Spark Ionization of Semi-metallic and Metallic Elements and of Ionic-crystals

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(Received April 21, 1961)

Inghram et al.[1-3] and Honig[4] have observed polyatomic molecular ions of carbon, silicon, and germanium by means of a mass spectrometer with a high-temperature effusion cell. These molecular ions have also been observed by Dörnenburg and Hintenberger[5] and by Sasaki et al.[6] using a double-focusing Mattauch-type mass spectrometer with a high frequency spark ionization source. However, the mechanism of the production of the molecular ion is still not clear. Therefore, primarily to find out qualitatively what kinds of electrode elements are capable of producing such molecular ions, experiments on the electrodes of semi-metallic and metallic elements and on ionic-crystals were performed by the author. In addition, some measurements for thermal ionization were also made in connection with the spark ionization.

Experimental

A double-focusing Mattauch-type mass spectrometer with a high frequency spark ionization source, which had been constructed by Sasaki et al.[6-8], was used. The sample to be examined was prepared in the form of rods. Two such rods for each sample were mounted in the spark ionization source with their tips approximately 1 mm. apart. The source was evacuated and, when the pressure had fallen to about 10^{-6} mmHg, spark voltage of 20 kV. was applied to the sample rods. The mass spectrum

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[1] W. A. Chupka and M. G. Inghram, *J. Chem. Phys.*, **21**, 1313 (1953).

[2] J. Drowart, G. De Maria, A. J. H. Boerboom and M. G. Inghram, ibid., **30**, 308 (1959).

[3] I. Drowart, R. P. Burns, G. De Maria and M. G. Inghram, ibid., **31**, 1131 (1959).

[4] R. E. Honig, ibid., **22**, 1610 (1954).

[5] E. Dörnenburg and H. Hintenberger, *Z. Naturforsch.*, **14**, 765 (1959).

[6] N. Sasaki, M. Onchi and J. Kai, *Mass Spectroscopy* (*Shitsuryo Bunseki*), No. **12**, 69 (1959).

[7] N. Sasaki, M. Onchi, J. Kai and Y. Abe, ibid., No. **12**, 61 (1959).

[8] N. Sasaki and J. Kai, ibid., No. **12**, 64 (1959).

TABLE I

Samples	Ions found
C	C_5^+, C_4^+, C_3^+, C_2^+, C^+, C^{2+}
Si	Si_6^+, Si_5^+, Si_4^+, Si_3^+, Si_2^+, Si^+, Si^{2+}
Ge	Ge_4^+, Ge_3^+, Ge_2^+, Ge^+, Ge^{2+}, Ge^{3+}, Ge^{4+}
Se	Se_3^+, Se_2^+, Se^+, Se^{2+}
Te	Te_2^+, Te^+, Te^{2+}
Sb	Sb_2^+, Sb^+, Sb^{2+}, Sb^{3+}, Sb^{4+}
Bi	Bi^+, Bi^{2+}, Bi^{3+}, Bi^{4+}, Bi^{5+}, Bi^{6+}
Al	Al^+, Al^{2+}
Ti	Ti^+, Ti^{2+}
Fe	Fe^+, Fe^{2+}, Fe^{3+}
Ni	Ni^+, Ni^{2+}, Ni^{3+}
Cu	Cu^+, Cu^{2+}
Zn	Zn^+, Zn^{2+}, Zn^{3+}
Zr	Zr^+, Zr^{2+}, Zr^{3+}
In	In^+, In^{2+}, In^{3+}
Sn	Sn^+, Sn^{2+}, Sn^{3+}
Pt	Pt^+, Pt^{2+}, Pt^{3+}, Pt^{4+}
Pt(Cu), Pt(Cu)	Pt^+, Pt^{2+}, Cu^+, Cu^{2+}
Au	Au^+, Au^{2+}, Au^{3+}
NaCl	Na^+, Na^{2+}, Cl^+
LiF	Li^+, Li^{2+}, Li^{3+}, Li^{4+}, F^+
KBr	K^+, K^{2+}, K^{3+}, Br^+
C, Si	$C_3^+ \sim C^+$, $Si_3^+ \sim Si^+ \sim Si^{2+}$
C, Ge	$C_4^+ \sim C^+$, $Ge_3^+ \sim Ge^+ \sim Ge^{4+}$
C, Pt	$C_3^+ \sim C^+$, $Pt^+ \sim Pt^{2+}$
Ge, Pt	$Ge_3^+ \sim Ge^+ \sim Ge^{4+}$, $Pt^+ \sim Pt^{4+}$
Ni, Pt	$Ni^+ \sim Ni^{3+}$, $Pt^+ \sim Pt^{4+}$
NaCl, KBr	$Na^+ \sim Na^{2+}$, $K^+ \sim K^{3+}$, Cl^+, Br^+
LiF, KBr	$Li^+ \sim Li^{4+}$, $K^+ \sim K^{3+}$, F^+, Br^+

