH_2)_2SiCl_3$. This new compound was prepared by the addition of a solution of Cl_3SiCH_2Cl (15.0 g; 0.081 mol) in 25 ml of Et_2O to Mg in Et_2O. Bubbling and the formation of a precipitate suggested that the Cl_3SiCH_2MgCl formed was beginning to react with unreacted Cl_3SiCH_2Cl. Therefore, $ClCH_2OCH_3$ (6.5 g; 0.081 mol) in 75 ml of ether was immediately added, and the mixture was refluxed under N_2 for 2 hr.

Purified $CH_3O(CH_2)_2SiCl_3$ (~2.5 g; 16% yield) was obtained by low-temperature vacuum distillation. Its infrared spectrum and those of the other members of the $CH_3O(CH_2)_nSiCl_3$ series[26] are similar to the published spectrum[19] of CH_3OSiCl_3. The ^{1}H NMR chemical shifts are given in Table I and are similar to results for the $CH_3O(CH_2)_nSiH_3$ compounds.[1]

The mass spectrum of $CH_3O(CH_2)_2SiCl_3$ presented a very simple fragmentation pattern (peaks >10% relative abundance): m/e 45 (100%), $CH_3OCH_2^+$; m/e 133 (11%), $^{35}Cl_3Si^+$; and m/e 135 (10%), $^{37}Cl^{35}Cl_2Si^+$.

CH_3OSiCl_3. This compound was prepared by the same reaction as $CH_3O(CH_2)_2SiCl_3$; however, the reaction mixture was refluxed under N_2 for 8 hr. The longer reflux time produced a thermal decomposition of $CH_3O(CH_2)_2SiCl_3$ to give CH_3OSiCl_3 and ethylene, a decomposition process common to β-functional silanes.[27] The product was purified by low-temperature vacuum distillation and identified by a gas-phase ir spectrum identical with that in the literature.[19]

Table II. Hydrogen Bonding Shifts ($\Delta\nu$) in the $CH_3O(CH_2)_nSiCl_3$ and $CH_3O(CH_2)_nSi(CH_3)_3$ Compounds[a]

Base	$\Delta\nu$ pyrrole
CH_3OSiCl_3	*b*
$CH_3OCH_2SiCl_3$	76
$CH_3O(CH_2)_2SiCl_3$	98
$CH_3O(CH_2)_3SiCl_3$	128
$CH_3OSi(CH_3)_3$	140
$CH_3OCH_2Si(CH_3)_3$	143
$CH_3O(CH_2)_2Si(CH_3)_3$	150
$CH_3O(CH_2)_3Si(CH_3)_3$	132

[a] cm^{-1}, extrapolated to infinite dilution, ±1 cm^{-1}. [b] Hydrogen-bonded peak not observed.

Results and Discussion

The relative base strengths (proton affinities) of the $CH_3O(CH_2)_nSiCl_3$ and $CH_3O(CH_2)_nSi(CH_3)_3$ compounds were determined by comparing the magnitudes of the infrared frequency shifts of free and hydrogen-bonded pyrrole (see Table II). The differences between the free and hydrogen-bonded N–H frequencies, $\Delta\nu$, has been shown to be directly related to the base strength of the ether[28] and thus can also be correlated with the electron availability on the Lewis base.

Pyrrole was chosen as the Lewis acid with the trichlorosilyl ethers because the Si–Cl bond is cleaved by the more acidic Lewis acids such as methanol. Spectra run with $CDCl_3$ proved to be unsatisfactory because of broad, poorly defined peaks. Since it has been shown that $\Delta\nu$ values of similar compounds are insensitive to changes in the concentration of Lewis acid over the range 0.005–0.2 M,[1] but occasionally vary with the concentration of Lewis base,[29] $\Delta\nu$ values were extrapolated to infinite dilution.

