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Gas phase ion chemistry of molybdenum hexacarbonyl

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Abstract

In an ion cyclotron resonance (ICR) cell, $Mo(CO)_n^+$ ions ($n = 0$–6), generated by electron ionization (EI) with 70 eV electrons, on collisions with $Mo(CO)_6$ undergo charge exchange (confirmed by isotopic experiments), collision-induced dissociation (CID), and association reactions to produce $Mo_m(CO)_n^+$ ions ($m = 1$–6). Reactions are essentially complete within 9 s at a pressure of 3×10^{-9} Torr, as recorded by the manifold ion gauge (uncalibrated); $Mo(CO)_n^+$ ions with $n = 0$–5 have been consumed within this time whereas $Mo(CO)_6^+$ ions have achieved a steady concentration. All $Mo_2(CO)_n^+$ ions ($n = 0$–11) were observed: the abundances of dimolybdenum-containing ions with $n < 7$ decrease at extended reaction times, whereas those with $n \geq 7$ remain steady or increase slowly, implying that reactivity decreases with increasing CO content. The major dimers have $n = 7$, 9, and 10. When subjected to CID the $Mo_2(CO)_7^+$ ion yields $Mo_2(CO)_n^+$ ions ($n = 0$–6). Most $Mo_3(CO)_n^+$ ions ($n = 0$–13) were observed, those with $n = 9$ being formed most readily. Similar observations apply to larger clusters, the most abundant ions being those with CO:Mo ratios of 2–3:1. $Mo(CO)_n^+$ ions ($n = 0$, 3–6) formed by EI with 15 eV electrons are unreactive for reaction times of at least 5 s at the same pressure. General reaction sequences are proposed. Negative ions generated with 70 eV electrons (~ 90% $Mo(CO)_5^-$) are much less reactive but also lead to cluster ion formation on reaction with $Mo(CO)_6$. (Int J Mass Spectrom 182/183 (1999) 53–61) © 1999 Elsevier Science B.V.

Keywords: Gas phase ion chemistry; Molybdenum hexacarbonyl

1. Introduction

We have observed that the mass spectrum of molybdenum hexacarbonyl generated by electron ionization (EI) with 70 eV electrons at an ion cyclotron resonance (ICR) cell pressure of $\sim 10^{-9}$ Torr (as recorded by the uncalibrated manifold ion gauge) exhibits, in addition to the expected $Mo(CO)_n^+$ species, ions containing multiple molybdenum atoms. Although clustering reactions of metal carbonyl ions have been reviewed [1] we could not find a precedent for association reactions of any carbonyl ions of transition group VI. Earlier work on carbonyl compounds of this group has included photoelectron [2], EI [3–6], and photoionization [7,8] studies of hexacarbonyls; electronic state energies of molybdenum hexacarbonyl ions [9], and internal energy distributions in tungsten hexacarbonyl ions [10,11]. For other transition metal groups the formation of polynuclear ions has been described. These studies include formation of large clusters from initial positive ions of

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Dedicated to the memory of Ben Freiser to commemorate his many seminal contributions to mass spectrometry and gas phase ion chemistry.

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triosmium carbonyl [12] and di- and tri-iron containing positive ions formed by EI of iron pentacarbonyl in an ICR cell resistively heated to 300–650 K at 1×10^{-7} Torr [13] although no reactions pathways were established. The existence of the iron-containing species had also been noted earlier [14]. The gas phase photochemistry of di-iron and di-chromium carbonyl negative ions formed from neutral dimers has also been reported [15].

Neutral polynuclear carbonyls of transition metals are well known but, significantly, none are known for transition group VI [16–18], possibly for steric reasons, as follows. Most carbonyls conform to the 18-electron rule; transition group VI metals conform to the rule in the monomeric hexacarbonyls, whereas transition group VIII metals conform in the pentacarbonyls. Transition group VII metals form dinuclear carbonyls containing metal–metal bonds in which the coordination number of the metal is six, e.g. in $Mn_2(CO)_{10}$. In contrast, a hypothetical dinuclear $Mo_2(CO)_{11}$ species conforming to the 18-electron rule by using one bridging CO, an Mo–Mo bond, and five terminal CO groups on each Mo atom, would have metal coordination numbers of seven. Not only this, the Mo-Mo distance may be unfavorably long for a bridging CO group [16,17], so that failure to prepare it can be rationalized, even though metal–metal bond strengths increase from the first to the second transition series. A hypothetical dinuclear species, such as $Mo_2(CO)_{10}$, can be proposed if a double bond between the metal atoms is invoked. In light of this discussion, the formation of polynuclear ions starting from molybdenum hexacarbonyl is interesting.

