23 October 1998

Chemical Physics Letters 295 (1998) 481–486

CHEMICAL
PHYSICS
LETTERS

Matrix isolation of fullerene-derived CO_2 at ambient temperature

Roger Taylor [a,*], Alain Pénicaud [b], Nicole J. Tower [a]

[a] *The Chemistry Laboratory, CPES School, Sussex University, Brighton BN1 9QJ, UK*
[b] *Centre de Recherche Paul-Pascal, C.N.R.S., Avenue Schweitzer, F-33600 Pessac, France*

Received 29 April 1998; in final form 26 August 1998

Abstract

Heating fullerene oxides, e.g. $C_{120}O$, $C_{70}O$, $C_{60}O$ and $C_{60}O_2$, in a KBr matrix at 225°C under 0.2 mbar vacuum, produces a sharp IR band at 2330 cm^{-1} due to matrix-isolated CO_2. The band is also obtained by heating a KBr matrix of the insoluble deposits that fullerenes form on standing in air. The matrices are extremely stable and are unchanged even by prolonged heating at 225°C under vacuum. Heating a KBr matrix of the deposit from C_{84} produces also a sharp stable band at 2035 cm^{-1} consistent with matrix-isolated C_3. Similar treatment of $C_{70}F_{38}O$ produces matrices containing both CO_2 and CO, the latter being of lower stability. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Various research groups have studied the IR spectrum of matrix-isolated CO_2 at low temperature ($\sim$ 10 K) in either hydrogen or rare gas matrices [1–4]. Multiplicity of peaks are seen due to occupancies of different matrix sites, various dimer orientations, and the presence of variable-size clusters, indicated by alteration in the relative band intensities upon annealing. The gas-phase IR spectrum of carbon dioxide shows antisymmetrical stretching fundamentals (ν_3) at 2360 cm^{-1} (P-branch) and 2342 cm^{-1} (R-branch) (shoulders on the latter are due to the ^{13}C isotope), together with the symmetrical bending fundamental (ν_2) centred at 670 cm^{-1} (inset to Fig. 1 shows the normal gas-phase spectrum). For CO_2 deposited on NaCl at -160°C, ν_3 appeared as a single band of $\sim$ 10 cm^{-1} half-height width at 2340 cm^{-1}, the shift to lower frequency compared to the gas phase being attributed to interactions with the salt surface [5].

2. Experimental and discussion

The IR spectra were obtained on a Perkin-Elmer 1710 FTIR spectrometer at 2 cm^{-1} resolution; the spectra show the usual wavenumber scale change at 2000 cm^{-1}.

2.1. Matrix isolation of CO_2

During measurement of the IR spectrum of pure $C_{120}O$ [6], we observed that on heating a KBr disc (formed in a standard 10 ton press) under 0.2 mbar vacuum (to eliminate moisture traces), a sharp band ($\sim$ 13 cm^{-1} half-height width) appeared in the spectrum at 2330 cm^{-1} (Fig. 1). To confirm that this was

---

[*] Corresponding author. Fax: +44-1273-677-196.

PII: S0009-2614(98)00979-8

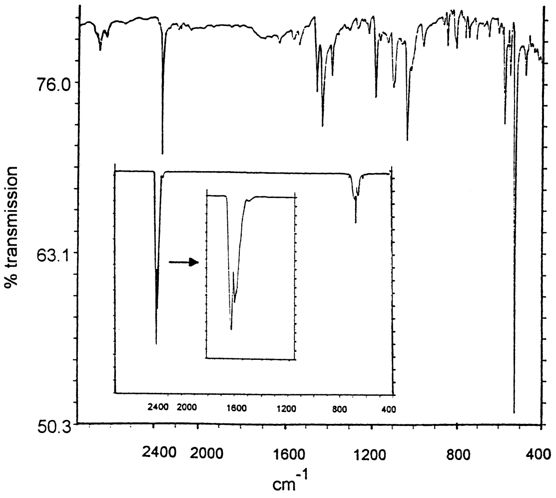

Fig. 1. IR spectrum (KBr disc) of $C_{120}O$, after heating at 225°C for 2 h; inset shows IR spectrum of CO_2 in air.

a trapped gas, the sample was dissolved in water (to remove the KBr) and then 1,2-dichlorobenzene (to allow the gas to fully escape), and after removal of the solvent, a fresh KBr disc was prepared. The band at 2330 cm^{-1} was now absent, but could be regenerated (with lower intensity) by further strong heating of the new disc.

