Negative Parent Ion in the Mass Spectrum of Hexacarbonylvanadium

By RICHARD E. SULLIVAN, MICHAEL S. LUPIN, and ROBERT W. KISER*

(*Department of Chemistry, University of Kentucky, Lexington, Kentucky* 40506)

Summary The first observation of a parent negative ion in the mass spectra of metal carbonyls is reported for $V(CO)_6$.

A SIGNIFICANT feature in the negative-ion mass spectra of metal carbonyls is the absence of the parent-molecule ion.[1–3] This is consistent with the view,[4] based on calculations for $Ni(CO)_4$[5] and $Cr(CO)_6$,[6] that the captured electron would have to be placed in an anti-bonding molecular orbital. The case of the paramagnetic hexacarbonylvanadium is different; the addition of an electron to the molecule to give the anion $V(CO)_6^-$ (which has been observed in solution) is expected since molecular orbital calculations indicate that the added electron would enter a bonding molecular orbital.[7] We report the observation of gaseous $V(CO)_6^-$ formed by electron capture from $V(CO)_6$, the first observation of a parent negative ion in metal carbonyls.

The complete negative ion mass spectrum of $V(CO)_6$ is given in the Table. The most intense negative ion corresponds to loss of one ligand from the parent molecule; also to be noted is the decrease in relative abundances with increasing fragmentation, a feature characteristic of other transition metal carbonyls.[1,2] Two metastable peaks were observed, corresponding to the transitions $V(CO)_5^- \rightarrow V(CO)_4^- + CO$ and $V(CO)_4^- \rightarrow V(CO)_3^- + CO$. By analogy with the negative[1,8] and positive[9] ion mass spectra of metal carbonyls, the $V(CO)_6^-$ ion is expected to fragment by a stepwise process; these data support the earlier expectations. However, the formation of $V(CO)_6^-$ by a simple electron capture process (presumably of secondary electrons) is not the only decomposition pathway available, and some of the $V(CO)_5^-$ may be formed by dissociative electron capture.

TABLE

Relative abundance at 70 ev(*uncorr.*)

Ion	Abundance	Ion	Abundance
$V(CO)^-$	0·1	$V(CO)_4^-$	60
$V(CO)_2^-$	1·0	$V(CO)_5^-$	100
$V(CO)_5^- \rightarrow V(CO)_4^- + CO$	0·3	$V(CO)_6^-$	0·02
$V(CO)_3^-$	10·0		
$V(CO)_4^- \rightarrow V(CO)_3^- + CO$	0·1		

All measurements were performed with an Hitachi RMU-6E double-focussing mass spectrometer at an ionizing energy of 70 ev(uncorr.). Inlet system and ion source temperatures were < 40° to suppress any thermal decomposition of the metal carbonyl. Sample pressures in the region between the electrostatic and magnetic sectors were *ca.* 3×10^{-6} torr. The hexacarbonylvanadium was prepared from $Na(diglyme)_2V(CO)_6$ by the method of Werner and Podall[10] and used within two hours of preparation. Tris(trifluoromethyl)-*s*-triazine was used as a convenient mass calibrant to bracket the $V(CO)_6^-$ ion (*m/e* 219) with ions at *m/e* 216 and 221.

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