$CH_3O(CH_2)_nSiCl_3$. The $\Delta\nu$ values obtained for the $CH_3O(CH_2)_nSiCl_3$ (n = 0–3) compounds are given in Table II. The increase in basicity from the n = 1 to the n = 3 members of the respective series is much greater in the $SiCl_3$ ethers (52 cm^{-1}) than in the analogous SiH_3 ethers[1] (20 cm^{-1}). The lesser basicity of the lower members of the $CH_3O(CH_2)_nSiH_3$ compounds was attributed to an intramolecular O → Si interaction between atoms which are not formally bonded to each other, an interaction which decreases in magnitude as n increases.[1]

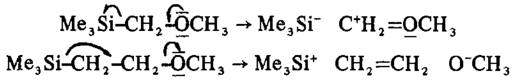
Group electronegativity considerations[30] suggest that the $SiCl_3$ group is considerably more electronegative than the SiH_3 group (χ_{SiCl_3} = 2.78, χ_{SiH_3} = 2.21). An inductive effect on the basicity in carbon chains is generally observable only between the n = 0 and n = 1 derivatives, and then only in small magnitude.[1,29] The electronegativity of the chlorine atoms, however, may indeed exert a significant effect in these compounds by inducing a greater positive charge on the silicon atom, contracting the silicon 3d orbitals, making the potential overlap with the oxygen lone pair electrons more efficient,[31] and thus lowering the basicity of the ether.

A positive charge on silicon would occur readily with a SiH_3 group (Si–H bond moment = Si^+–H^- = 1.0 D),[15,32] and even more with a $SiCl_3$ group (Si–Cl bond moment = Si^+–Cl^- = 2.5 D).[15,32] In the case of a $Si(CH_3)_3$ group, however (Si–CH_3 bond moment = Si^+–CH_3^- = 0.2 Debye),[15,32] it would be expected that O → Si interactions would be less important.

Additional evidence in support of an O → Si intramolecular interaction in $CH_3O(CH_2)_nSiCl_3$ compounds can be found in the mass spectra of the compounds, which all show rearrangement ions in which the oxygen has migrated to the silicon.[26] Such rearrangement ions have been associated with intramolecular O → Si interactions in studies by Weber,[33] and have also been observed in analogous compounds in which similar intramolecular interactions have been postulated.[1,15,34-38]

$CH_3O(CH_2)_nSi(CH_3)_3$. The $\Delta\nu$ values of pyrrole for the $CH_3O(CH_2)_nSi(CH_3)_3$ (n = 1 to 3) series are also listed in Table II. The relative order of increasing basicity is $n = 0 < n = 1 < n = 2 > n = 3$.

It might be noted that this order is identical with that which has been found for several other $Y(CH_2)_nM(CH_3)_3$ series, for example, the $CH_3O(CH_2)_nC(CH_3)_3$ and $NH_2(CH_2)_nSi(CH_3)_3$ compounds.[7,9,16,39,40] Chvalovský has interpreted the relative base strengths of (ω-aminoalkyl)trimethylsilanes in terms of hyperconjugation,[39,40] and analogous hyperconjugative limiting structures can also be written for the (ω-methoxyalkyl)trimethylsilanes, although the relative importance of these structures is not clear.



$$Me_3Si{-}CH_2{-}\underline{\overline{O}}CH_3 \rightarrow Me_3Si^- \quad C^+H_2{=}\underline{O}CH_3$$

$$Me_3Si{-}CH_2{-}CH_2{-}\underline{\overline{O}}CH_3 \rightarrow Me_3Si^+ \quad CH_2{=}CH_2 \quad O^-CH_3$$

In summary, the presence of an intramolecular O → Si interaction is consistent with the basicity trend of trichlorosilyl compounds, but as noted above this interaction is less important in $Si(CH_3)_3$ (and also the $Si(C_6H_5)_3$[41]) compounds than in SiH_3 or $SiCl_3$ species, and an O → Si interaction would not account for the relative order of basicities in the $CH_3O(CH_2)_nSi(CH_3)_3$ (n = 2 and 3) compounds. In both the trimethylcarbon and the trimethylsilicon compounds, the fact that the $n = 2$ homolog is the strongest base is consistent with the examples in which hyperconjugation was postulated to provide the principal correlation.

