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Reactions of Metal Ions (M^+) with Chromium Hexacarbonyl as Studied by Laser Ablation-Molecular Beam Method. Distinct Difference between the First and Second Series of Transition Metals Revealed in the Distribution of Product Ions $[MCr(CO)_n]^+$ (n=0-6)

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The distribution of product ions in the title reactions was studied for 24 metals. The most abundant ions were those with n = 3, 4, 5, 6, 4, 3, and 3 for M = Ti, V, Cr, Mn, Fe, Co, and Ni. Those in the second series of transition metals were dominated by n = 3 (or 3 and 4). Such a difference among metals was qualitatively interpreted in terms of strengths of M^+-Cr bonds.

In the laser ablation-molecular beam method proposed by the present authors,[1-4] metal ions laser-ablated by a pulsed laser react with an organic or organometallic compound in a pulsed molecular beam injected nearby. Product ions are probed with a quadrupole mass spectrometer. This method is much simpler and also less expensive compared to the methods used hitherto in the investigations of gas-phase reactions of metal ions, e.g., ICR or FTMS methods.[5,6] In the present letter, the method was applied for reactions of metal ions with chromium hexacarbonyl.

The experimental setup was essentially the same as reported previously.[1-3] Metals and $Cr(CO)_6$ were purchased from Japan Lamp Industries and Wako, respectively.

In the absence of a molecular beam, laser ablation of a metal substrate gave only atomic monocation (M^+). When the molecular beam of $Cr(CO)_6$ was injected, mixed-metal carbonyl ions $[MCr(CO)_n]^+$ (n=0-6) due to the ion-molecule reaction were observed, besides the substrate metal ion M^+ and parent and fragment ions of the carbonyl $[Cr(CO)_n]^+$ (n=0-6). Mass spectra obtained for Mn^+- and Nb^+-$Cr(CO)_6$ systems are shown in Fig. 1.

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Distributions of product ions among the series $[MCr(CO)_n]^+$ (n=0-6) are shown in Table 1.[7)] Numerals in the table are relative abundances of product ions (total = 100), corrected for the relative transmittance of the mass filter. In the first series of transition metals, the most abundant ions for Ti^+, V^+, Cr^+, Mn^+, Fe^+, Co^+, and Ni^+ are those with n = 3, 4, 5, 6, 4, 3, and 3, respectively. For the second series of transition metals, no or very small amount of n=5 and n=6 ions are found; the most abundant ions for Y^+-Pd^+ are those with n=3 (or n=3 and 4). Zn^+ and Cd^+ do not form any mixed-metal ions, nor Li^+, Na^+, and K^+. Laser light is focused so that comparable amounts of ions are formed for each metal. Then a tight focus is necessary for metals with high boiling points. This leads to the difference in the kinetic energy (KE) distributions of metal ions. However, observed distribution of product ions did not depend on the laser fluence within the used range, 150-380 mJ cm^{-2}. Therefore,

