Light-induced Oxygen Incision of C_{60}

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Light-induced opening of the fullerene C_{60} cage due to reaction with excited molecular oxygen ($^1O_2$) generated *via* C_{60} triplet energy transfer with $^3O_2$ has been studied in thin films by differential IR spectroscopy, mass spectroscopy and quantum chemical simulation.

Gram-quantity availability[1] of the highly symmetrical C_{60} cluster[2] is allowing a number of remarkable investigations. Results reported to date include the highest transition temperature for superconductivity of an organic compound,[3] promising nonlinear optical properties[4] and progress in characterization of these molecules.

Here we describe the photochemical degradation of solid C_{60} giving rise to $C_{60}O_2$ and $C_{60}O_4$ through a simple process. In this process, one C=C of the C_{60} framework is severed *via* reaction with electronically excited molecular oxygen, $^1O_2$ ($^1\Delta_g$), which is produced by triplet energy transfer from photogenerated triplet C_{60} and ground-state oxygen triplet $^3O_2$ ($^3\Sigma_g$). The two C=O groups present at both sides of the slit make $C_{60}O_2$ a suitable reactant to make derivatives of C_{60} including possibly the insertion of dopants inside the cage.

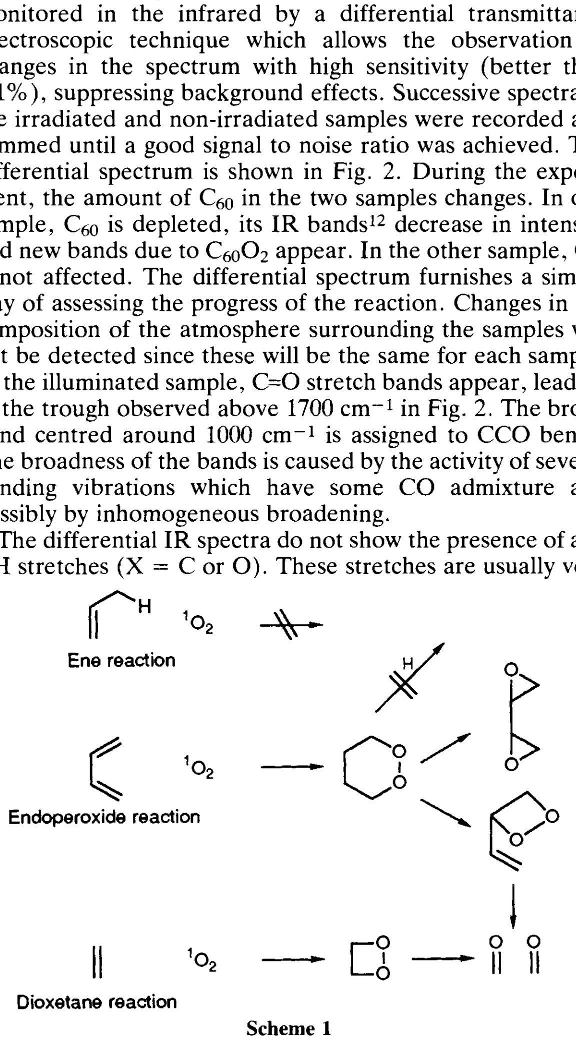
To date, C_{60} has been reported to interact with molecular oxygen in three major ways. $C_{60}O$ is prepared upon UV irradiation in benzene solution saturated with oxygen.[5] If heated, or following high-energy photoexcitation, C_{60} itself reacts chemically with oxygen through an as yet unknown mechanism[6] and eventually forms CO and CO_2.[7] Under milder conditions, electronic excitation of C_{60} in the presence of oxygen produces with unit efficiency molecular oxygen in the highly reactive singlet $^1O_2$ state.[8]

The oxygen formed can react with unsaturated C=C bonds of the type present in C_{60} *via* three mechanisms (see Scheme 1). The ene reaction forms hydroperoxides and requires hydrogen atoms to stabilize the final product.[9] The endoperoxide reaction[10] gives rise to products different from those of the dioxetane reaction[11] in which a four-membered ring is formed. Dioxetanes are usually explosive. They are converted into very stable dicarbonyl compounds upon mild heating.

In the reaction with O_2, C_{60} acts first as a generator of molecular oxygen in the $^1\Delta_g$ singlet electronic state, which then reacts with C_{60} itself. In the final product, one photon and one O_2 molecule cleave a C=C bond to open an entrance in the cage guarded by two carbonyl groups (see Fig. 1).

