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Negative Ions Formed by Vacuum Spark Discharge. IV.[1] Polyatomic Negative Ions of the Elements in B-Subgroups on the Periodic Table

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Polyatomic negative ions for almost all of the elements in B-subgroups on the periodic table were tested by the spark discharge type ion source mass spectroscopy. Polyatomic negative ions such as hydride negative ions, oxide negative ions, and carbide negative ions could be detected. The results are discussed with reference to the reported results by other methods of formation.

A study on negative ion spark source mass spectroscopy has been carried out using a Mattauch-Herzog type double focusing mass spectrograph. Formation of atomic negative ions of 48 elements,[2] relative sensitivity coefficients for negative ions,[3] and polyatomic negative ions of the elements in A-subgroups on the periodic table[1] have already been reported.

In the previous report,[1] polyatomic negative ions of the elements in A-subgroups on the periodic table were described; these were formed by the spark discharge type ion source and were detected with use of the Mattauch-Herzog type double focusing mass spectrograph. They were classified into five types: (1) "polymer" negative ions, (2) hydride negative ions, (3) oxide negative ions, (4) carbide negative ions and (5) other types of negative ions. The results were discussed with reference to the reported values of electron affinities and to the other methods of formation.

In the present report, polyatomic negative ions of the elements in B-subgroups on the periodic table which can be detected experimentally by a spark discharge type ion source are described, along with the polyatomic positive ions. Sample materials used were: (1) elementary materials in the form of solid metals or powdered metals, (2) oxide compounds, (3) binary compounds such as ZnSe or CdS, (4) various metal alloys, and (5) other types of compounds, including almost all of the elements in B-subgroups (transition metal elements) on the periodic table, except for the element Tc.

The detected polyatomic negative ions are classified into three types: (1) hydride negative ions, (2) oxide negative ions, and (3) carbide negative ions. No "polymer" negative ions can be detected for these elements in this experiment, in contrast to the case of the elements in A-subgroups (typical elements), in which many "polymer" negative ions were detected.[1]

Although there are fewer examples in the literature that describe the formation of polyatomic negative ions of the elements of B-subgroups by various methods of formation, as compared with the case of A-subgroups, the results obtained here are compared with such reports as do exist.

Few electron affinity values for the molecules containing transition metal elements are also available in the literature,[4,5] except for those of the molecular ions WO_3^-,[6] HWO_4^-,[6] and PtN^-.[7] This is just the opposite situation to the case of the molecular ions of the A-subgroups (typical elements), in which many examples of determination of the values of the electron affinities are reported. For example, experimental techniques for determining the electron affinity values include the following: photodetachment,[8,9] spectroscopy,[10] photoelectron spectroscopy,[11] photoionization,[12,13] charge exchange,[14] dissociative electron attachment,[15,16] thermochemistry,[17] surface ionization,[18,19] and electron impact.[20,21] Empirical techniques applied to the electron affinity values of molecular ions is the method of isoelectronic model (NO^- [22]).

Few theoretical calculations of the electron affinity values for the molecules containing transition metal elements are in the literature, though some for molecular ions containing the typical elements are reported.[4,5] Methods include variational calculation,[23] Hartree-Fock calculation,[24] configuration interactions,[25] and Rydberg-Klein-Rees calculations.[26]

The experimental results given here are thus considered to be very valuable from the standpoint of the study of electron affinity values for the molecular ions of the transition metal elements. They give experimental evidence that the molecular ions detected here have the positive electron affinity values. The results are also very valuable in the interpretation of negative ion mass spectra formed by the spark discharge type ion source.

Experimental

Apparatus. The instrument used was a Mattauch-Herzog type double focusing mass spectrograph equipped with an r. f. spark discharge type ion source (Mitsubishi Denki Electric Co., Ltd.). Since details of the instrumentation were reported elsewhere,[27–29] only the operationing conditions are given here: spark voltage 20 kV, pulse width 200 μs, repetition rate 100 s^{-1}, ion accelerating voltage 15 kV for both positive and negative ions.

Materials. Sample materials studied are (1) elementary materials in the form of solid metals or powdered metals, (2) oxide compounds, (3) binary compounds such as ZnSe or CdS, (4) various metal alloys, (5) other types of compounds. They are listed in Table 1.