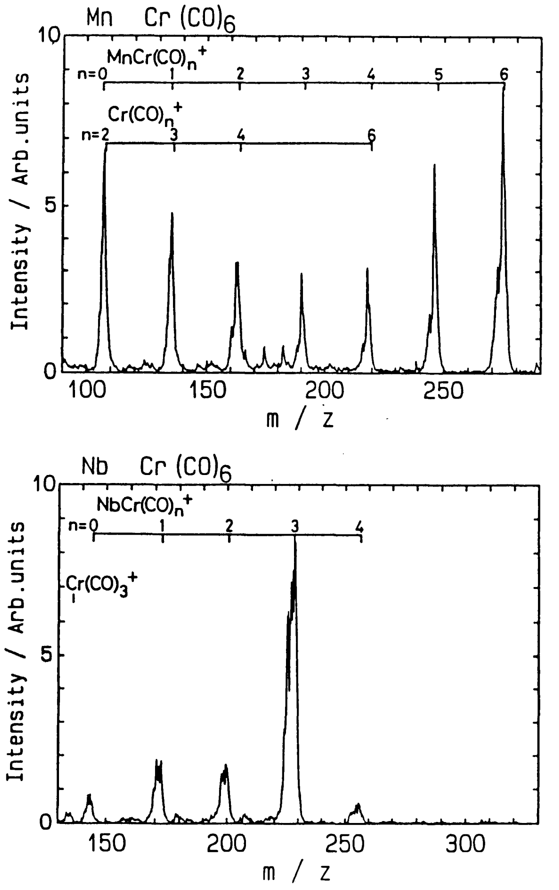

Fig. 1. Mass spectra for (a) Mn^+- and (b) Nb^+-$Cr(CO)_6$ systems.

Table 1. Relative yield of mixed-metal carbonyl ions $[MCr(CO)_n]^+$, n=0-6 (total=100), and the average number of n ($\bar{n}$)

M	n=0	1	2	3	4	5	6	$\bar{n}$
Mg	1	2	4	7	9	40	37	4.9
Al	25	21	8	9	11	23	3	
Ca	7	7	10	14	11	50	1	3.7
Ti	4	6	14	25	51	0	0	3.1
V	7	7	12	12	44	18	0	3.3
Cr	8	10	15	12	17	31	7	3.4
Mn	11	10	11	12	8	19	29	
Fe	23	14	13	9	33	8	0	2.4
Co	3	9	12	38	37	1	0	3.0
Ni	0	12	20	60	8	0	0	2.6
Cu	3	6	11	10	13	57	0	3.9
Ga	10	14	19	15	16	8	18	
Y	9	11	9	35	36	0	0	2.8
Zr	11	19	29	33	7	1	0	2.1
Nb	6	15	14	61	4	0	0	2.4
Mo	2	8	13	40	37	0	0	3.0
Ru	2	14	17	65	2	0	0	2.5
Rh	2	13	17	52	16	0	0	2.7
Pd	9	16	14	47	11	3	0	2.4
Ag	2	5	8	12	10	43	20	4.3
In	2	5	12	32	16	8	25	3.8
Sn	0	0	5	10	16	62	7	4.6
Ta	5	14	32	46	2	1	0	2.3
Pb	8	15	20	27	30	0	0	2.6

observed difference in reactivity among metals reflects the intrinsic property of each element M.

In the course of reaction of a metal ion with a $Cr(CO)_6$ molecule, the initial collision must lead to a labile 1:1 addition complex with an appreciable amount of internal energy. It is then stabilized either by the collision with another molecule, or by successive elimination of CO moieties. Relative importance of various stabilization channels is manifested in the distribution in the number of released carbonyl(s).

For Ti^+ through Ni^+, Kappes and Staley[6)] studied the reaction with $Cr(CO)_6$ by ICR technique. While the 1:1 addition (with no loss of CO's) was observed for Cr^+ and Mn^+, loss of one or two CO molecules was commonly observed. These authors argued that the variation in the number of CO molecule(s) lost should reflect the differences in the metal-carbonyl bond strength in the intermediate and the exothermicity of the overall reaction. However, they did not discuss the problem any further.

The explanation of observed distribution is tried for transition metals.[8)] The energy needed (ΔE) for the reaction

$$M^+ + Cr(CO)_6 \rightarrow [MCr(CO)_n]^+ + (6-n)CO \qquad (1)$$

can be estimated by

$$\Delta E = (6-n)D(Cr\text{-}CO) - D(M^+\text{-}Cr) \qquad (2)$$

where D(Cr-CO) is dissociation energy of a Cr-CO bond.[9)] $D(M^+\text{-}Cr)$ is that of an M^+-Cr bond newly formed in the complex. The relationship

$$D(M^+\text{-}Cr) = D(M\text{-}Cr) + IP(M) - IP(MCr) \qquad (3)$$

holds,[10)] where D(M-Cr) is dissociation energy of a neutral M-Cr bond in the diatomic molecule M-Cr, and IP's are relevant ionization potentials. Experimental values of D(M-Cr) are, however, not presently available. Their values (in kJ mol^{-1}) have been estimated by[11)]

$$D(M\text{-}Cr) = \frac{1}{2}\{D(M\text{-}M)+D(Cr\text{-}Cr)\} + 96(\chi_M-\chi_{Cr})^2 \qquad (4)$$

where D(M-M) and D(Cr-Cr) are the relevant single-bond energy of the diatomic molecule,[12)] and χ_M and χ_{Cr} are, respectively, electronegativity (in Pauling's scale) of each atom. Because we have no IP(MCr) data available, we use IP(MFe) obtained by Freiser et al.[10)] as a substitute.