2. Experimental

A Bruker (Bruker Daltonics, Bremen, Germany) Fourier transform ion cyclotron resonance mass spectrometer, which has a 7T magnet and is operated by XMASS software, was used. Molybdenum hexacarbonyl (used as purchased) was admitted, through an adjustable leak valve at room temperature, to the ion source at ambient temperature, to a constant pressure of 3.0×10^{-9} Torr, as read by the manifold ion gauge (i.e. significantly higher than the background pressure reading of $\sim 3 \times 10^{-10}$ Torr). After ionization by 70 eV electrons, the product ions could be selected, if desired, by a correlated sweep [19]. In such cases, molybdenum-containing ions were selected in two ways: (1) by using a safety belt wide enough to select all the isotopes present in a given ion type, and (2) by using a narrow safety belt so that only ions containing the abundant ^{96}Mo isotope (mainly) were selected. (The mass-to-charge ratio dependent widths of these safety belts were optimized for each case. Isolation of a single isotope involved a compromise between selectivity and ion yield). Selected ions were then allowed to react with neutral molybdenum hexacarbonyl for varying times, after which a mass spectrum was recorded. For kinetic studies relative ion abundances were measured in the following way. From each ion type the area of a specific isotopic mass-to-charge ratio peak, not susceptible to interferences, was recorded. In subsequent data manipulation its area was multiplied by a factor (which differs mainly according to the molybdenum content of the ion type) to obtain the total relative abundances for the ion type. This approach was necessary because integration of the total signal over all isotopes for ion types of low abundance was unreliable because of the slope of, and noise in, the baseline.

3. Results and discussion

At 70 eV electron beam energy the positive ion mass spectrum yields the ions $Mo(CO)_n^+$ ($n = 0$–6) [Fig. 1(a)] whereas the negative ion spectrum (to which we shall return) contains mainly $Mo(CO)_5^-$ ($\sim$ 90% of the total negative ion current). Fig. 1(a) shows small peaks at mass-to-charge ratio values higher than that of $Mo(CO)_6^+$; these can be assigned to dimolybdenum-containing species. The heights of these peaks are sensitive both to the ion source pressure and to the delay time (i.e. reaction time) between ion generation and detection. They can be rendered insignificant at pressure readings (uncalibrated) in the 10^{-10} Torr range and without an imposed delay time. At a pressure reading of 3 ×

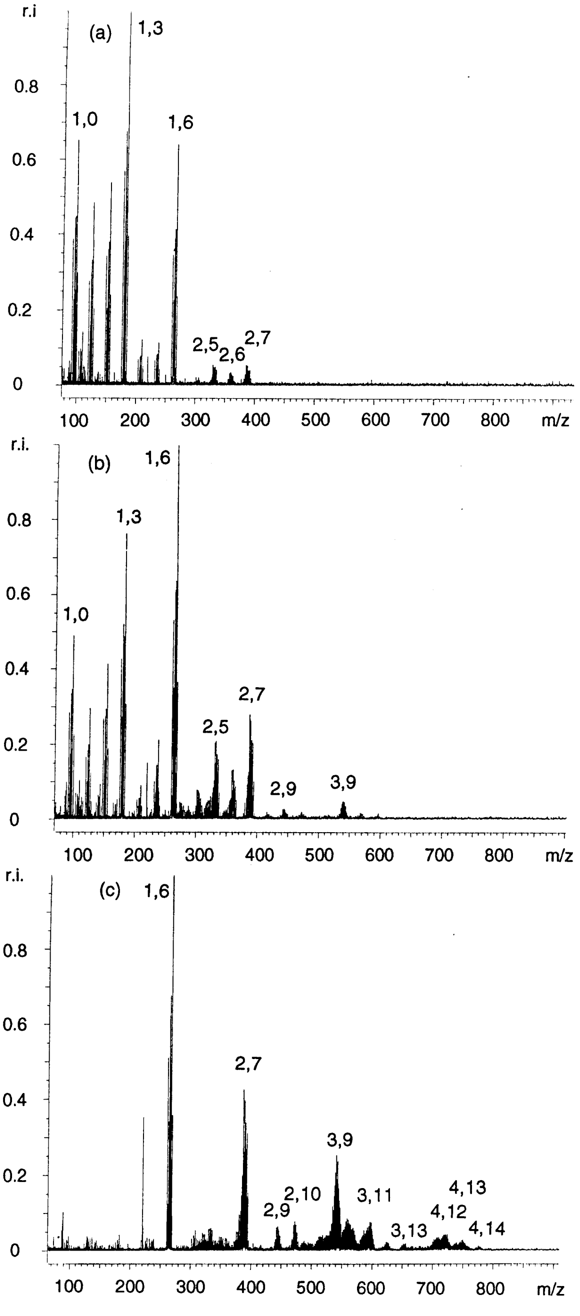

Fig. 1. Positive ion mass spectra generated from $Mo(CO)_6$ ionized by 70 eV electrons and subsequent reactions with $Mo(CO)_6$ at a pressure gauge reading of 1.1×10^{-9} Torr after reaction times of (a) 0.1 s, (b) 1.5 s, (c) 10 s. (Shorthand notation used: m, n = $Mo_m(CO)_n^+$.)