Experimental procedures for measuring mass spectra o negative ions for these sample materials, and the method and procedure for the assignment of the mass spectral peaks obtained, are essentially the same as described in the previous report.[1,2)]

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TABLE 1. SAMPLE MATERIALS FOR THE POLYATOMIC NEGATIVE IONS

Group	Element	Sample materials	Group	Element	Sample materials
IB	Cu	Copper metal Copper alloy		Ta	Tantalum metal Tatalum(V) oxide, Powder
	Ag	Silver metal Silver alloy Silver(I) oxide, Powder Silver bromide, Powder	VIB	Cr	Chromium metal Chromium(III) oxide, Powder
				Mo	Molybdenum metal Ammonium molybdate, Powder
	Au	Gold metal Gold, powder Gold alloy		W	Tungsten metal Tungsten(VI) oxide, Powder
IIB	Zn	Zinc(II) selenide Zinc(II) oxide, Powder	VIB	Mn	Manganese metal Manganese(II) carbonate
	Cd	Cadmium(II) telluride, Crystal Cadmium(II) sulfide, Crystal Cadmium(II) oxide, Powder		Re	Rhenium, Filament Rhenium, Powder
	Hg	Mercury(I) chloride, Powder Mercury(II) oxide, Powder	VIII	Fe	Iron metal Iron alloy Iron(III) oxide, Powder Meteorite
IIIB	Sc	Scandium metal Scandium(III) oxide, Powder		Co	Cobalt alloy Meteorite
	Y	Yttrium metal Yttrium(III) oxide, Powder		Ni	Nickel metal Nickel alloy Meteorite
	La	Lanthanum metal Lanthanum(III) oxide, Powder Monazite		Ru	Ruthenium, Powder
IVB	Ti	Titanium metal Titanium(IV) oxide, Powder		Rh	Rhodium, Powder Rhodium-platinum alloy
	Zr	Zirconium metal Zirconium (IV) oxide, Powder Monazite		Pd	Palladium metal Palladium alloy
				Os	Osmium, Powder
				Ir	Iridium, Powder
	Hf	Hafnium metal		Pt	Platinum metal Platinum alloy
VB	V	Vanadium metal Vanadium(V) oxide, Powder			
	Nb	Niobium metal Niobium(V) oxide, Powder			

Results and Discussion

Experimental results for the polyatomic negative ions are tabulated in Table 2, along with the experimental results for atomic negative ions[2] and for polyatomic positive ions which were detected in the positive ion spark source mass spectra using the same samples.

Group IB Elements. In this group, for the elements Cu, the oxide ion CuO^- and the carbide ions CuC^- and CuC_2^- are detected. For the element Ag, the carbide negative ion AgC^-; for the element Au, oxide negative ions AuO^- and AuO_2^-, and carbide negative ions AuC^-, AuC_2^-, AuC_3^-, and AuC_4^- are detected. The positive ion Ag_2^+ is detected.

In the literature,[30] Cu^+—Cu_5^+ ions were detected by spark source mass spectroscopy. NO electron affinity values for the molecules that are detected in this experiment are available in the literature.

Group IIB Elements. For all of the elements in this group, no polyatomic negative or positive ions are detected by the experiment. Spark electrodes in this experiment were ZnSe(crystal)/Pt, or ZnO(powder)/Pt, Zn-alloy/Pt; CdS(crystal)/Pt, CdTe(crystal)/Pt, CdO(powder)/Pt; Hg_2Cl_2(powder)/Pt, HgO(powder)/Pt.

In the literature,[31] CdO^-, CdO_3^-, CdO_6^-, and CdO_7^- ions are reported to form by surface ionization. No electron affinity values are available for the molecules in this group.

Group IIIB Elements. In this group, negative ions of YO^-, LaO^-, LaO_2^-, LaO_3^-, $LaOH_2^-$, and $LaO_2H_2^-$ are detected. Positive ions of YO^+, YOH_3^+, and LaO^+ are also detected. When the pure metals of Y/Y and La/La electrodes are used as sample materials, these ions are detected. The oxygen and hydrogen atoms in these detected ions may derive from the contamination on the electrodes or from the background gas molecules. Carbide negative ions for these elements can not be detected. There are no reports on polyatomic negative ions or electron affinity values