The above results would seem to be consistent with previous suggestions[27] that no single concept (inductive effects, hyperconjugation, d orbital participation) adequately accounts for the observed behavior of organosilicon compounds, and that a combination of these effects is required to correlate observed results.

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Registry No. CH_3OSiCl_3, 1825-97-4; $CH_3OCH_2SiCl_3$, 33415-27-9; $CH_3O(CH_2)_2SiCl_3$, 56629-79-9; $CH_3O(CH_2)_3SiCl_3$, 18171-65-8; $CH_3OSi(CH_3)_3$, 1825-61-2; $CH_3OCH_2Si(CH_3)_3$, 14704-14-4; $CH_3O(CH_2)_2Si(CH_3)_3$, 18173-63-2; $CH_3O(CH_2)_3Si(CH_3)_3$, 18387-32-1; Cl_3SiCH_2Cl, 1558-25-4; $ClCH_2OCH_3$, 107-30-2.

References and Notes

(1) J. M. Bellama and L. L. Gerchman, *Inorg. Chem.*, **14**, 1618 (1975).
(2) A. Marchand, J. Mendelsohn, M. Lebedeff, and J. Valade, *J. Organomet. Chem.*, **17**, 379 (1969).
(3) J. T. Wang and C. H. Van Dyke, *Inorg. Chem.*, **6**, 1741 (1967).
(4) R. West and R. H. Baney, *J. Am. Chem. Soc.*, **81**, 6145 (1959).
(5) R. West, R. H. Baney, and D. L. Powell, *J. Am. Chem. Soc.*, **82**, 6269 (1960).
(6) R. West, L. S. Whatley, and K. J. Lake, *J. Am. Chem. Soc.*, **83**, 761 (1961).
(7) E. W. Abel, D. A. Armitage, and S. P. Tyfield, *J. Chem. Soc. A*, 554 (1967).
(8) E. W. Abel, D. A. Armitage, and G. R. Wiley, *Trans. Faraday Soc.*, **60**, 1257 (1964).
(9) E. Lukevits, M. G. Voronkov, E. E. Shestakov, and A. E. Pestunovich, *J. Gen. Chem. USSR (Engl. Transl.)*, **41**, 2243 (1972).
(10) Z. Pacl, M. Jakoubková, R. Řeřicha, and V. Chvalovský, *Collect. Czech. Chem. Commun.*, **36**, 1588 (1971).
(11) Z. Pacl, M. Jakoubková, R. Řeřicha, and V. Chvalovský, *Collect. Czech. Chem. Commun.*, **36**, 2181 (1971).
(12) J. Rejhon, J. Hetflejš, M. Jakoubková, and V. Chvalovský, *Collect. Czech. Chem. Commun.*, **37**, 3054 (1972).
(13) E. A. V. Ebsworth, "Organometallic Compounds of the Group IV Elements", Vol. 1, Part 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N.Y., 1968, Chapter 1.
(14) H. Bock and B. G. Ramsay, *Angew. Chem., Int. Ed. Engl.*, **12**, 734 (1973), and references therein.
(15) J. M. Bellama and A. G. MacDiarmid, *J. Organomet. Chem.*, **24**, 91 (1970).
(16) J. Pola, J. M. Bellama, and V. Chvalovský, *Collect. Czech. Chem. Commun.*, **39**, 3705 (1974).
(17) A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *J. Am. Chem. Soc.*, **82**, 5102 (1960).
(18) J. J. Daly and F. Sanz, *J. Chem. Soc., Dalton Trans.*, 2051 (1974).
(19) R. Forneris and E. Funck, *Z. Elektrochem.*, **62**, 1130 (1958).
(20) V. F. Mironov, L. N. Kalinina, and T. K. Gar, *Zh. Obshch. Khim.*, **41**, 878 (1971).
(21) J. Valade and R. Calas, *C. R. Hebd. Seances Acad. Sci.*, **243**, 386 (1956).
(22) R. O. Sauer, *J. Am. Chem. Soc.*, **66**, 1707 (1944).
(23) J. L. Speier, *J. Am. Chem. Soc.*, **70**, 4142 (1948).
(24) R. Calas, J. Valade, and M. Josien, *C. R. Hebd. Seances Acad. Sci.*, **249**, 826 (1959).
(25) R. Calas, N. Duffaut, J. Valade, *Bull. Soc. Chim. Fr.*, 790 (1955).
(26) J. B. Davison, Ph.D. Dissertation, University of Maryland, 1974.
(27) A. W. P. Jarvie, *Organomet. Chem. Rev., Sect. A*, **6**, 153 (1970).
(28) R. S. Drago and T. D. Epley, *J. Am. Chem. Soc.*, **91**, 2883 (1969).
(29) A. Allerhand and P. R. Schleyer, *J. Am. Chem. Soc.*, **85**, 371 (1963).
(30) J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965).
(31) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).
(32) J. M. Bellama, R. S. Evans, and J. E. Huheey, *J. Am. Chem. Soc.*, **95**, 7242 (1973).
(33) W. P. Weber, *Intra-Sci. Chem. Rep.*, **7**, 109 (1973).
(34) J. M. Bellama and C. J. McCormick, *Inorg. Nucl. Chem. Lett.*, **7**, 533 (1971).
(35) J. A. Morrison and J. M. Bellama, *J. Organomet. Chem.*, **92**, 163 (1975).
(36) J. A. Morrison and J. M. Bellama, *Inorg. Chem.*, **14**, 1614 (1975).
(37) J. M. Bellama and J. B. Davison, *Inorg. Chim. Acta*, in press.
(38) A. L. Rheingold and J. M. Bellama, *J. Organomet. Chem.*, in press.
(39) V. Fialová, V. Bažant, and V. Chvalovský, *Collect. Czech. Chem. Commun.*, **38**, 3837 (1973).
(40) V. Chvalovský, plenary lecture, Third International Symposium on Organosilicon Chemistry, Madison, Wis., 1972.
(41) L. A. Harmon and J. M. Bellama, unpublished data.