10^{-9} Torr, and by increasing the delay time, many ion–molecule reactions occur, to generate complex mass spectra, as illustrated by the remaining panels in Fig. 1. At long enough reaction times ions containing up to at least six molybdenum atoms can be generated. To investigate the reaction pathways leading to these ions each of the $Mo(CO)_n^+$ ($n = 0$–6) ions was individually selected and then allowed to react with $Mo(CO)_6$ for varying times. To illustrate our approach, we discuss the reactions of $Mo(CO)_3^+$ with $Mo(CO)_6$ in some detail. Fig. 2 shows the spectra generated at a few chosen reaction times for $Mo(CO)_3^+$ selected with a safety belt wide enough to include all isotopes without significant distortion of the isotopic pattern. The relative abundances of the ionic products as a function of reaction time are shown in Fig. 3.

Initially, the $Mo(CO)_3^+$ ions, in addition to their translational energy, can be expected to be vibrationally and electronically excited. Fig. 3(a) shows that $Mo(CO)_n^+$ ($n = 0$–6) species are formed. The $Mo(CO)_n^+$ species with $n \leq 2$ can be formed directly from $Mo(CO)_3^+$ by collisionally induced dissociation (CID) through collisions with $Mo(CO)_6$, whereas $Mo(CO)_6^+$ can be formed by charge exchange with $Mo(CO)_3^+$; $Mo(CO)_6^+$ can subsequently lose CO molecules. Eventually, $Mo(CO)_6^+$ becomes nonreactive because of deactivating collisions with neutral species, but $Mo(CO)_n^+$ species ($n = 0$–5) continue to react and eventually become insignificant.

Fig. 3(b) shows the formation of $Mo_2(CO)_n^+$ species, where n takes all values from 0–11, inclusive. Since only species with $n \leq 9$ can be formed in a collision of the initial $Mo(CO)_3^+$ reactant with $Mo(CO)_6$ then at least two reaction steps are needed to form species with $n = 10$ or 11. At reaction times up to 2–3 s the abundances of all species are increasing. After this time the abundances of species with $n < 7$ start to decrease indicating that their rates of formation have declined to the point at which they are slower than the combined CID and further association reactions. When $n = 7$ or 8 the abundances are nearly constant, decreasing slightly at the longest reaction times. When $n \geq 9$ the abundances increase slowly. Because the rates of formation of species with $n \geq 7$

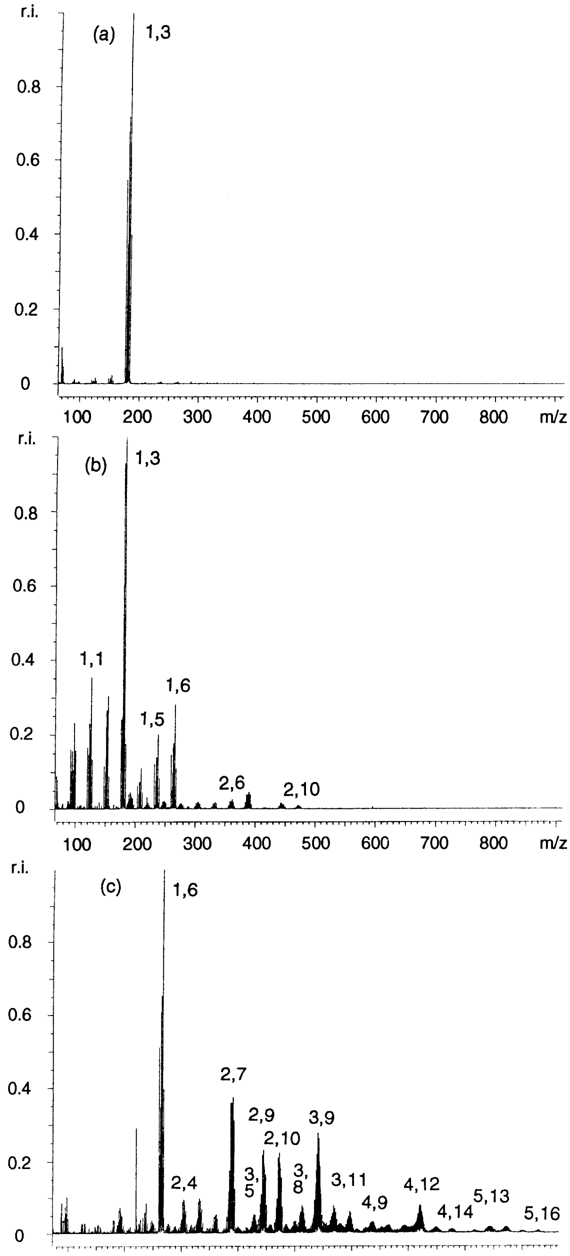

Fig. 2. Positive ion mass spectra generated by reaction of $\mathrm{Mo(CO)}_3^+$ (all isotopes included) with $\mathrm{Mo(CO)}_6$ at a pressure gauge reading of 3.2×10^{-9} Torr after reaction times of (a) 0 s, (b) 0.5 s, (c) 4.5 s.

have now become slow, their reaction rates are also slow, implying that they are now stable. Of these stable species, that with $n = 7$ is formed most readily, followed by species with $n = 9$ and 10.

