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An FT-IR and TGA Study of the Thermal Oxidation of C_{60}

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The thermal stability of C_{60} in pure oxygen has been investigated by in-situ FT-IR and thermogravimetric analysis (TGA). It is shown that at temperatures of about 250 °C, the C_{60} loses its spherically symmetric structure and is oxidized to an anhydride type species. The anhydride on exposure to air is converted to an acid which however reverts to the anhydride on heating in a nitrogen or oxygen atmosphere. On heating beyond 250 °C, the C_{60} is completely oxidized probably to CO and CO_2, but this complete oxidation appears to take place in two stages with the anhydride part of the molecule getting oxidized first. It is postulated that the lower oxidative stability of C_{60} compared to graphite is probably due to the greater reactivity towards oxygen of the pentagon–hexagon junction, compared to the hexagon–hexagon junction, present in C_{60}.

The chemistry of the C_{60} molecule has been the subject of very intense study ever since the large scale production of this compound was reported.1) A novel aspect of this icosahedral molecule is that the chemical bonding requirements on the surface are completely satisfied and therefore, unlike the other forms of carbon, there are no dangling bonds. A graphite like sheet of 60 atoms for instance would have 20 dangling bonds. However, rather surprisingly, it has been shown that although C_{60} is stable at high temperatures of upto 900 °C in an inert atmosphere, it is oxidatively less stable than graphite.2)

The interaction of C_{60} films with solid O_2 on exposure to high and low energy photon sources has been investigated by high resolution photoemission studies3) and its interaction with gaseous oxygen or air at 300 K has been studied by X-ray photoelectron spectroscopy (XPS).4) It has been shown that there is evidence for the formation of oxygenated C_{60} species whereas graphite under similar conditions does not react with oxygen.4) Subsequently, the first fullerene epoxide has been produced5) by the UV-irradiation of C_{60} in benzene saturated with oxygen. More recently the light induced opening of the fullerene C_{60} cage by reaction with singlet oxygen leading to the formation of $C_{60}O_2$ has been reported.6) The thermal stability of C_{60} in an oxygen–argon atmosphere has been studied by emission FT-IR spectroscopy7) and its interaction with pure oxygen has been investigated by differential scanning calorimetry/thermogravimetric analysis (DSC/TGA) studies.8) In both cases, there is evidence that the final decomposition of C_{60} to CO and CO_2 at temperatures of 400 °C and above proceeds through the formation of intermediate carbon–oxygen compounds which are variously speculated to be anhydrides or cyclopentanone type species.

The elucidation of the oxidation pathway of C_{60} is important for understanding its lower oxidative stability compared to graphite and with this aim we have in the present work investigated by in-situ FT-IR and TGA studies the thermal stability of C_{60} in pure oxygen. A comparison with the thermal stability in oxygen of the soot generated for the production of C_{60} has also been made in order to have a better understanding of the oxidation pathway of C_{60}.

Experimental

The C_{60} species was produced by the contact arc vaporization of graphite1) and the soot generated was extracted with hot toluene. From the toluene extract, C_{60} was seperated from the other fullerenes by column chromatography9,10) wherein typically 20 mg of the extracted material was dispersed onto 2 g of silica and loaded onto the top of a column of neutral alumina. The column was then eluted with hexane and 5% toluene in hexane mixture. From the fractions containing pure C_{60}, the product obtained after solvent removal was dried in vacuum at 100 °C for 48 h. The infrared spectra of the isolated C_{60} did not show any of the typical bands due to C_{70} at 674 and 795 cm^{-1} indicating that the sample was not contaminated with C_{70}. For the infrared measurements, a layer of C_{60} was deposited on a KBr disc by evaporation of a solution of C_{60} in toluene and the sample mounted into the transmission probe of the AABSPEC model 2000 multi-mode FT-IR cell. This cell made up of a single block of 316 stainless steel, permits the in-situ heating of samples in a controlled atmosphere and was mounted into the sample compartment of a Nicolet 710 FT-IR spectrometer. The sample was heated under an oxygen flow of 150 ml min^{-1} at the rate of 5 °C min^{-1} and the infrared spectrum was recorded at each specified temperature after maintaining the sample at that temperature for 30 min. The spectrum was also scanned continuously as the temperature of the sample was being raised at the specified heating rate. The spectra of a pellet of plain KBr mounted in the transmission probe of the cell was also recorded at different temperatures under conditions identical to those employed while recording the spectra of C_{60},