TABLE 2. POLYATOMIC NEGATIVE IONS AND POSITIVE IONS

Group	Element	Atomic	Polyatomic negative ions	Polyatomic positive ions
IB	Cu	D[a)]	CuO^-; CuC^-, CuC_2^-	
	Ag	D	AgC^-	Ag_2^+
	Au	D	AuO^-, AuO_2^-; AuC^-—AuC_4^-	
IIB	Zn	ND[b)]		
	Cd	ND		
	Hg	ND		
IIIB	Sc	ND		
	Y	D	YO^-	YO^+, YOH_3^+
	La	D	LaO^-—LaO_3^-; $LaOH_2^-$, $LaO_2H_2^-$	LaO^+
IVB	Ti	ND		
	Zr	D	ZrO^-	ZrO^+
	Hf	ND		
VB	V	(ND)		
	Nb	D	NbO^-—NbO_3^-; NbO_2H^-, NbO_3H^-; NbC^-, NbC_2^-	
	Ta	ND		TaO^+—TaO_3^+
VIB	Cr	D	CrO^-—CrO_3^-	
	Mo	D	MoO^-—MoO_4^-; MoC^-—MoC_4^-; $MoOH^-$—MoO_3H^-; MoH^-	
	W	D	WO^-—WO_4^-; WC^-—WC_3^-	
VIIB	Mn	ND		
	Tc			
	Re	ND		
VIII	Fe	D		
	Ru	D		
	Os	D		
	Co	D		
	Rh	D	RhH^-; RhO^-; RhC^-, RhC_2^-	
	Ir	D		
	Ni	D		
	Pd	D	PdH^-	
	Pt	D	PtO^-, PtO_2^-; PtC^-—PtC_4^-; PtH^-; $PtCH^-$—PtC_3H^-	

a) Detected. b) Not detected.

of these elements.

Group IVB Elements. In this group, ZrO^- and ZrO^+ are detected by this experiment, For the elements Ti and Hf, no polyatomic negative and positive ions are detected.

In the literature,[30] Ti^+—Ti_5^+ ions were reported to form by the spark discharge ion source. No electron affinity values are available in the literature.

Group VB Elements. For the element Nb, we detected in the Nb/Pt spark discharge oxide negative ions, NbO^-, NbO_2^-, and NbO_3^-; hydride oxide negative ions NbO_2H^- and NbO_3H^-; and carbide ions NbC^-, and NbC_2^-. For the elements V and Ta, no atomic or polyatomic negative ions are detected. The positive ions TaO^+, TaO_2^+, and TaO_3^+ ions are detected.

There are no reports on the polyatomic negative ions for these elements and their electron affinity values.

Group VIB Elements. For the element Cr, oxide negative ions CrO^-, CrO_2^-, and CrO_3^- are detected by Cr/Cr spark discharge, for Mo, we detected oxide negative ions MoO^-, MoO_2^-, MoO_3^-, and MoO_4^-; hydride oxide negative ions $MoOH^-$, MoO_2H^-, and MoO_3H^-; carbide negative ions MoC^-, MoC_2^-, MoC_3^-, and MoC_4^-; and hydride negative ions MoH^- by Mo/Mo spark discharge. For the element W, oxide negative ions WO^-, WO_2^-, WO_3^-, and WO_4^- and carbide negative ions WC^-, WC_2^-, WC_3^- are detected by W/W spark discharge. No polyatomic positive ions for these elements are detected.

TABLE 3. HYDRIDE NEGATIVE IONS

Group	VIB	VIII		
Element	Mo	Rh	Pd	Pt
M^-	D	D	D	D
MH^-	D	D	D	D

The literature reports detection of WO_6^- and WO_8^- ions by surface ionization,[31] and WO^+, WO_2^+, and WO_3^+ ions by the reaction of incandescent W-filament with oxygen gas followed by the electron-impact.[32] Electron affinity values for the molecular ions WO_3^- and HWO_4^- are reported to be 3.6 eV and 4.4 eV respectively from a thermochemical measurement,[6] but HWO_4^- ion could not be detected in this experiment.