Fig. 3(c) shows the formation of $\mathrm{Mo_3(CO)}_n^+$ ions, where most ions up to $n = 13$ are observed. The species with $n = 9$ is formed most readily. The abundances of ions with $n \leq 8$ decrease at longer reaction times indicating participation in further reactions, whereas the abundances of species with $n \geq 9$ remain sensibly constant or increase slowly. Fig. 3(d) shows the formation of $\mathrm{Mo_4(CO)}_n^+$ ions, where n takes the values 2–14, inclusive. The abundances of ions with $n = 6, 7$, and 12–14 increase steadily, with $\mathrm{Mo_4(CO)}_{12}^+$ being formed most readily. Penta- and hexa-molybdenum-containing ions are of much lower abundance; the abundances were difficult to measure accurately because the signal-to-noise ratio was poor. The major ions were $\mathrm{Mo_5(CO)}_n^+$ ($n = 12$–16, with $n = 13$ being the major contributor) and $\mathrm{Mo_6(CO)}_{17}^+$.

The reactions of all the other $\mathrm{Mo(CO)}_n^+$ ions with $\mathrm{Mo(CO)}_6$ were studied in a similar way. As for $\mathrm{Mo(CO)}_3^+$, the $\mathrm{Mo(CO)}_n^+$ ions undergo both CID and charge exchange with $\mathrm{Mo(CO)}_6$ but the kinetic details differ so that the time-dependent relative abundance profiles for the mono-Mo-containing species are not exactly the same as those in Fig. 3. The differences are conveniently expressed in terms of relative reaction rates (or branching ratios), a point to which we shall return. With minor differences in detail, the time-dependent relative abundance profiles of the poly-Mo-containing species resemble those in Figs. 3(b)–3(d).

The foregoing experiments were performed on ions selected after generation by a 70 eV electron beam and not deactivated by collisions prior to reaction with $\mathrm{Mo(CO)}_6$. Upon decreasing the electron beam energy to 15 eV the major ions in the spectrum were $\mathrm{Mo(CO)}_6^+$ and Mo^+, with small amounts of $\mathrm{Mo(CO)}_3^+$, $\mathrm{Mo(CO)}_4^+$, and $\mathrm{Mo(CO)}_5^+$. Even without collisional deactivation these ions were now unreactive at delay times up to 5 s. We therefore infer that some electronic or vibrational excitation of $\mathrm{Mo(CO)}_n^+$ ions is necessary for reaction to occur.

Experiments were also performed on isotopically selected $^{96}\mathrm{Mo(CO)}_n^+$ ions ($n = 0$–6) by using a narrow safety belt (selection was imperfect owing to the need to compromise between selectivity and sensitivity). These experiments confirmed the charge