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and these spectra were used as the background and were ratioed to the single beam spectra of C_{60} at each particular temperature. Typically 1000 scans using a Mercury Cadmium Telluride (MCT) B detector were coadded for each spectrum.

The TGA experiments were run on a Mettler TG50 model with a TC 11 TA processor, in an atmosphere of pure oxygen at a flow rate of 150 $\mathrm{ml\,min^{-1}}$ and at a heating rate of 5 $\mathrm{°C\,min^{-1}}$.

Results and Discussion

FT-IR Studies. The C_{60} molecule belongs to the I_h point group and because of its highly symmetrical nature, out of the 174 normal vibrational modes, only four modes are allowed as fundamentals. These four characteristic[11] bands at 527, 577, 1183, and 1429 $\mathrm{cm^{-1}}$ are clearly visible in the infrared spectra of the C_{60} sample at room temperature (Fig. 1). The absence of any bands at 674 and 795 $\mathrm{cm^{-1}}$ which are unique for C_{70} confirms that there is no contamination of C_{70} in the sample. On heating to 100 °C and subsequently to 200 °C the four bands due to the C_{60} molecule remain essentially unchanged. At 240 °C, a broad band around 1740 $\mathrm{cm^{-1}}$ first appears but the bands due to C_{60} are also present although with much reduced intensity. On heating to 250 °C however, the characteristic bands due to C_{60} disappear and a strong broad band centred at 1780 $\mathrm{cm^{-1}}$ with shoulders at 1840 and 1745 $\mathrm{cm^{-1}}$ is observed along with relatively weaker broad bands at 1595 and 910 $\mathrm{cm^{-1}}$. These bands remain essentially unaltered at 280 °C but on further heating to 300 °C, there is a drastic reduction in the intensity of the band at 1780 $\mathrm{cm^{-1}}$ along with the virtual disappearence of the band at 910 $\mathrm{cm^{-1}}$ but the 1595 $\mathrm{cm^{-1}}$ band remains essentially unaffected. It is only on heating to 350 °C and above that the 1595 $\mathrm{cm^{-1}}$ band also disappears.

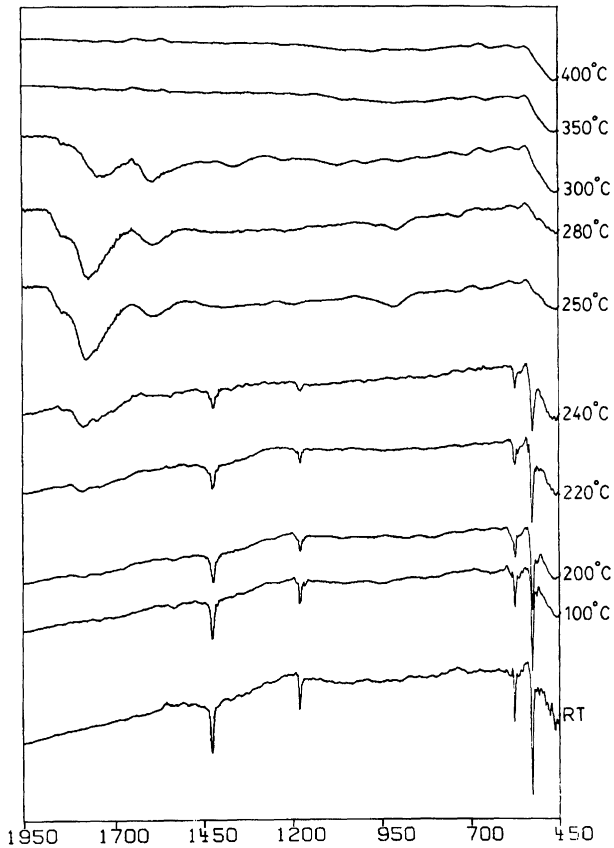

Fig. 1. FT-IR spectra of C_{60} heated in oxygen from room temperature to 400 °C.