Group VIIB Elements. For this group, no atomic or polyatomic negative ions are detected, nor are any

Table 4. Oxide Negative ions

Group	IB		IIIB		IVB	VB	VIB			VIII	
Element	Cu	Au	Y	La	Zr	Nb	Cr	Mo	W	Pt	Rh
M^-	D	D	D	D	D	D	D	D	D	D	D
MO^-	D	D	D	D	D	D	D	D	D	D	D
MO_2^-		D		D		D	D	D	D	D	
MO_3^-				D		D	D	D	D		
MO_4^-				—		—		D	D		
MOH_2^-				D		—					
MO_2H^-				—		D					
$MO_2H_2^-$				D		—					
MO_3H^-						D					

Table 5. Carbide Negative ions

Group	IB			VIB		VIII	
Element	Cu	Ag	Au	Mo	W	Rh	Pt
M^-	D	D	D	D	D	D	D
MC^-	D	D	D	D	D	D	D
MC_2^-	D		D	D	D	D	D
MC_3^-			D	D	D		D
MC_4^-			D	D			D
MCH^-							D
MC_2H^-							D
MC_3H^-							D

positive polyatomic ions.

In the literature,[31] ReO_2^- and ReO_4^- ions were reported to form by surface ionization. No electron affinity values are available here.

Group VIII Elements. For the element Rh, hydride RhH^-, oxide RhO^-, and carbide negative ions RhC^- and RhC_2^- are detected by Pt–Rh/Pt–Rh spark discharge. For Pd, the hydride negative ion PdH^- is detected by Pd/Pd spark discharge. For the element Pt, we detected hydride negative ion PtH^-, oxide negative ions PtO^- and PtO_2^-, carbide negative ions PtC^-, PtC_2^-, PtC_3^-, and PtC_4^-; and carbide hydride negative ions $PtCH^-$, PtC_2H^-, and PtC_3H^-, by Pt/Pt spark discharge. For the other elements in this group, no polyatomic negative or positive ions are detected.

Fe_2^+—Fe_6^+ ions were detected by spark discharge.[30] The electron affinity value for PtN^- ion was reported to be >0 eV.[7]

In summary, we described the ionic species of polyatomic negative ions for the elements in B-subgroups on the periodic table, in addition to the polyatomic positive ions which are detected in this experiment. The polyatomic negative ions described here are classified into the following three types: (1) hydride negative ions, (2) oxide negative ions, and (3) carbide negative ions. They are tabulated in Tables 3, 4, and 5. Polyatomic positive ions are classified into (1) "polymer" positive ions, and (2) hydride positive ions. They are shown in Tables 6 and 7. From these tables, the following features are observed concerning the formation of polyatomic negative and positive ions by the spark discharge type ion source in the elements of B-subgroups on the periodic table.

Table 6. "Polymer" positive ions

Group	IB
Element	Ag
M_2^+	D

Table 7. Oxide positive ions

Group	IIIB		IVB	VB
Element	Y	La	Zr	Ta
MO^+	D	D	D	D
MO_2^+	—			D
MO_3^+	—			D
MOH_3^+	D			

(1) No polyatomic negative ions can be detected for the elements in which atomic negative ions can not be detected. (Zn, Cd, Hg, Sc, Ti, V, Ta, Re).

(2) No "polymer" negative ions can be detected for the elements of the B-subgroups, in contrast to the case of the elements of A-subgroups, in which many "polymer" negative and positive ions are detected. The only "polymer" positive ion detected in an element of B-subgroup is Ag_2^+.

(3) Hydride negative ions can be detected for the elements Mo, Rh, Pd, and Pt. No hydride positive ion can be detected.

(4) Oxide negative ions are detected in a large number of the ionic species, than in the case of the elements of A-subgroups.[1] Oxide positive ions are detected for the elements Y, La, Zr, and Ta.

(5) Carbide negative ions are also detected in a large number of ionic species than in the elements of A-subgroups.[1] No carbide positive ions can be detected in the elements of B-subgroups.

The electron affinity values for the molecular ions detected here are not available in the literature, except for the molecular ion of WO_3^- (3.6 eV[6]). Therefore, the comparison between the experimental results given here and the reported values of electron affinities is impossible. However, in the case of atomic negative ions,[2] and in the polyatomic negative ions of the elements of A-subgroups,[1] there were no exceptions to the assumption that the ionic species detected in these experiments had positive electron affinity values in the literature. If this assumption is correct also in the case of the polyatomic negative ions of the elements of B-subgroups on the periodic table, the results presented here give experimental evidence that the ionic species described in this report have positive electron affinity values.

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