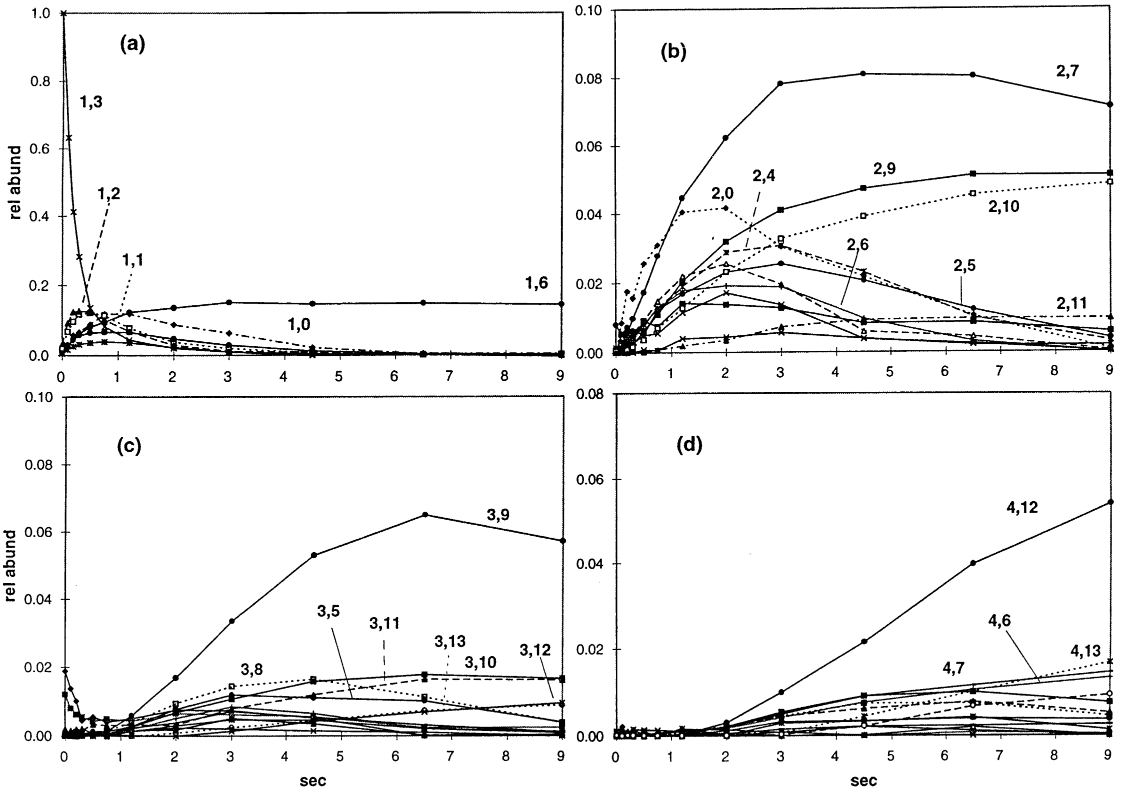

Fig. 3. Time-dependent relative abundance profiles for reaction of $Mo(CO)_3^+$ with $Mo(CO)_6$ at a pressure gauge reading of 3.2×10^{-9} Torr: (a) mono-Mo-containing species, (b) di-Mo-containing species, (c) tri-Mo-containing species, (d) tetra-Mo-containing species.

exchange processes alluded to earlier, as illustrated here for reactions of $^{96}Mo(CO)_3^+$ ions by the spectra in Figs. 4(a)–4(c). For short reaction times, $^{96}Mo(CO)_n^+$ ions ($n = 0$–2) are observed, indicating that they are formed directly from $^{96}Mo(CO)_3^+$ by CID. On the other hand, the $Mo(CO)_6^+$ ions produced have a natural isotopic distribution indicating that they are formed from $Mo(CO)_6$ by electron loss. $Mo(CO)_n^+$ ions with $n = 4$ or 5 also exhibit the natural isotopic distribution indicating their formation by dissociation of $Mo(CO)_6^+$. For longer reaction times the natural isotopic distribution starts to grow in the $Mo(CO)_n^+$ ions with $n = 0$–3 at the expense of the enriched isotope as the $Mo(CO)_{4-6}^+$ ions decompose. All the other $^{96}Mo(CO)_n^+$ ions behave similarly, i.e. ions in which n has increased have the natural isotopic distribution. Those in which n is the same, or lower, initially contain the ^{96}Mo isotope but the natural isotopic content grows with reaction time. Unfortunately, the isotopic distribution in poly-Mo-containing ions was indistinguishable from the natural distribution so that isotopic information has been lost.

Ionization energies (Table 1) indicate that ground state $Mo(CO)_n^+$ ions should not undergo charge exchange with $Mo(CO)_6$, though the excitation energy requirements would not be large. The only experimental values [20] are for Mo and $Mo(CO)_6$; these indicate an energy requirement of ~ 1.1 eV. The density functional theory (DFT) calculations, to be reported later [21], also indicate energy requirements ranging from 0.08–~ 2.0 eV for the various charge exchanges. The DFT calculations were performed by using the program DMOL (Biosym Technologies, Inc., San Diego, CA, v2.3 and 2.36) with double numerical basis sets and a BLYP functional [22–24]. The DFT values are consistent with the experimental

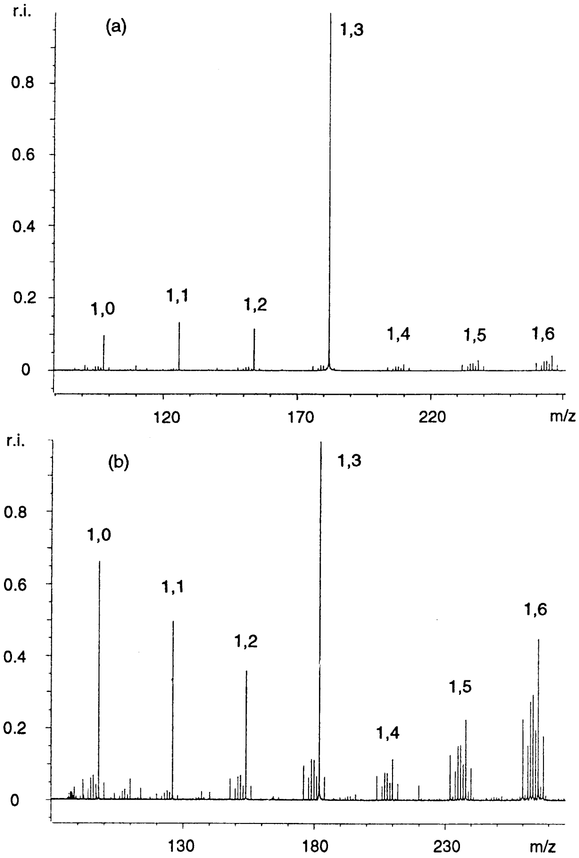

Fig. 4. Positive ion mass spectra generated by reaction of $^{96}Mo(CO)_3^+$ with $Mo(CO)_6$ at a pressure gauge reading of 3.2×10^{-9} Torr after reaction times of (a) 0.1 s, (b) 0.5 s.

observations, i.e. charge exchange occurs for freshly generated ions, having translational energy and internal excitation, colliding with $Mo(CO)_6$ but ceases after a while as the ions become cooled by collisions.

In another experiment $Mo_2(CO)_7^+$ ions, when allowed to collide with $Mo(CO)_6$, underwent CID to $Mo_2(CO)_n^+$ ($n = 0$–6) rather than undergoing association reactions. This result implies that this and other unreactive long-lasting survivor ions, such as di-Mo-containing ions with $n \geq 7$, are not further involved in association reactions.