The broad band centered at 1780 $\mathrm{cm^{-1}}$ is in the region of the ketone carbonyl absorption of five-membered ring systems and five-membered ring lactones. However, the presence of two bands at 1780 and 1840 $\mathrm{cm^{-1}}$ (which appears as a shoulder on the main band) with a difference of about 60 $\mathrm{cm^{-1}}$ strongly suggests the presence of a cyclic anhydride. Anhydrides are characterized[12,13] by two bands in the carbonyl region due to the symmetric and antisymmetric stretching vibrations, with the lower frequency antisymmetric stretch being more intense in the case of five-membered ring anhydrides. Cyclic six membered ring anhydrides condensed to aromatic systems also show two bands but they occur at lower frequencies and the separation between the bands is smaller (about 35 $\mathrm{cm^{-1}}$). Consequently the bands at 1780 and 1840 $\mathrm{cm^{-1}}$ can probably be assigned to a cyclic anhydride species. A similar suggestion has tentatively been made earlier.[7] The band at 910 $\mathrm{cm^{-1}}$ in contrast to the 1595 $\mathrm{cm^{-1}}$ band would appear to be associated with the anhydride species, since it also disappears on heating to 300 °C, whereas the 1595 $\mathrm{cm^{-1}}$ band remains virtually unaffected. Cyclic anhydrides infact are known[13] to absorb strongly in the 955—895 $\mathrm{cm^{-1}}$ and 1300—1000 $\mathrm{cm^{-1}}$ regions due to the stretching of the C–C–O–C–C bonds. Consequently, the band at 910 $\mathrm{cm^{-1}}$ and the broad weak absorption centered at 1215 $\mathrm{cm^{-1}}$ can also be assigned to a cyclic anhydride species. The 1595 $\mathrm{cm^{-1}}$ band on the other hand can probably be attributed to the stretching mode of a graphitic six-membered ring, since it is known[14] that graphite has an infrared active mode (E_{1u}) involving out of phase intralayer displacement at 1588 $\mathrm{cm^{-1}}$.

The nature of the oxidation product of C_{60} was further investigated by studying its behavior on exposure to different atmospheres. It was observed (Fig. 2) that the oxidized species obtained on heating C_{60} to 250 °C in oxygen with infrared bands at 1840, 1780, 1590, and 910 $\mathrm{cm^{-1}}$, when brought in contact with air, gave a different infrared spectrum with bands at 1710 and 1590 $\mathrm{cm^{-1}}$ and the bands at 1780, 1840, and 910 $\mathrm{cm^{-1}}$ disappeared almost completely. In addition a broad band centered at 3540 $\mathrm{cm^{-1}}$ was observed in the O–H stretching region. The bands at 1710 and 3540 $\mathrm{cm^{-1}}$ can be assigned to the CO and OH of a dicarboxylic acid. (phthalic acid for instance has a single CO band at 1695 $\mathrm{cm^{-1}}$).

