

REACTION OF C_{60} WITH $SbCl_5$

W.R. Datars, P.K. Ummat, T. Olech and R.K. Nkum*

Department of Physics & Astronomy, McMaster University, Hamilton,
Ontario L8S 4M1, Canada

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C_{60} was doped with $SbCl_5$ by the direct reaction with liquid $SbCl_5$ or with $SbCl_5$ dissolved in CCl_4 . Mass spectrometer analysis showed that the compound consisted of Cl_2 , $SbCl_3$ and C_{60} . The $SbCl_5$ was removed by sublimation leaving Cl_2 in C_{60} . The doped compound was electrically conducting at room temperature. The resistivity increased with decreasing temperature corresponding to a semiconducting energy gap of 1.1 eV.

THERE IS a great deal of interest in new carbon compounds since the discovery of the new form of carbon that has the formula C_{60} and is a fullerene called a bucky ball [1]. The molecule $SbCl_5$ is an acceptor or Lewis acid that accepts electrons in graphite to provide electrical conduction in the valence band of graphite [2]. The complexes in graphite are of the form $SbCl_x$ with $x = 3, 4, 5, 6$. Thus, it is of interest to react C_{60} and $SbCl_5$.

The C_{60} was prepared in the usual manner. Carbon soot was made by electrically eroding 6 mm carbon rods in a large chamber containing helium gas maintained at a pressure of 100 torr. A mixture of C_{60} and C_{70} was obtained by using a Soxhlet extractor with toluene as the solvent. After removing the solvent by a rotary vapour unit, the C_{60} was separated from the mixture of fullerenes in a column chromatograph with an eluent of hexane to which 3% toluene had been added. Finally, the C_{60} was cleaned and purified by a vapour transport method to remove solvents and other impurities. Work was done with the C_{60}/C_{70} mixture and with pure C_{60} . Similar results were obtained with both materials.

Samples were prepared in two ways. In the first, a solid pellet of C_{60} or C_{60}/C_{70} was reacted for two days directly with liquid $SbCl_5$ in an h-shaped tube which was placed in a horizontal furnace at 150°C with the liquid and the solid pellet in one arm of the tube. After it was removed from the furnace the arm containing the reaction products was kept at 50°C and the second arm was placed in liquid nitrogen to

distil the $SbCl_5$ into the second arm. In addition a white, crystalline material sublimed on the cooler part of the tube. The direct reaction product in the first arm was an orange–brown solid.

The second method was done at 40–50°C with the $SbCl_5$ dissolved in CCl_4 . This low temperature reaction had the advantage that it was done at a temperature at which $SbCl_5$ does not dissociate appreciably. The product of the reaction with C_{60} was a solid with a brownish colour.

The mass analysis was performed with a double-focusing mass spectrometer (ZAB-E) with a resolution, $m/\Delta m$, of 1000 at the McMaster Regional Centre for Mass Spectrometry. The samples were heated in the source chamber of the spectrometer from 20 to 350°C and were ionized by an electron beam with an energy of 70 eV. The infrared spectrum between 500 and 2500 cm^{-1} was determined with a Fourier transform interferometer.

The mass spectra of pure $SbCl_3$ and $SbCl_5$ are compared in Fig. 1. This is presented for use in the analysis of the reaction products of $SbCl_5$ and C_{60} . The observed ions are produced by the electron bombardment of the parent compounds. There is a small dependence of the relative amount of each ion on the sample temperature and the time in the heating cycle when a spectrum is taken. However, the following is characteristic of the $SbCl_3$ and $SbCl_5$ spectra. For both compounds, the abundance of $SbCl_2^+$ is the largest with those of Sb^+ and $SbCl^+$ 10–12% of it and that of $SbCl_3^+$ 45–50% of it. The $SbCl_4^+$ ion is 20% abundant from $SbCl_5$ and does not exist from $SbCl_3$. This is the main difference between the spectra of the two compounds. $SbCl_5^+$ and Cl_2^+ are not detected from either compound.

*Present address: Department of Physics, University of Science and Technology, Kumasi, Ghana.