In our experiment, a C_{60} thin film was evaporated onto two freshly cleaved KBr crystals. The thickness of the films was 0.5 μm. Two identical samples were mounted on a rotating wheel inside a chamber filled with O_2. Only one of the samples was irradiated by Ar^+ laser radiation. The reaction was monitored in the infrared by a differential transmittance spectroscopic technique which allows the observation of changes in the spectrum with high sensitivity (better than 0.1%), suppressing background effects. Successive spectra of the irradiated and non-irradiated samples were recorded and summed until a good signal to noise ratio was achieved. The differential spectrum is shown in Fig. 2. During the experiment, the amount of C_{60} in the two samples changes. In one sample, C_{60} is depleted, its IR bands[12] decrease in intensity and new bands due to $C_{60}O_2$ appear. In the other sample, C_{60} is not affected. The differential spectrum furnishes a simple way of assessing the progress of the reaction. Changes in the composition of the atmosphere surrounding the samples will not be detected since these will be the same for each sample. In the illuminated sample, C=O stretch bands appear, leading to the trough observed above 1700 cm^{-1} in Fig. 2. The broad band centred around 1000 cm^{-1} is assigned to CCO bends. The broadness of the bands is caused by the activity of several bending vibrations which have some CO admixture and possibly by inhomogeneous broadening.

The differential IR spectra do not show the presence of any XH stretches (X = C or O). These stretches are usually very



Scheme 1

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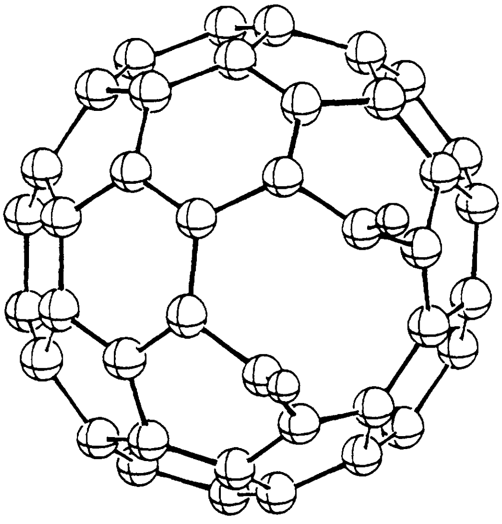

Fig. 1 Incision of the C_{60} cage *via* reaction with $^1O_2$. Only the 47 atoms of the upper part of the molecule are shown to allow a better view of the slit.

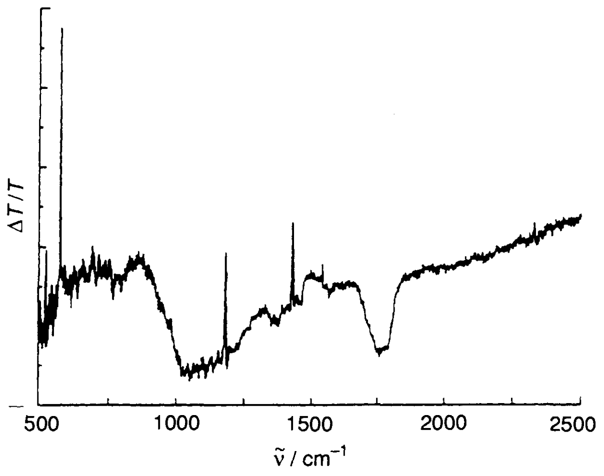

Fig. 2 Differential transmittance spectrum of two samples of C_{60} in O_2 atmosphere. The photoreaction is monitored by following the ratio of the transmittance of the irradiated *versus* the non-irradiated sample. The laser wavelength was $\lambda = 488$ nm, its power density $D = 800$ mW cm^{-2}. The downward features reflect the appearance of $C_{60}O_2$ while the upward bands reflect the depletion of C_{60}.

intense in IR spectra and would be expected to occur about 3000 cm^{-1}. Their absence means that only the dioxetane reaction takes place and that only $C_{60}O_2$ is produced. Notable in the spectra also is the absence of CO and CO_2 stretches which occur[13] above 2000 cm^{-1}, a fact that indicates that reaction is far from completion.

To lend further support to our experiment, we used electron ionization (EI) mass spectometry positively to identify the presence of $C_{60}O_2$ (*m/z* 752). In Fig. 3, we show the mass spectrum obtained at 480 °C; the signal to noise ratio was >30 : 1. Samples obtained from films irradiated for longer times showed the presence of $C_{60}O_4$ (*m/z* 784).