In Fig. 2 the average number of released CO molecules ($6-\bar{n}$) is plotted against $D(M^+\text{-}Cr)$ obtained by Eq. 3 where data are available. Apparently there is a tendency that

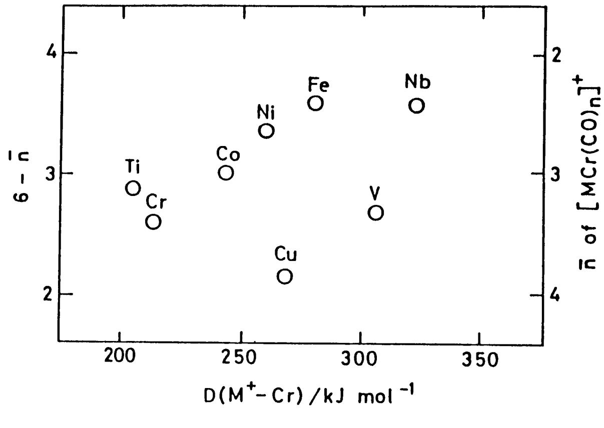

Fig. 2. Plot of ($6-\bar{n}$) vs. $D(M^+\text{-}Cr)$.

$(6-\bar{n})$ is larger, for the metals with a larger $D(M^+-Cr)$ value. Very roughly speaking, numbers of released CO groups are determined by the strengths of M^+-Cr bonds.

Transition metals in the second series (Y-Pd) show reactivities much distinct from those in the first series, as mentioned above. Discussion in terms of $D(M^+-Cr)$ cannot be made for them (except for Nb), however, because of the lack of their IP(MFe) data.10) These elements are characterized with large D(M-M) values (>260 kJ mol^{-1} except for Y and Pd12)), leading to large D(M-Cr) values (see Eq. 4). It is highly probable that this leads, in turn, to large $D(M^+-Cr)$ values for them.

Such a treatment is very rough and simple-minded. Nevertheless, it can shed new light on the organometallic ion chemistry in that it suggests the important role of metal-metal bond strengths in the chemistry of organo-bimetallic ions. Refined treatments should follow when the lacuna of our knowledge on the strengths of intermetallic bonds is filled.

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7) The average number ($\bar{n}$) is not given for Al, Ga, and Mn, because the distribution for these metals is very diffuse, suggesting the presence of more than one reaction channel.
8) Discussion is limited to transition metals here. For some of typical elements, discussion should be made along a different line (e.g., M-O-C-Cr bond formation).
9) D(Cr-CO) is n-dependent: 155 and 105 kJ mol^{-1} for n = 5 and 4, respectively (K. E. Lewis, D. M. Golden and G. P. Smith, J. Am. Chem. Soc., 106, 3905 (1984); T. R. Fletcher and R. N. Rosenfeld, ibid., 110, 2097 (1988)). However, its value for n = 3-0 is not known. Therefore, we use the average value derived from gas-phase heat of formation values, 108-113 kJ mol^{-1} (J. A. Connor, Curr. Top. Chem., 71, 71 (1977), D. A. Pittam, G. Pilcher, D. S. Barnes, H. A. Skinner, and D. Todd, J. Less-Common Met., 42, 217 (1975); G. Pilcher, M. J. Ware, and D. A. Pittam, ibid., 42, 223 (1975)). The essential feature of discussion in the present paper does not depend on the exact value of D(Cr-CO) for each step of CO elimination.
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