3.1. Reaction rates

Under the conditions of these experiments the reactions should initially follow simple first order rate laws. Deviations from first order behavior occur because of competing reactions. For example, an attempt to determine a rate constant by applying the integrated rate law to the relative abundance of $Mo(CO)_3^+$ as it reacts with $Mo(CO)_6$ generated a curved semilog plot because, after charge exchange with $Mo(CO)_6$, some $Mo(CO)_3^+$ is regenerated by dissociation of $Mo(CO)_6^+$. Consequently, pseudo-first order rate constants were estimated by the initial rate method. The values given in Table 2 for reactions of all $Mo(CO)_n^+$ ions have no absolute significance because the ICR cell pressure is not accurately known but, because they were obtained at the same pressure readings, the relative values can be compared. For each reactant ion the rate constants for formation of product ions are shown with positive values and (for clarity) those for consumption of the reactant ions with negative values. The sum of the positive and negative values for each reactant ion should be zero if formation of mono-Mo-containing ions only is occurring. A positive value for the total reflects inaccuracy in the rate constant measurements whereas a negative value (also subject to corresponding inaccuracies) suggests that association reactions are occurring after very short reaction times. The reactivity of the ions seems to increase from $n = 0$–3, and then to decrease. When $n = 0$ charge exchange is the dominant

Table 1
Ionization energies (eV) of $Mo(CO)_n$ species and average Mo–CO bond energies (eV) in $Mo(CO)_n^+$

	Mo	Mo(CO)	$Mo(CO)_2$ (C_{2v})	$Mo(CO)_3$ (C_{3v})	$Mo(CO)_4$ (C_{2v})	$Mo(CO)_5$ (C_{4v})	$Mo(CO)_6$ (O_h)	CO
IE(Expl) [20]	7.10	–	–	–	–	–	8.23	14.01
IE(DFT) [a] [21]	6.92	6.77	6.87	8.44	8.56	8.65	8.73	–
BE(DFT) [21]	–	1.08	1.22	1.41	1.37	1.36	1.35	–

[a] Density functional theory. The DFT results are given for the indicated preferred geometries; all Mo-C-O linkages are linear.

Table 2
Pseudo first order rate constants (s^{-1}) for reaction of $Mo(CO)_n^+$ with $Mo(CO)_6$ at a pressure gauge reading of 3.1×10^{-9} Torr at ambient ICR cell temperature

Product	Reactant ion						
Ion	Mo^+	$Mo(CO)^+$	$Mo(CO)_2^+$	$Mo(CO)_3^+$	$Mo(CO)_4^+$	$Mo(CO)_5^+$	$Mo(CO)_6^+$
Mo^+	−0.90	0.95	0.37	0.29	0.24	0.30	0.03
$Mo(CO)^+$	–	−1.87	0.94	0.39	0.10	0.21	0.04
$Mo(CO)_2^+$	0.13	0.13	−2.43	0.45	0.61	0.22	0.14
$Mo(CO)_3^+$	0.20	0.15	0.12	−2.94	0.65	0.16	0.38
$Mo(CO)_4^+$	0.12	0.04	0.05	0.10	−2.55	0.27	0.46
$Mo(CO)_5^+$	0.21	0.11	0.10	0.19	0.38	−2.64	0.69
$Mo(CO)_6^+$	0.64	0.22	0.21	0.20	0.78	0.41	−1.45
Total	0.40	−0.27	−0.64	−1.32	0.19	−1.07	0.19

For clarity, the rate constants for the disappearance of reactant ions are artificially shown with negative values and those for formation of product ions with positive values.

process. Association reactions appear to be most significant for intermediate values of n (2, 3, and 5).

It is possible to propose the following general reaction steps, although specific details have not yet been established.

70 eV EI:

$$Mo(CO)_6 \rightarrow Mo(CO)_n^+ + (6 - n)CO + e^-$$

$$(n = 0\text{–}6)$$

Charge exchange:

$$Mo(CO)_n^+ + Mo(CO)_6 \rightarrow Mo(CO)_n + Mo(CO)_6^+$$

CID or unimolecular dissociation:

$$Mo(CO)_n^+ \rightarrow Mo(CO)_m^+ + (n - m)CO$$

Association reactions:

$$Mo(CO)_n^+ + Mo(CO)_6 \rightarrow [Mo_2(CO)_{6+n}^+]$$

$$\rightarrow Mo_2(CO)_{6+n-x}^+ + xCO$$

$$Mo_2(CO)_y^+ + Mo(CO)_6 \rightarrow [Mo_3(CO)_{6+y}^+]$$

$$\rightarrow Mo_3(CO)_{6+y-x}^+ + xCO$$

$$Mo_3(CO)_z^+ + Mo(CO)_6 \rightarrow [Mo_4(CO)_{6+z}^+]$$

$$\rightarrow Mo_4(CO)_{6+z-x}^+ + xCO$$

etc.