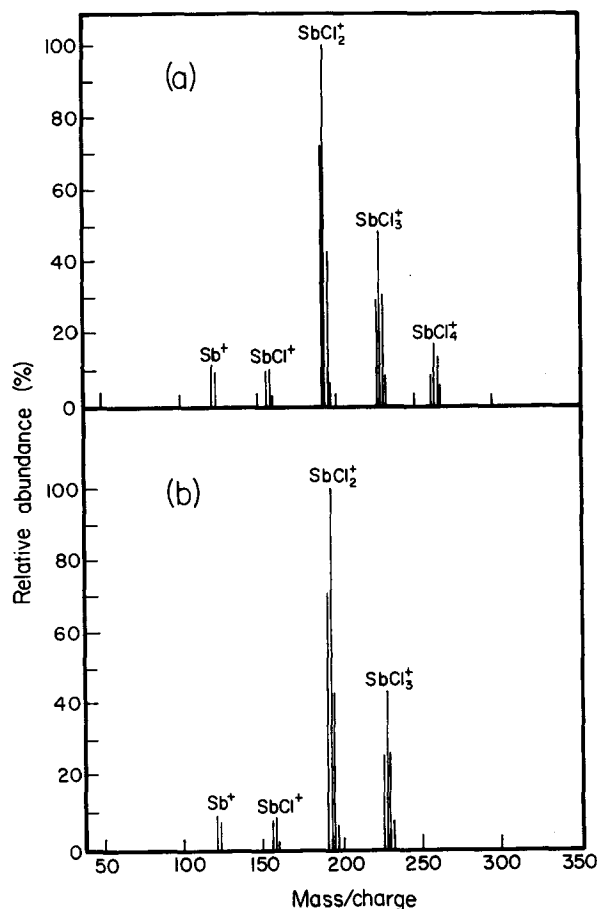


Fig. 1. Mass spectra of ions from (a) $SbCl_5$ (b) $SbCl_3$.

The mass spectrum of the white, crystalline sublimate from the first reaction is the same as that of $SbCl_3$.

The mass spectra from the reaction products of the two methods of preparation are shown in Fig. 2. The spectrum of $SbCl_x$ ($0 < x \leq 3$) ions for a sample produced by the direct reaction of C_{60} with $SbCl_5$ [Fig. 2(a)] is very similar to that for $SbCl_3$: The relative abundance of the ions is similar and there is no $SbCl_4^+$ to identify it with $SbCl_5$. The spectra of $SbCl_x$ ions from the samples made in CCl_4 are also similar to that for $SbCl_3$. The spectrum in Fig. 2(b) for a C_{60} sample reacted with $SbCl_5$ in CCl_4 has the greatest difference with a larger abundance of Sb^+ and $SbCl^+$. However, it is similar to the spectrum of $SbCl_3$ since it has no $SbCl_4^+$ ions.

A significant amount of Cl_2^+ is indicated in the spectra of Fig. 2; 54% in Fig. 2(a) and 38% in Fig. 2(b). A significant amount of Cl_2^+ was detected from all the samples that were analyzed with the mass spectrometer. The abundance relative to that of $SbCl_2^+$ was between 33% and 300%. The largest

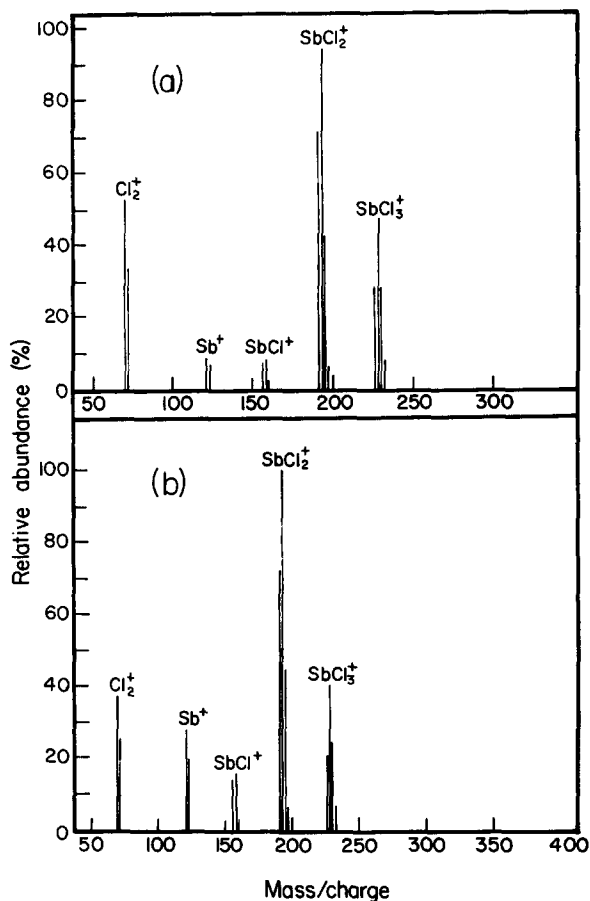
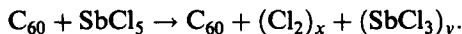


Fig. 2. Mass spectra of ions from C_{60} with $SbCl_5$ reacted in (a) liquid $SbCl_5$ (b) a solution of $SbCl_5$ and CCl_4 .

amount was from C_{60}/C_{70} reacted with $SbCl_5$ in CCl_4 . This indicates that Cl_2 is a constituent of the samples.