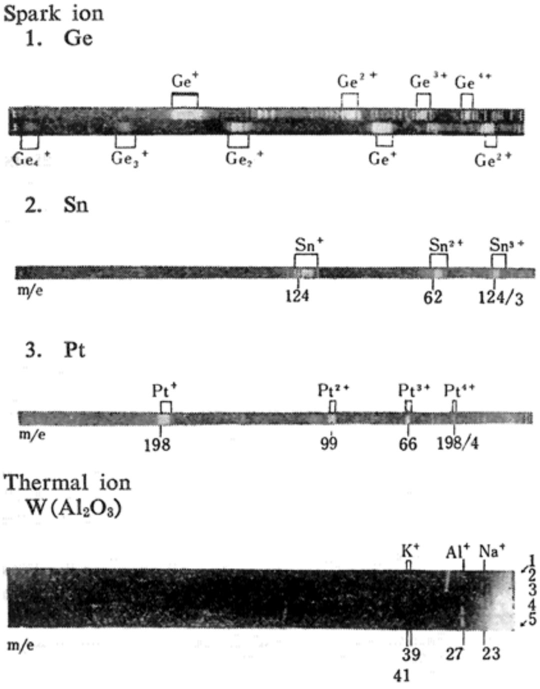

Fig. 1. Mass spectra.

was recorded, at the ion-accelerating voltage of 16 kV., on an Ilford Q-2 photographic plate. The time of exposure required for taking mass spectrographs clearly for the samples of elements and of ionic-crystals were 1～5 min. and 10 min. respectively. Typical results obtained for samples of germanium, tin (white tin), and platinum are given in Fig. 1. Gaseous species for each sample were examined on the mass spectrograph; those results are summarized in Table I, in which the sample Pt(Cu) is a platinium rod plated with copper. The results obtained in the spark between the electrodes of the different kinds of sample rods are also given in Table I.

Furthermore, mass spectra of positive ions emitted by electrical heating from a filament which has been mounted at both ends of the sample holder of the electrodes were investigated.

The thermal ionization source $W(Al_2O_3)$ shown in Fig. 1 is an alumina-coated tungsten filament, 0.055 mm. in diameter.

Results and Discussion

Thermal Ionization.—The mass spectrographs (Nos. 1—5) of the thermal ion given in Fig. 1 were taken during the gradual rise of temperature in one filament. The observed color of the filament and the time of exposure at each temperature were as follows: 1) dark red, 10 min.; 2) red, 10 min.; 3) yellowish red, 10 min.; 4) yellow, 5 min.; 5) yellowish white, 5 min. The experimental results can be summarized as follows.

The positive ions emitted from the filament are Na^+ and K^+ (39) at somewhat low tempertures, and K^+(41) and Al^+ in addition to Na^+ and K^+(39) at still higher temperatures, perhaps above 1000° C. At still higher temperatures these impure ions of alkali disappear and the emission of the only Al^+ ion is rich. Thus, the variation in positive ion emission caused by the gradual rise in temperature of the filament was successfully tracked out by taking a mass spectrograph of the ion emitted.

For the ion source of the platinum filament, 0.06 mm. in diameter, only alkali ions such as Na^+ and K^+ were observed.

Spark between Different Kinds of Electrode Elements.—Species found in the spark between the electrodes of different kind were found in just the same mixture as had been produced in the sparks of each electrode. For instance, in the spark between the electrodes of carbon and silicon elements no molecular ion such as silicon carbide was observed (cf. Table I).

Spark between the Same Kind of Electrode Elements.—Multiply-charged monatomic ions are given for all samples, whereas polyatomic ions are given only for several kinds of samples, and these are only singly charged ones (cf. Table I). This seems to show that monatomic molecules in the gas phase can be readily ionized to multiply-charged ions, whereas polyatomic molecules are too unstable to form doubly-charged ions without decomposition of the molecules.

Polyatomic ions are produced only for the semi-metallic elements (cf. Table I). (This result was obtained in a significant concentration of mass spectra under experimental conditions concerning spark voltage, the time of exposure, etc., such as has been described in the experimental section. No experiments under other conditions were carried out.)

