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Preliminary communication

GAS PHASE ION MOLECULE REACTIONS INVOLVING THE FORMATION OF METAL TO CARBON BONDS

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Summary

Results of an ion cyclotron resonance study of the gaseous ion chemistry observed in mixtures of alkyl halides and transition metal complexes are reported. Two different types of processes give rise to metal—carbon bonds. From observation of the process $M^+ + CH_3X \rightarrow MCH_3{}^+ + X$ limits on gas phase metal—carbon bond strength are inferred: 68 kcal/mol $> D(M^+—CH_3) >$ 56 kcal/mole for M = Fe, Co. Limits on several metal ion—olefin bond strengths are inferred from HX elimination reactions. Reactions of propyl and allyl cations with $Co(CO)_3NO$ and $Fe(CO)_5$ are also described.

The study of ion molecule reactions in the gas phase has proved useful in characterizing the thermodynamic and chemical properties of ions and molecules in the absence of solvent [1]. The gaseous ion chemistry of metals and metal compounds has received relatively little attention, but the results that have been reported are quite promising [2]. The emphasis in the reported studies is on reactions forming polynuclear metal complexes and reactions involving ligand substitution. In examining the gas phase ion chemistry of mixtures of transition metals and alkyl halides we have observed a number of reactions involving formation of metal to carbon bonds. Moreover, the nature of several of the observed reactions is such that thermochemical properties of the metal to carbon bonds may be inferred. In our experiments ionization is initiated by electron impact and reactions of the ions produced are followed using standard ion cyclotron resonance techniques**. Ion cyclotron double resonance identifies reactions 1 and 2, for example, in a mixture of $Co(CO)_3NO$ and CH_3I. The Co^+ ion is produced by electron impact on the $Co(CO)_3NO$. Similar processes are observed in mixtures of $Fe(CO)_5$ and CH_3I (reactions 3 and 4). Although the rates of 2 and 4 are comparable with those of 1 and 3, reactions of Fe^+ and Co^+ with CH_3Br yields

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[**] For a recent review of ion cyclotron resonance techniques see ref. 3.

$$Co^+ + CH_3I \begin{cases} \rightarrow CoI^+ + CH_3 & (k \times 10^{10} = 1.1^*) \quad (1) \\ \rightarrow CoCH_3{}^+ + I & (k \times 10^{10} = 0.8) \quad (2) \end{cases}$$

$$Fe^+ + CH_3I \begin{cases} \rightarrow FeI^+ + CH_3 & (k \times 10^{10} = 1.9) \quad (3) \\ \rightarrow FeCH_3{}^+ + I & (k \times 10^{10} = 1.9) \quad (4) \end{cases}$$

only MBr^+. From 2 and 4 we can deduce lower limits on the transition metal to carbon bond strengths in the absence of a coordinate sphere on the metal.

Under the conditions of the typical ion cyclotron resonance experiment, activated or endothermic processes are much too slow to be observed. The rates of 1 and 3 are fast ($k \sim 10^{-10}$ cm^3 mol^{-1} sec^{-1} = 6×10^{10} liter mole^{-1} sec^{-1}) and are not observed to depend on the energy of the impacting electrons. This indicates that the reactions involve ground state ions and are thermoneutral or exothermic which implies the lower limit on $D(M^+—CH_3)$ in Table 1. The upper limit in Table 1 is obtained by assuming that $MCH_3{}^+$ is not a product of reaction between M^+ and CH_3Br because $D(M^+—CH_3) < D(Br—CH_3)$. Also noted in Table 1 are results of several calorimetric determinations of transition metal to carbon bonds. The data are few but it appears that the coordination sphere weakens the bond significantly. The charge on the gaseous ion may also contribute to the difference between the gas phase and solution results. The electrostatic interaction between a methyl group and a point charge at a distance of 2.0 Å is about 20 kcal/mol.

TABLE 1

METAL—CARBON BOND STRENGTHS [a]
$56 < D(Fe^+—CH_3) < 68$ [b]
$56 < D(Co^+—CH_3) < 68$ [b]
$D(CH_3—Mn(CO)_5) = 27.9 \pm 2\ 3, 30.9 \pm 2.3$ [c]
$D(CH_3—Re(CO)_5) = 53.2 \pm 2.5$ [c]
$D((CH_3)_2(\pi\text{-}C_2H_5)Pt—CH_3) = 39 \pm 5$ [d]
$D(CH_3—PtCl(CH_3)(COCH_3)(P(CH_3)_2C_6H_5)_2) = 37.8$ [e]

[a] In kcal/mole. [b] Present results. See text. [c] Ref. 8. [d] Ref 9. [e] Ref. 10.