The tendency to undergo association reactions appears to be greatest for intermediate CO:Mo ratios (i.e. 2–3:1). At higher ratios the polymeric ions are less reactive (as has been noted) whereas precursor ions with lower ratios are not formed to any great extent. If the Mo–CO bond energies listed in Table 1 are typical of those in the polynuclear ions then, unless the Mo–Mo bonds are very strong, the association reactions will be endothermic for ground state ions having little translational energy.

3.2. Negative ions

The negative ion mass spectrum (at an electron beam energy of 70 eV) is very simple, consisting mainly of $Mo(CO)_5^-$ (~ 90% of the total ion current). The negative ions (without any selection or collisional deactivation) were allowed to react with $Mo(CO)_6$. Fig. 5 shows that the negative ions are much less reactive than the positive ions, with significantly lower relative abundances of poly-Mo-containing species being observed, even after significantly longer reaction times at the same pressure. The abundance of $Mo(CO)_5^-$ is still decreasing slowly even at reaction times of 150 s [Fig. 5(a)]. The main $Mo_2(CO)_n^-$ ions at 150 s [Fig. 5(b)] are $Mo_2(CO)_6^-$ and $Mo_2(CO)_9^-$ (each ~ 3% relative abundance). At shorter reaction times $Mo_2(CO)_8^-$ is also formed, but its relative abundance then decreases with increasing reaction

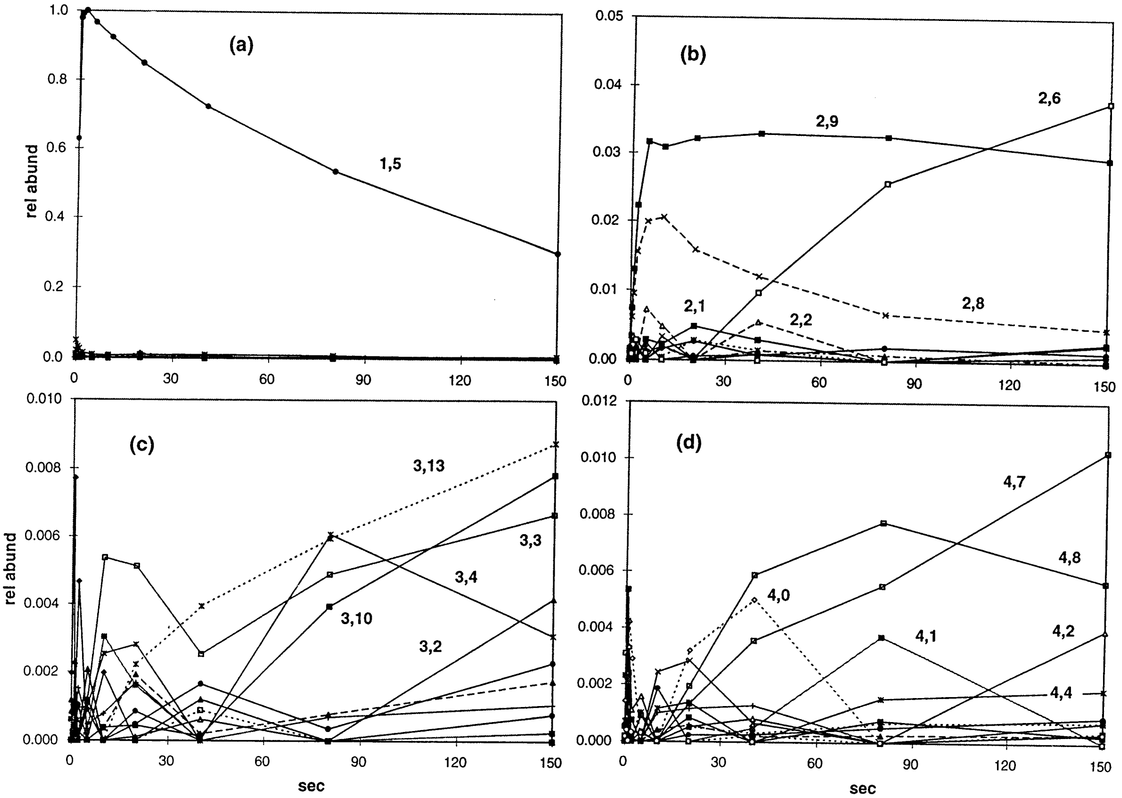

Fig. 5. Time-dependent relative abundance profiles for reaction of negative ions (~ 90% $Mo(CO)_5^-$) with $Mo(CO)_6$: (a) mono-Mo-containing species, (b) di-Mo-containing species, (c) tri-Mo-containing species, (d) tetra-Mo-containing species.

time. The major poly-Mo-containing ions formed during long reaction times are $Mo_3(CO)_{13}^-$ (~ 0.9%), $Mo_2(CO)_{10}^-$ (~ 0.8%), $Mo_4(CO)_7^-$ (~ 1.0%), $Mo_4(CO)_8^-$ (~ 0.6%), $Mo_5(CO)_{11}^-$ (~ 0.15%), $Mo_5(CO)_{12}^-$ (~ 0.06%), and $Mo_6(CO)_{14}^-$ (~ 0.06%). Presumably, the general reaction sequences for formation of the negative ion clusters parallel (with differences in detail) those proposed for the positive ions, although it is possible that trapped electrons could also play a part.