The above observations provide further evidence in

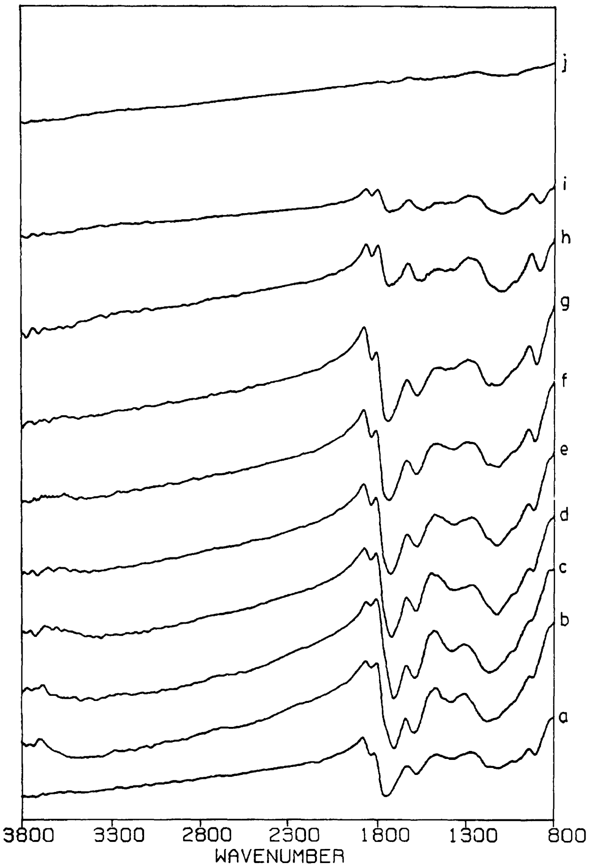

Fig. 2. FT-IR spectra of (a) C_{60} heated in oxygen at 250 °C for 1 h. (b) sample **a** on exposure to air. (c) sample **b** in oxygen atmosphere at room temperature and on heating to (d) 100 °C, (e) 150 °C, (f) 200 °C, (g) 250 °C, (h) 300 °C, (i) 350 °C, and (j) 400 °C.

support of the formation of an anhydride on heating C_{60} in oxygen which on exposure to air is converted to the acid. At the same time, the drastic reduction in the intensity of the 910 cm^{-1} band also along with those at 1840 and 1780 cm^{-1} on exposure of the oxidized C_{60} to air, strongly suggests that the 910 cm^{-1} band is indeed associated with the anhydride species.

On heating the acid species in oxygen to 100 °C, the bands at 910 and 1840 cm^{-1} grow in intensity while the band at 1710 cm^{-1} shifts to higher frequency and on further heating up to 300 °C, the original bands of the anhydride are restored. On heating to 350 °C however, the intensity of the bands is reduced and at 400 °C, the bands disappear completely indicating total oxidation of C_{60}.

The behavior of the oxidation product of C_{60} in a nitrogen atmosphere is similar (Fig. 3). The bands due to the anhydride produced on heating C_{60} to 250 °C in oxygen persist when nitrogen is introduced into the infrared cell instead of oxygen. However, with the introduction of air, the typical bands due to the acid species are observed. Once again, on heating the acid in nitrogen atmosphere to 200 °C the bands due to the anhydride are regenerated.

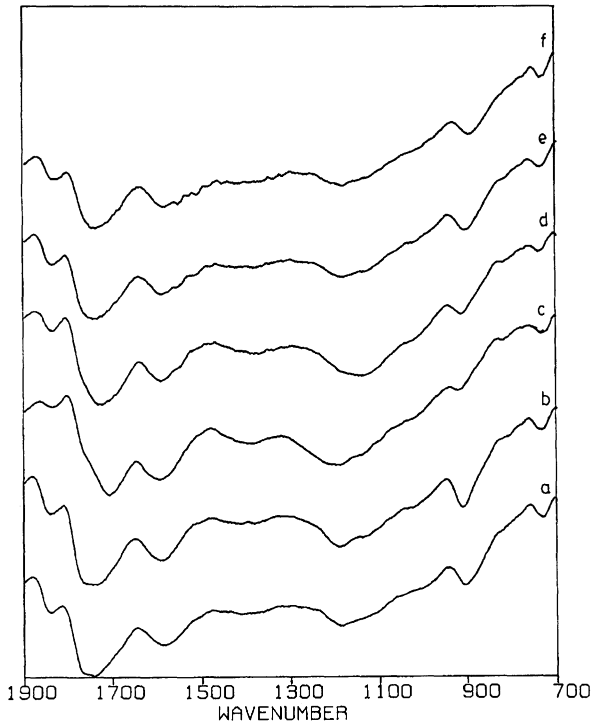

Fig. 3. FT-IR spectra of (a) C_{60} heated in oxygen at 250 °C for 1 h. (b) sample **a** in a nitrogen atmosphere. (c) sample **a** on exposure to air. (d) sample **c** in nitrogen atmosphere at room temperature and on heating to (e) 100 °C and (f) 200 °C.

