FORMATION OF NEGATIVE ALUMINUM, GALLIUM, INDIUM AND THALLIUM IONS ON THE CAPTURE OF ELECTRONS BY MOLECULES OF HALIDES OF THESE ELEMENTS

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Negative ions of aluminum, gallium, indium, and thallium were observed when electrons interacted with molecules of halides of these elements. These were the first observations of negative gallium and indium ions. Negative ions of aluminum, indium, and thallium were formed on the interaction of electrons with $AlCl_3$, InBr, and thallium halide molecules through the resonance capture of electrons by molecules followed by the dissociation of the latter into negative ions and neutral halogen atoms.

ATOMS of B, Al, Ga, In, and Tl, which belong to group III in the periodic table, have one p-electron in the outer electron shell; therefore, we may assume that all these atoms have electron affinity, i.e., they may form stable negative ions.[1]

B^- ions were detected by Branscomb and Smith in a BF_3 discharge;[2] Fogel' et al. obtained these ions by the double charge-exchange of B^+ ions in various gases.[3] Blewett and Jones[4] investigated the ion emission of hot Al_2O_3; they noted a weak mass-spectrometric line representing negative ions of mass number 27 and ascribed it to Al^- ions. Ions of mass number 27 were recorded also in the spectrum of negative ions emitted by barium-oxide cathodes.[5] The existence of Tl^- ions was established by Dukel'skiĭ and Zandberg[1] by analyzing ions produced by a discharge in thallium halide vapor.

The purpose of the present work was to find whether it is possible to form negative Al^-, Ge^-, In^- and Tl^- ions on the interaction of molecules of halides of these elements with electrons. To observe and identify the ions, we used a magnetic mass spectrometer in which ions were recorded by an open electron multiplier (with a threshold sensitivity of 5×10^{-18} A per scale division). The electron current in the ion source was 1—50 μA, and the electron energy ranged from 0.1 to 100 eV.

Aluminum. It is difficult to identity Al^- ions because aluminum is a one-isotope element. The same mass number 27 may represent ions of HCN^- and $C_2H_3^-$ radicals, as well as CN^- ions containing C^{13} or N^{15} atoms. CN^- ions are formed easily by surface ionization and give one of the strongest "background lines" in investigations of negative ion spectra. A background line of mass number 26 was also observed in our work.

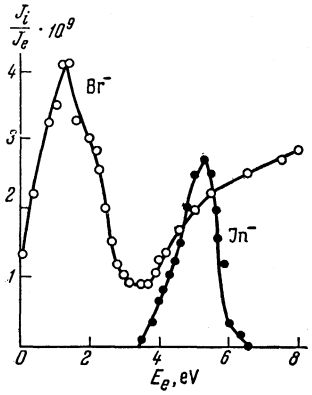
We used $AlCl_3$ as the working substance because it is least subject to dissociation in vacuum. On the introduction of a vapor of this compound into an ion source, Cl^-, $AlCl^-$ and $AlCl_2^-$, as well as ions of mass number 27, were observed in the negative ion spectrum.

The ion current, corresponding to the mass number 27, increased when the $AlCl^3$ vapor pressure increased. To check whether ions of mass number 27 were Al^- ions, and not $C_2H_3^-$, HCN^-, $(C^{13}N^{14})^-$, or $(C^{12}N^{15})^-$ ions, we investigated the spectrum of negative ions formed on the introduction into the ion source of vinyl cyanide (acrylonitrile) C_2H_3CN. An intense line of mass number 26 and a weak line of mass number 27 were observed in the same spectrum. The former was much more intense and the latter much less intense than the lines of the same mass numbers observed on the introduction of $AlCl_3$ vapor into the ion source. When $AlCl_3$ vapor and C_2H_3CN vapor were introduced simultaneously, both lines, 26 and 27, were observed, but the intensity of the 27 line depended only on the vapor pressure of $AlCl_3$, while the intensity of the 26 line depended on the vapor pressure of C_2H_3CN. The results of these control tests gave ground for believing that the negative ions of mass number 27, appearing on the introduction of $AlCl_3$ vapor into the ion source, were Al^- ions. These were observed only over a narrow range of electron energies (2—4.5 eV), i.e., they were formed as the result of the resonance capture of electrons by molecules.

Gallium. Negative Ga^- ions were observed on the introduction of GaI_3 vapor into the ion source. The identification presented no difficulties since

the relationship between the intensities of the lines with mass numbers 69 and 71 corresponded to the isotopic composition of gallium. The formation of Ga^- ions was observed at electron energies from 4 to 8 eV.

Indium. In^- ions were observed on the introduction of InBr vapor into the ion source. The lines of the two isotopes In^{113} (4%) and In^{115} (96%) were completely resolved by the mass spectrometer. The figure shows the dependence of the yield of In^- and Br^- ions on the energy of the electrons interacting with InBr molecules. In^- ions were formed only on the capture of 3.5—6.5 eV electrons by InBr molecules:



Dependence of the yield of Br^- and In^- ions on the energy of electrons interacting with InBr molecules.

$InBr + e \rightarrow (InBr)^{-*} \rightarrow In^- + Br$. The curve for Br^- ions shows that, apart from the resonance capture of 0—3 eV electrons, InBr molecules may be dissociated by electron impact into In^+ and Br^- ions (this is represented by a part of the curve in the 3.5—8 eV region).

Thallium. The introduction into the ion source of TlCl, TlBr, or TlI vapor caused the appearance, in the negative ion spectrum, of two lines corresponding to the two isotopes of thallium with mass numbers 203 and 205, with the same ratio of intensities as in the spectrum of positive thallium ions. The dependence of the negative ion yield on the electron energy was studied in detail for thallium halides and the appearance potentials of thallium ions and of other positive and negative ions were carefully determined. The results will be published in a separate communication.

In conclusion, the authors express their gratitude to Professor V. M. Dukel'skiĭ for suggesting the problem and directing the present work.

[1] V. M. Dukel'skiĭ and É. Ya. Zandberg, DAN SSSR **86**, 263 (1952).

[2] L. M. Branscomb and S. J. Smith, J. Chem. Phys. **25**, 598 (1956).

[3] Fogel', Kozlov, and Kalmykov, JETP **36**, 1322 (1959), Soviet Phys. JETP **9**, 937 (1959).

[4] J. P. Blewett and E. J. Jones, Phys. Rev. **50**, 464 (1936).

[5] W. Grattidge and A. A. Shepherd, Proc. Phys. Soc. (London) **67B**, 177 (1954).

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