Resonant Electron Capture in Silicon Tetraisocyanate and Silicon Tetrachloride

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NEGATIVE ions may be formed in the ion source of the mass spectrometer by three processes as the energy of the bombarding electrons is varied:

(1) Ion-pair production
$CH_3F + e^- \rightarrow CH_3^+ + F^- + e^-$ ($E_e > 9$—10 ev)

(2) Dissociative electron capture
$SF_6 + e^- \rightarrow SF_5^- + F$ ($E_e = 0$—10 ev)

(3) Resonance electron capture
$SF_6 + e^- \rightarrow SF_6^-$ ($E_e = 0$ ev)

Although it has been suggested[1] that the conditions existing in the ion source of the mass spectrometer are not conducive to the formation of parent negative ions negative parent ions have been detected by resonance electron capture[2] and by charge-transfer reactions in negative ion–molecule reactions.[3]

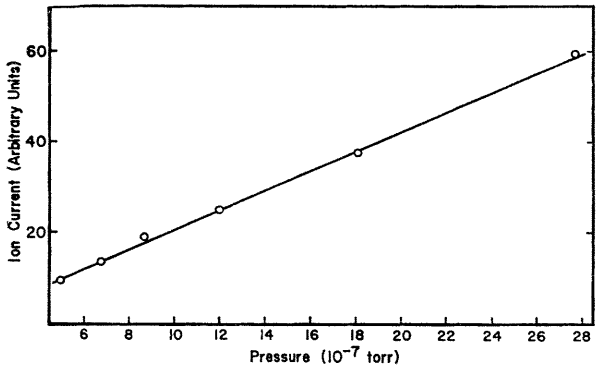

FIGURE. $Si(NCO)_4^-$ *Ion current* vs. *pressure.*

We have detected $Si(NCO)_4^-$ in silicon tetraisocyanate and $SiCl_4^-$ in silicon tetrachloride at low electron-energies and also at electron energies of *ca.* 50 ev. The formation at the higher electron-energies is no doubt by secondary electron capture. At low electron-energies the ionization efficiency curve for $Si(NCO)_4^-$ and $SiCl_4^-$ were identical with that for SF_6^- and $Ph_5NO_2^-$. Since it has been demonstrated[2] that SF_6^- and $PhNO_2^-$ are formed by resonance electron capture, we suggest that $Si(NCO)_4^-$ and $SiCl_4^-$ are formed by a similar reaction. That the processes do not result from collisional stabilization of an excited parent negative ion, or from the capture of secondary electrons, or any other second order process is deduced from the pressure dependence of the $Si(NCO)_4^-$ and $SiCl_4^-$ ion currents. The ion current measured at the maximum in the electron capture ionization efficiency curve for $Si(NCO)_4^-$ clearly shows first-order pressure dependence (Figure). Similar pressure dependence was noted for $SiCl_4$. The results and the data on the formation of the $Si(NCO)_4^-$ and $SiCl_4^-$ as a function of electron energy support the conclusion that the parent negative ions are formed in resonance electron capture reactions.

Additional species in the negative-ion mass spectrum $Si(NCO)_3^-$, $Si(NCO)_2^-$, $Si(NCO)^-$, Si^-, and NCO^-; $SiCl_3$, $SiCl_2^-$, $SiCl^-$, Si^-, and Cl^- are formed by dissociative electron-capture processes. An investigation of metastable transitions in the negative-ion mass spectra may aid in establishing the unimolecular reactions which lead to the formation of these fragment ions.

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