Spark between the Electrodes of Ionic-crystal.—When the spark voltage was applied to the electrodes of an alkali halide single crystal, the crystals were brightly colored in the run, violet for sodium chloride, yellow for lithium fluoride, and cobalt blue for potassium bromide.

As shown in Table I, the gaseous species for each crystal are positive ions of alkali and halogen, including their isotopes, and the concentration of the spectral line of halogen ions is, in general, less then that of the corresponding alkali ions. For alkalis, their multiply-charged monatomic ions are given, whereas for halogens, only singly-charged monatomic ions are given. Molecular ions such as $NaCl^+$ and Na_2^+, for instance, were not observed.

When the crystals were taken out from the spark source after sparking, it was observed that the crystals still held their original shape and, moreover, that color centers had been formed finely, yellow for sodium chloride, yellowish brown for lithium fluoride, and cobalt blue for potassium bromide. These color centers seem to have been formed by electron impact on the crystals.

The species found in the spark between electrodes of different kinds (e. g., sodium chloride and potassium bromide) were in just the same mixture as what had been produced in the sparks of each electrode (cf. Table I). Similar results to the case of the same kind of electrodes were also obtained in the matters of the brightness of crystals during sparking and of the color centers after sparking.

Concentration of Mass Spectral Line of Spark Ion.—The results obtained from an examination of the mass spectral line in the significant concentration are as follows:

For all elements, as shown in Fig. 1, for instance, their isotopes are simultaneously given in the spark, and the relative intensity in the lines of an isotope corresponds approximately to their abundance ratio.

For each sample element (X), the relative intensity of multiply-charged monatomic ions is $X^+ > X^{2+} > X^{3+} \cdots\cdots$. In the case of polyatomic molecular ions, the relative intensity is $X^+ > X_2^+ > X_3^+ \cdots\cdots$ for silicon, germanium, and selenium, $X^+ > X_2^+$ for tellurium and antimony, and $X^+ > X_3^+ > X_2^+ > X_5^+ > X_4^+$ for carbon. Furthermore, the intensity of polyatomic ions is, in general, less than that of multiply-charged monatomic ions of the same element.

Discussion.—Gaseous species observed in the thermal ionization were usually singly-charged monatomic ions for the ion sources of alumina-coated tungsten filament, bare platinum filament, etc.[9-11], whereas, in the spark, multiply-charged monatomic ions were always observed. In addition, an estimation of quite a high temperature can be given for the tips of element rods during sparking, for, the tips have been observed in a melting state after sparking. These results seem to show a difference between the mechanism of ion formation by sparking and that by thermal ionization[9-11]. In the case of a spark, as is well known, electrons are produced through a kind of chain reaction, and most of the experimental results obtained here can well be understood as an effect of the

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9) T. Yuasa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 996 (1958).

10) T. Yuasa, ibid., **79**, 999 (1958).

11) T. Yuasa, ibid., **80**, 1117 (1959).

electron impact on the electrodes or gaseous particles.

In the condition of such an electron impact on gaseous particles, the ionization (or decomposition) process for the atom, ion, or molecule seems to overcome other processes such as the recombination of atom and ion.

Therefore, one of the two alternative mechanisms considered—the formation of polyatomic ions by recombining the atom with the ion in the gas phase—seems to be unlikely, and another formation process appears probable. That is, first, large gaseous molecules are emitted from the rods, then the substances are decomposed in the gas phase; thus a series of molecular ions as given in Table I are produced, or such a series of ions may be sublimated simultaneously from the first. (These two processes may take place simultaneously.) If this process, in which no polyatomic ions can be formed as long as polymerized substances are not sublimated from the solid, is applied to the experimental results, the conclusion can be drawn that the sublimation products from the metallic crystal are only a group of free monoatomic molecules, whereas for the semi-metallic crystal with a covalent bond some gaseous polymer must exist in the sublimation products.

Summary

Using a mass spectrometer, the nature of the mass spectrum produced by the spark ionization source of semi-metallic and metallic elements and of ionic-crystals was studied, and it was found that only semi-metallic elements are capable of producing their polyatomic ions in a significant concentration.

When the samples of alkali halide single crystals were taken out from the spark source after sparking, it was observed that the crystals held their shape and, moreover, that color centers had been formed finely.

In the light of the experimental results, the mechanism of the ion formation in the spark was discussed, and it was pointed out that some relation might exist between the crystal structure of the solid sample and the formation of the gaseous molecular ion.

The author wishes to express his thanks to Mr. S. Nas for his cooperation in the experiments.

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