4. Conclusions

In the ion chemistry of molybdenum hexacarbonyl, a multitude of polynuclear ions are observed. The preferred positive ions in the various clusters are $Mo_2(CO)_7^+$, $Mo_2(CO)_9^+$, $Mo_2(CO)_{10}^+$, $Mo_3(CO)_9^+$, $Mo_4(CO)_{12}^+$, $Mo_5(CO)_{13}^+$, and $Mo_6(CO)_{17}^+$, and preferred negative ions are $Mo_2(CO)_6^-$ and $Mo_2(CO)_9^-$. Interestingly, a *trace* of $Mo_2(CO)_{11}^+$ is also observed, despite its expected lack of stability (see introduction). Electron counting does not allow predictions as to the number of bridging or terminal groups. It is tempting to propose polyhedron structures, i.e. tetrahedron, square pyramid or trigonal bipyramid, and octahedron for the 4, 5, and 6 membered metal atom skeletons, respectively. Some of the stable stoichiometries parallel those of compounds of known structures. For example, neutral $Ir_4(CO)_{12}$ has a tetrahedron of Ir atoms, each having three terminal CO groups whereas $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ each have a tetrahedron of metal atoms but instead three of the CO groups are bridging and are located above three edges of one face of the tetrahedron [18]. In the case of neutral $Rh_6(CO)_{16}$, four CO groups are each bridged to three Rh atoms and are located alternately above four of the eight faces of an octahedron of Rh atoms [16]. The latter compound conforms to Wade's rules and contains seven skeletal electron pairs [25,26]. However, the six-membered Mo-containing clusters are electron deficient and do not contain sufficient electrons to populate the skeletal bonding orbitals of the octahedral cluster and so structural predictions should be treated with caution.

Acknowledgements

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References

[1] D.P. Ridge, in C.Y. Ng, T. Baer, I. Powis (Eds.), Unimolecular and Bimolecular Reaction Dynamics, Wiley, New York, 1994, Chap. 7, pp. 337–370.
[2] B.R. Higginson, D.R. Lloyd, P. Burroughs, D.M. Gibson, A.F. Orchard, J. Chem. Soc., Faraday Trans. 2 69 (1973) 1659.
[3] R.E. Winters, R.W. Kiser, Inorg. Chem. 4 (1965) 157.
[4] A. Foffani, S. Pignataro, B. Cantone, F. Grasso, Z. Phys. Chem. 45 (1965) 79.
[5] D.R. Bidinosti, N.S. McIntyre, Can. J. Chem. 45 (1967) 641.
[6] G.A. Junk, H.J. Svec, Z. Naturforsch. B 23 (1968) 1.
[7] F.I. Vilesov, B.L. Kurbatov, Dokl. Akad. Nauk SSSR 140 (1961) 1364.
[8] D.R. Lloyd, E.W. Schlag, Inorg. Chem. 8 (1969) 2544.
[9] F.M. Harris, P.J. Jackson, J.A. Rontree, S.R. Andrews, D.E. Parry, J. Mass Spectrom. 30 (1995) 601.
[10] V.H. Wysocki, H.I. Kenttamaa, R.G. Cooks, Int. J. Mass Spectrom Ion Processes 75 (1987) 181.
[11] R.G. Cooks, T. Ast, B. Kralj, V. Kramer, D. Žigon, J. Am. Soc. Mass Spectrom. 1 (1990) 16.
[12] S.L. Mullen, A.G. Marshall, J. Am. Chem. Soc. 110 (1988) 1766.
[13] S.M. Peterman, D.H. Russell, Proceedings of the 45th ASMS Conference on Mass Spectrometry and Allied Topics, Palm Springs, CA, June 1–7, 1997.
[14] J.V. Oriede, D.H. Russell, Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, TN, May 19–24, 1991.
[15] B.T. Cooper, S.W. Buckner, Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, TN, May 19–24, 1991.
[16] K.F. Purcell, J.C. Kotz, Inorganic Chemistry, W.B. Saunders, Philadelphia, 1977, Chap. 16, pp. 855–863.
[17] J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry (4th Ed.), Harper Collins, New York, 1993, Chap. 15, pp. 630–639.
[18] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry (5th Ed.), Wiley, New York, 1998, Chap. 22, pp. 1021–1028.
[19] A.J.R. Heck, L.J. de Koning, A.F. Pinkse, N.M.M. Nibbering, Rapid Commun. Mass Spectrom. 5 (1991) 406.
[20] S.G. Lias, J.F. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (1988) 281, 630 (suppl.).
[21] K.J. Fisher, I.G. Dance (unpublished).
[22] B. Delley, M. Wrinn, H.P. Luthi, J. Chem. Phys. 100 (1994) 5785.
[23] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[24] A.D. Becke, Phys. Rev. A. 38 (1988) 3098.
[25] See [18], pp. 1068–1070.
[26] K. Wade, Adv. Inorg. Chem. Radiochem. 18 (1976) 1.