The integrity after the reaction with respect to C_{60} or C_{60}/C_{70} is shown in Fig. 3. The sample prepared from pure C_{60} shows only the C_{60} mass spectrum in Fig. 3(a) and that made from a C_{60}/C_{70} mixture has C_{60}^+ and C_{70}^+ ions in Fig. 3(b). There is no evidence of ions of the form $C_{60}Cl_x^+$.

The reaction products of C_{60} and $SbCl_5$ are $SbCl_3$ and Cl_2 . This follows the reaction



The evidence for Cl_2 is clear from the mass spectroscopy analysis. $SbCl_3$ is indicated from the analysis and from $SbCl_3$ obtained from the solution of the reaction. Values of x and y are not derived from the analysis.

The infrared spectrum is given in Fig. 4 to show spectroscopic evidence of the doped species. The lines at 1117cm^{-1} , 1312cm^{-1} and 1615cm^{-1} are attrib-

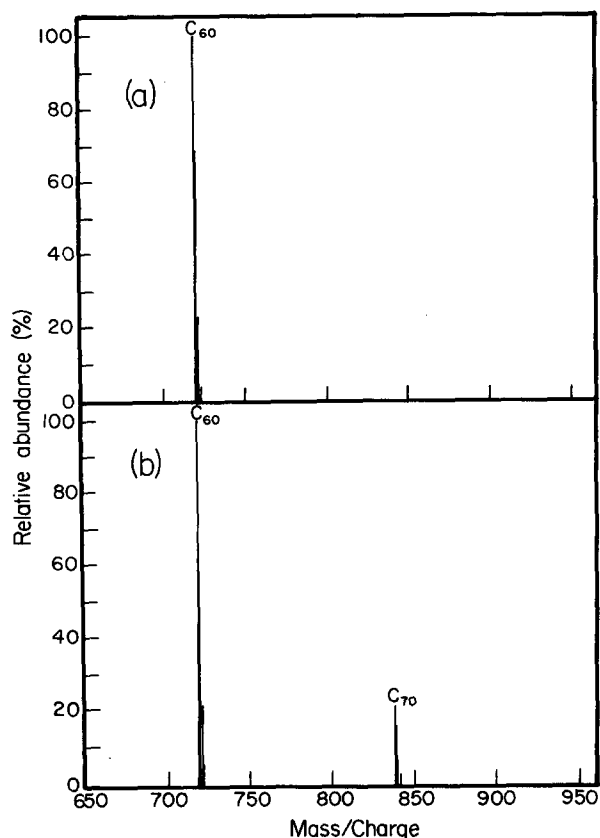


Fig. 3. Mass spectra of (a) C_{60} (b) C_{60}/C_{70} reacted with $SbCl_5$.

uted to C_{60} because they are within 5% of those reported by Tebbe *et al.* [3] for authentic C_{60} . However, the broader width of the lines relative to that of pure C_{60} indicates that there are interactions with C_{60} in the compound. The strong absorption at 880 cm^{-1} in Fig. 4 is attributed to the strong C-Cl

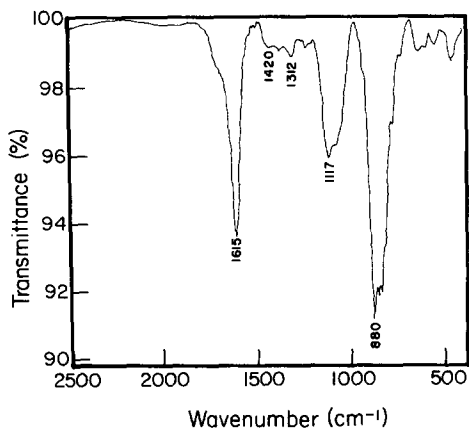


Fig. 4. Far infrared spectrum of C_{60} reacted with $SbCl_5$.

stretching mode which is expected at a frequency of approximately 850 cm^{-1} [3, 4]. The interaction could be with the Cl from the Cl_2 or the $SbCl_3$.

Thus, both the mass spectra and far infrared spectrum indicates that the C_{60} is doped. It is this material that is used for the resistivity measurements.