Two different processes involving the formation of organometallic species occur in mixtures of secondary and tertiary alkyl halides with $CoNO(CO)_3$ and $Fe(CO)_5$. The first process is exemplified by reaction 5 which seems to be quite general for a variety of metal ions. Li^+ reacts in this way [5] and we have

$$M^+ + i\text{-}C_3H_7Cl \rightarrow MC_3H_6{}^+ + HCl \qquad (M = Fe, Co) \qquad (5)$$

observed that Na^+ reacts similarly with tertiary chlorides [6a][**]. From these and related processes, the limits on metal olefin bond strengths in Table 2 may be inferred.

The second type of process is exemplified by reactions 6-9. The $C_3H_7{}^+$ and $C_3H_5{}^+$ are formed by electron impact on $i\text{-}C_3H_7Cl$ and are probably predom-

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[*] Rate constants in cm^3 mol^{-1} sec^{-1} determined using the method of Marshall and Buttrill [4].

[**] Alkali metal ions for this study were generated in the gas phase by thermionic emission, see ref. 6b.

TABLE 2

LIMITS ON OLEFIN METAL—ION BOND STRENGTHS [a]

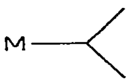
Reaction		Inference [b]
$M^+ + i\text{-}C_3H_7Cl \rightarrow C_3H_6M^+ + HCl$	(M = Li, Fe, Co)	$D(C_3H_6\text{—}M^+) > 18.9$
$M^+ + t\text{-}C_4H_9Cl \rightarrow C_4H_8M^+ + HCl$	(M = Li, Na, Fe, Co)	$D(C_4H_8\text{—}M^+) > 17.0$
$C_3H_6M^+ + i\text{-}C_3H_7Cl \rightarrow (C_3H_6)_2M^+ + HCl$	(M = Fe, Co)	$D(C_3H_6M^+\text{—}C_3H_6) > 18.9$
$C_4H_8Li^+ + t\text{-}C_4H_9Cl \rightarrow (C_4H_8)_2Li^+ + HCl$		$D(C_4H_8Li^+\text{—}C_4H_8) > 17.0$
$M^+ + CH_3COCl \rightarrow CH_2COM^+ + HCl$	(M = Li, Fe, Co)	$D(CH_2CO\text{—}M^+) > 20.5$

[a] The numbers are inferred from the observed reactions and data in ref. 11. [b] Limits are in kcal/mol.

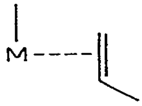
inantly isopropyl and allyl cations respectively. The product of 6 and 9 is probably a π-allyl complex, but the products of 7 and 8 could be either I, II or III or a

$$C_3H_5^+ + Co(NO)(CO)_3 \rightarrow Co(NO)(CO)(C_3H_5)^+ + 2CO \qquad (k \times 10^{10} = 3.1) \quad (6)$$

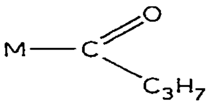
$$C_3H_7^+ + Co(NO)(CO)_3 \rightarrow \left\{\begin{array}{lll} Co(NO)(CO)_2(C_3H_7)^+ + CO & (k \times 10^{10} = 2.4) & (7) \\ Co(NO)(CO)(C_3H_7)^+ + 2CO & (k \times 10^{10} = 0.7) & (8) \\ Co(NO)(CO)(C_3H_5)^+ + 2CO + H_2 & (k \times 10^{10} = 0.2) & (9) \\ Co(NO)(CO)_3H^+ + C_3H_6 & (k \times 10^{10} = 0.2) & (10) \end{array}\right.$$



(I)



(II)



(III)

mixture of the three. The product of reaction 8 loses CO in a subsequent reaction suggesting that structures I and II are important. Proton transfer from $C_3H_7^+$ to $CoNO(CO)_3$ is exothermic [7] but relatively unimportant suggesting that I may be more stable than II. Proton transfer dominates the reaction of $C_3H_7^+$ with $Fe(CO)_5$ (reactions 10-13), however, suggesting structures I and II to be relatively unstable for the product of (12). Allyl cation reacts with $Fe(CO)_5$ by both

$$C_3H_7^+ + Fe(CO)_5 \rightarrow \left\{\begin{array}{lll} Fe(CO)_5H^+ + C_3H_6 & (k \times 10^{10} = 1.5) & (11) \\ Fe(CO)_4C_3H_7^+ + CO & (k \times 10^{10} = 0.2) & (12) \\ Fe(CO)_3(C_3H_5)^+ + 2CO + H_2 & (k \times 10^{10} = 0.1) & (13) \end{array}\right.$$

$$C_3H_5^+ + Fe(CO)_5 \rightarrow \left\{\begin{array}{lll} Fe(CO)_5H^+ + C_3H_4 & (k \times 10^{10} = 1.0) & (14) \\ Fe(CO)_3(C_3H_5)^+ + CO & (k \times 10^{10} = 0.2) & (15) \\ Fe(CO)_2(C_3H_5)^+ + 2CO & (k \times 10^{10} = 0.6) & (16) \end{array}\right.$$

proton transfer and carbonyl displacement in approximately equal proportions (reactions 14-16). The subsequent chemistry of these organometallic ions is under study to obtain more evidence regarding their structure and other properties.

Acknowledgements

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