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Kinetic Study of the Iodine Cleavage of $(CH_3)_2As\overline{C{=}CAs(CH_3)_2CF_2C}F_2Mn_2(CO)_8$ and Related Complexes

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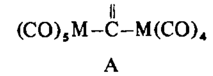
It is well-known that most dinuclear metal carbonyl compounds containing a metal-metal bond are cleaved by halogen to afford the corresponding halogenometal carbonyl derivative.[1] In particular the standard preparation of $M(CO)_5X$ (M = Mn, Tc, Re; X = Cl, Br, I) involves the cleavage of the M-M bonds of $M_2(CO)_{10}$ by halogens.[2,3] Despite numerous reports there have been relatively few mechanistic studies and these have been confined to reactions of the following species with halogen: $Mn_2(CO)_{10}$,[4] $Re_2(CO)_{10}$,[5] $Os_3(CO)_{12}$,[6] $[dienylFe(CO)_2]_2$.[7]

The reaction of iodine with $Mn_2(CO)_{10}$ follows a pseudo-first-order rate law $k_{obsd} = k_a + k_b[I_2]$ where k_a is equal to the rate constant for decomposition in oxygenated solution.[4] The activation enthalpy for the bimolecular path is 31 kcal/mol. A similar rate law is obtained from the reaction of iodine with $Re_2(CO)_{10}$ although the activation enthalpy for the bimolecular path has the lower value of 16.9 kcal/mol.[5] The most recent interpretation of these results[8] would seem to be as in Scheme I. One reaction is iodine independent and governed by k_a and the other bimolecular. In the original publications[4,5] the free-radical intermediate was replaced by the metal-migrated and carbonyl-bridged species



$$(CO)_5M{-}\overset{\overset{\large O}{\|}}{C}{-}M(CO)_4$$

A

Poë and coworkers[4,5] suggested that the difference in activation energies for the bimolecular pathway (M = Mn, Re) indicates a difference in the reaction mechanism but they said little