Material prepared in CCl_4 was pressed into pellets for resistivity measurements. This was done in a dry box to make sure that there was no reaction of the material with air that might increase the surface contact resistance between the grains in the pellet. The resistivity was measured with two current point contacts and two potential point contacts that were applied in the dry box. The sample with the contacts was sealed in a container before it was removed from the dry box for the resistivity measurements. This maintained the integrity of the material. Both directions of current were used to eliminate possible thermal emfs for the measurement at each temperature as the sample warmed after the cryostat had been cooled with liquid nitrogen. The resistivity was $0.08\ \Omega\text{-cm}$ at room temperature. It increased with decreasing temperature and could not be measured below 200 K.

The temperature dependence of the resistance is shown in Fig. 5. It indicates a semiconductor behaviour. A plot of the log of resistance versus reciprocal temperature is linear for temperatures between 200 and 250 K. The slope of the plot corresponds to an energy gap of $(1.1 \pm 0.1)\text{ eV}$.

C_{60} is an insulator at room temperature with an energy gap of 1.8 eV. The $SbCl_3$ and Cl_2 in the compounds can accept electrons if they have an unoccupied energy band in the energy gap. Thermal

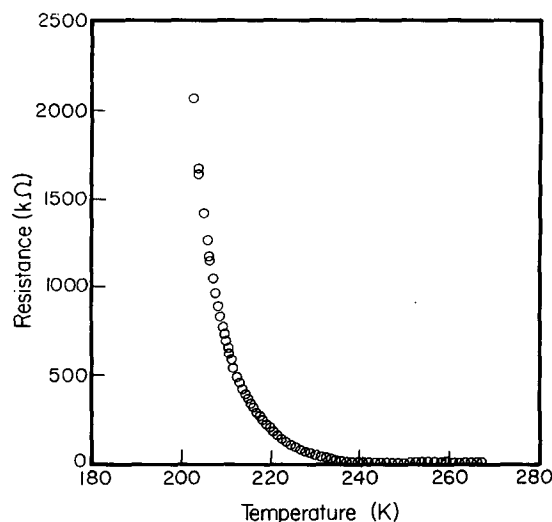


Fig. 5. The resistance of C_{60} reacted with $SbCl_5$ as a function of temperature.

excitation of electrons from the C₆₀ valence band to these energy levels gives carrier conduction in the valence band. The observed energy gap of 1.1 eV is probably between the top of the valence band and an energy level of Cl₂ or SbCl₃.

The chlorination of C₆₀ has been achieved previously in two ways. Tebbe *et al.* [3] reacted C₆₀ with liquid chlorine to form C₆₀Cl_x where x varied from 12 to 15. Olah *et al.* [4] passed Cl₂ gas at a high temperature through C₆₀ to form a dark brown product. Our work shows that there is also chlorination of C₆₀ by the reaction with SbCl₅. After the reduced product, SbCl₃ was removed by sublimation, the compound was dark brown which was the colour of the chlorinated compound. This method of chlorination is done at room temperature in an organic chloro solution such as CH₂Cl₂ or CCl₄.

The present results maybe compared with those of other C₆₀ compounds that have been prepared [5]. The reaction with AsF₅ gives a green compound. It is semiconducting with an energy gap of 0.16 eV. Reaction with SbF₅ produces a dark green compound that is semiconducting with an energy gap of 0.31 eV. Reaction with Cl₂ gives a brown compound that is not electrically conducting at room temperature.

In conclusion, high purity C₆₀ was prepared and

used in the reaction with SbCl₅. The reaction was done by the direct immersion of C₆₀ in SbCl₅ or in a solution of SbCl₅ and CCl₄. The compounds were analyzed with a mass spectrometer and far infrared spectrometry. The observed ions show the presence of C₆₀, SbCl₃ and Cl₂ in the compounds. Resistivity measurements showed that the compound is a semiconductor with an energy gap of 1.1 eV and is conducting at room temperature.

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REFERENCES

1. H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl & R.E. Smalley, *Nature* **318**, 162 (1985).
2. M.S. Dresselhaus & G. Dresselhaus, *Adv. Phys.* **30**, 139 (1981).
3. F.N. Tebbe, J.Y. Becker, D.B. Chase, L.E. Firment, E.R. Holler, B.S. Malone, P.J. Krusic & E. Wasserman, *J. Am. Chem. Soc.* **113**, 9900 (1991).
4. G.A. Olah, I. Bucsi, C. Lambert, R. Aniszfeld, N.J. Trivedi, D.K. Sensharma & G.K. Surya Prakash, *J. Am. Chem. Soc.* **113**, 9385 (1991).
5. W.R. Datars, P.K. Ummat, R.K. Nkum & T.R. Chien (to be published).