TGA Studies. The TGA of C_{60} (Fig. 4A) supports the data from the infrared experiment. The weight gain which starts around 250 °C and is maximum at 310 °C corresponds to the formation of the intermediate oxidation product and the weight loss commencing at about 350 °C and reaching a maximum at 455 °C is due to complete oxidation. It is however interesting to note from the derivative thermogram that the total oxidation takes place in two stages which agrees with the observation from the infrared data that the bands at 1840, 1780, and 910 cm^{-1} disappear first whereas the 1595 cm^{-1} band disappears only at higher temperatures. This suggests that initially the anhydride part of the molecule undergoes complete oxidation followed by the residual fragments of the C_{60} molecules. The higher temperatures of partial and complete oxidation observed in the TGA experiments compared to the infrared data is due to the fact that in the infrared experiment the C_{60} was heated at each temperature for 30 min whereas in the TGA experiment the weight change was scanned against a continuous increase in temperature. Infact in the TGA experiment, when the temperature was kept constant at 250 °C for 30 min the weight gain observed was similar to that obtained during the continuously scanned TGA experiment. Similarly complete weight loss corresponding to total oxidation of C_{60} was also observed when the temperature was held constant at 350 °C for 30 min during the TGA experiment.

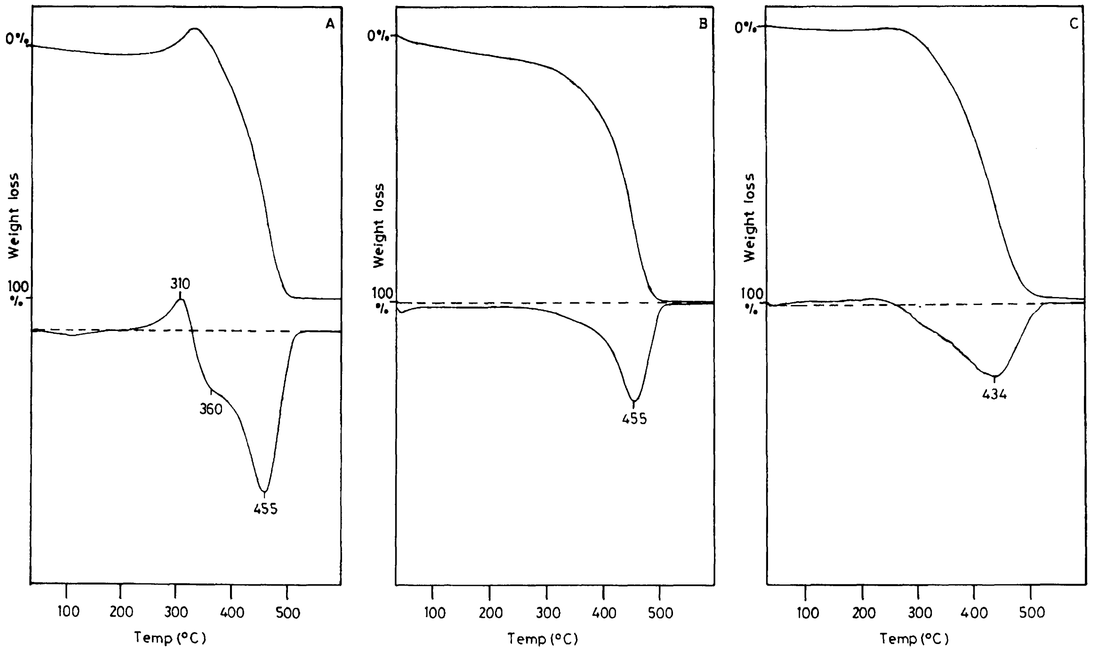

Fig. 4. TGA and first derivative TGA scans in oxygen atmosphere of (a) C_{60}. (b) product obtained on heating C_{60} in oxygen to 250 °C for 1 h followed by exposure to air and (c) residual soot.