Finally, a quantum-chemical procedure was used to simulate the IR spectrum of $C_{60}O_2$. The same method allowed us to predict with good accuracy the IR bands of C_{60} before they were experimentally available.[14] Subsequent comparison[15] with the experiment yielded a maximum wavenumber difference for IR bands of 30 cm^{-1}. The simulation‡ is carried out in steps. First, we optimize the structure of $C_{60}O_2$. Then we calculate the vibrational frequencies and the normal modes of

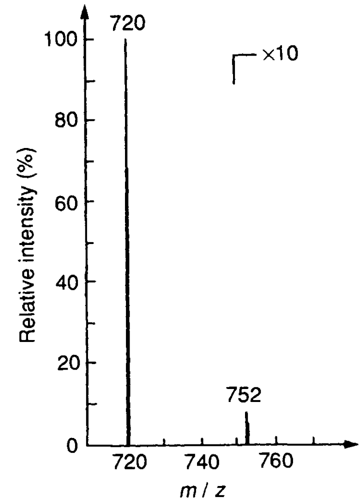

Fig. 3 Electron ionization mass spectrum of C_{60} and $C_{60}O_2$ measured by a VGZAB2F double-focus, reverse-geometry instrument operating at 70 eV, 200 mA, with a source temperature of 200 °C. The sample was introduced by a direct insertion probe and heated to 480 °C.

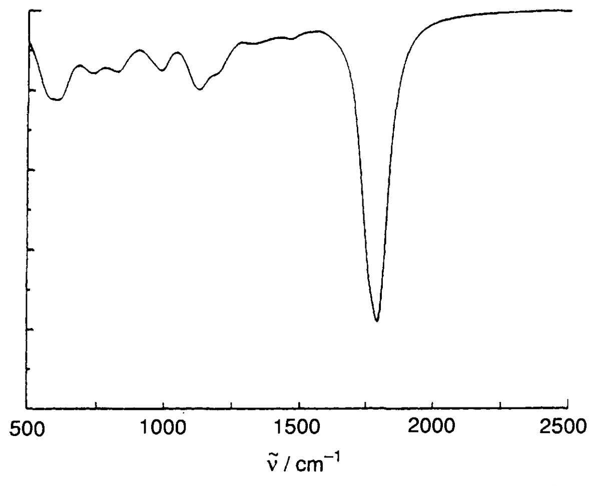

Fig. 4 IR spectrum of $C_{60}O_2$ simulated by the QCFF/PI procedure.[19] The calculated intensities were convoluted with a Lorentzian linewidth of 100 cm^{-1}. The CO stretches are calculated at 1798 and 1752 cm^{-1}.

vibration which are subsequently used to calculate the IR intensities. Fig. 4 shows the calculated IR spectrum of $C_{60}O_2$. Bands due to CO stretches and bends are present, since they have large transition dipole moments and would dominate the IR spectrum. The agreement is good despite the fact that, if the 1000 cm^{-1} band is entirely due to the dicarbonyl $C_{60}O_2$, the CCO bend intensities are somewhat underestimated. We take the good agreement between experiment and theory as further confirmation that we have really detected formation of $C_{60}O_2$. The calculation also allows us to gauge quantities which are not determined experimentally, *e.g.* the size of the slit formed in the cage by the reaction. In the optimized structure shown in Fig. 1, the distance between the previously bound carbon atoms is 2.68 Å. The slit length is 4.12 Å. Similar results were obtained for the other possible isomer of $C_{60}O_2$. We choose to present this isomer because the reaction between $^1O_2$ and unsaturated bonds usually occurs with π-electron-poor systems.[11]

The agreement between highly sensitive photomodulation spectroscopy, quantum chemical calculations and mass spectroscopy makes us confident of the identification of the solid state photoproduct. The success of the photosynthetic route in opening the C_{60} cage is due to the absence of solvent or other molecules that can effectively compete with the dioxetane

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‡ The CO σ bond parameters were set to $b_0 = 1.37$ Å, $D_b = 110$ kcal mol^{-1} and $a = 2.0$ Å^{-1}. These quantities are defined in ref. 17.

reaction.[5] The initial attachment of $^1O_2$ can thus proceed only through the formation of a four-membered ring. This photoreaction together with the fluorination[16], chlorination[17] and bromination[17] reactions of C_{60} is further proof that the O=C bonds of this molecule have much in common with ethylenic bonds as far as reactivity is concerned.

These results are also a warning relevant to the possible applications of unprotected C_{60} thin films in photonic applications.

A few straightforward applications for $C_{60}O_2$ come to mind. The carbonyl groups introduced offer the possibility to exploit the full arsenal of organic chemistry to bind or functionalize the cluster. Reactions with organometallic reagents can change the CO group into CC bonds external to the molecule. The slit in the C_{60} framework could also be used to make small atoms or ions slip into the cage. The incision could then be sealed by reaction with titanium dispersed on potassium-doped graphite[18] restoring the original carbon–carbon double bond.

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