The TGA pattern of the acid species produced by heating C_{60} in oxygen at 250 °C for one hour followed by exposure to air is shown in Fig. 4B. In conjunction with the infrared studies, the gradual loss of weight up to 250 °C can be attributed to dehydroxylation to the anhydride. The subsequent total oxidation of this anhydride species takes place at the same temperature at which the total oxidation of C_{60} (Fig. 4A) takes place indicating that the anhydride originally formed on oxidation of C_{60} is indeed regenerated from the acid species.

The TGA pattern (Fig. 4C) of the residual soot, after extraction of C_{60} and higher fullerenes from it with toluene, is quite revealing (a more detailed study of soot will be published elsewhere). It is observed that the complete oxidation of soot takes place at a temperature lower than that of C_{60} and considerably lower than that of graphite (used in the production of C_{60}) whose complete oxidation peak temperature, from the derivative of the TGA scan, was found to be 740 °C under identical experimental conditions.

The C_{60} molecule has two different types of bonds, one at the fusion of two six-membered rings (6–6) and the other at the fusion of a five-membered and a six-membered ring (6–5). The 6–6 bonds are shorter than the 6–5 bonds and have the most double bond character.[15)] Quite understandably therefore all addition reactions of C_{60} including the formation of metal complexes[16)] and the epoxide,[5)] take place at 6–6 bonds. However, in the case of the oxidation of C_{60} in oxygen, the disappearance of all the characteristic C_{60} bands clearly indicate that the spherically symmetric C_{60} structure is opened up and the most likely site for the cleavage of a bond through attack by oxygen would be a 6–5 junction. In this context the observation that the thermal stability in oxygen of soot is comparable with that of C_{60} and much lower than that of graphite is quite relevant. It has been shown[16)] by laser desorption–time of flight (LD–TOF) and fast atom bombardment (FAB) mass spectroscopic studies that the residual soot contains very large fullerenes up to about C_{400}. It is therefore quite surprising that the thermal stability in oxygen of the residual soot is lower than that of C_{60} since the larger the fullerene the more contiguous six-membered rings will be present and the closer its electronic structure will be to that of the more highly aromatic and oxidatively more stable graphite. A very likely reason for this, as in the case of C_{60}, could be the strain induced by the presence of five-membered rings. However, in the perfectly symmetrical C_{60} molecule, this strain can be delocalized over the entire molecule whereas in the higher fullerenes the reduced symmetry would cause the strain energy to be more localized, thus making the 5–6 ring junctions more susceptible to cleavage on oxygen attack. This could account for the lower oxidative stability of residual soot compared to C_{60}.

In essence therefore, the lower oxidative stability of both C_{60} and soot compared to graphite can probably be attributed to the presence of pentagons in their structure. The oxidation of C_{60} can be visualized as involving the attack of molecular oxygen at the junction between a six-membered and a five-membered ring resulting in the opening up of the spherical structure of C_{60}. Infact a very recent report[17)] on the laser desorption mass spectra of $C_{60}O$ obtained by the reaction of C_{60} with O_3 indicates that the oxygen insertion does indeed take place at a 6–5 ring junction.

Conclusions

From the present work, the following conclusions may be drawn:

(1) On heating solid C_{60} in oxygen to a temperature of about 250 °C, the spherically symmetric structure of C_{60} is lost and an anhydride type species is produced. This oxidation product on exposure to air transforms to an acid, but the original anhydride is regenerated on heating the acid species in nitrogen or oxygen atmosphere.

(2) On heating beyond 250 °C the C_{60} is oxidized completely to probably a mixture of CO and CO_2. However, the complete oxidation appears to take place in two stages with the anhydride part of the molecule getting oxidized first.

(3) The lower oxidative stability of C_{60} compared to graphite is probably due to the greater reactivity towards oxygen of the pentagon–hexagon junction present in C_{60} compared to the totally hexagon based structure of graphite.

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