Further experiments have been carried out with HPLC purified $C_{60}O$ and $C_{60}O_2$. Neither of these compounds shows any band in the CO_2 region, but on heating either of them (225°C for 2 h), an intense band again appears at 2330 cm^{-1}. Higher oxides of [60]fullerene, and $C_{70}O$ behave in the same way. In each spectrum, ν_2 appears as a single band at 653 ± 1 cm^{-1}. Fig. 2 shows the results of heating $C_{60}O$ at various times/temperatures and the development of the main CO_2 band [which shows evidence of being comprised of a mixture of molecules which are matrix isolated (sharp band at 2330 cm^{-1}) and some which are able to rotate freely (shoulder at ~ 2360 cm^{-1})]. The shoulder was obtained only from the oxides which generate such large numbers of CO_2 molecules that failure to isolate all of them is not unexpected. The evolution of CO_2 from $C_{60}O$ was also monitored and confirmed by EI mass spectrometry of the heated (matrix-free) solid. Fig. 3 shows the plot of the intensities of the total ion current and the 44 amu peak with increasing probe temperature. So great was the CO_2 generation that the mass spectrometer shut down temporarily due to ion current overload.

The loss of CO_2 (rather than CO) from the oxides is unexpected and indicates that a bimolecular reaction must be involved. This predicts (Eq. (1)) that pure $C_{60}O$ should produce C_{119} (1429 amu) on heating, and this was confirmed by EI mass spectrometry.

$$2\,C_{60}O \rightarrow CO_2 + C_{119}\,. \qquad (1)$$

C_{119} has been produced previously from the reaction of $C_{60}O$ with C_{60}, the mechanism being assumed to involve loss of CO from the epoxide to give a carbene which then either adds across a 6:6-bond [7,8], or inserts (mainly) into a 6:5-bond [8]; subsequent bond formation produces two isomers of C_{119} one of which has been characterised

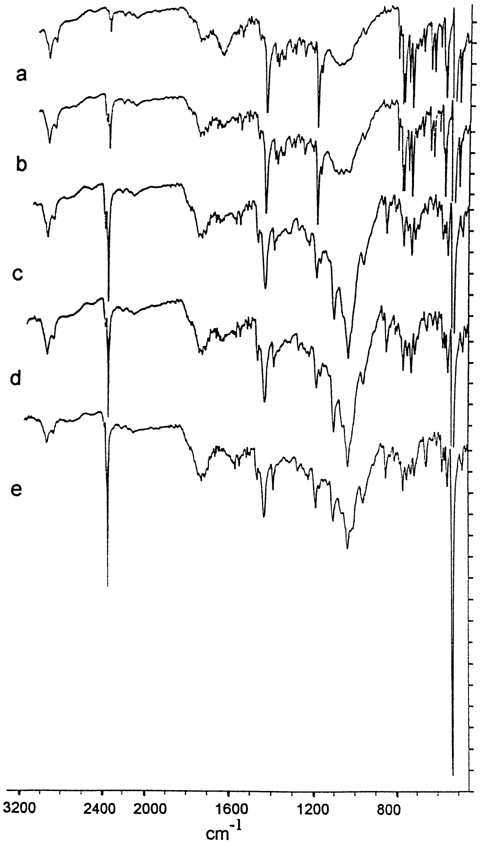

Fig. 2. IR spectra (KBr disc) of $C_{60}O$: (a) unheated; (b)–(e), heated for 30 min at 100, 150, 200 and 250°C, respectively.

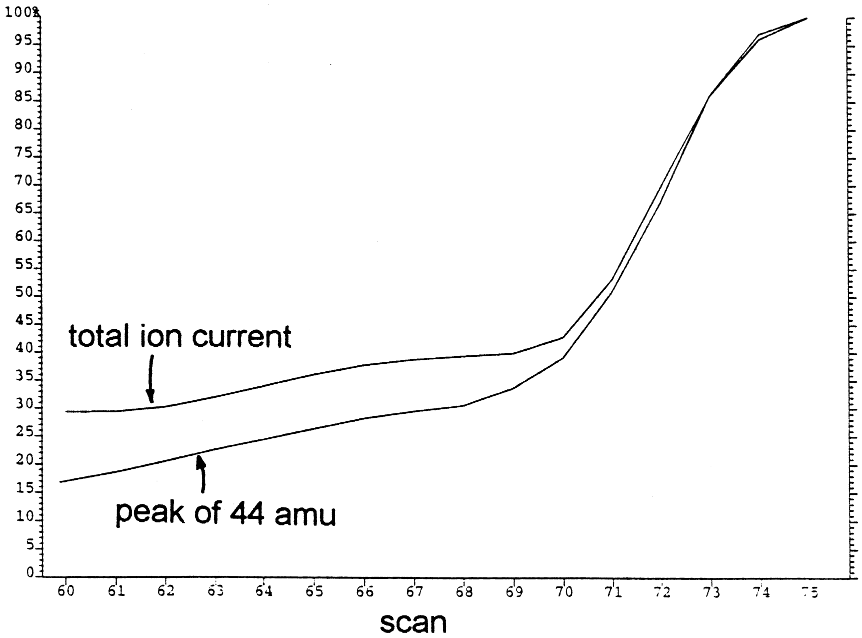

Fig. 3. Plot of intensities (EI mass spectrometry) of the total ion current and of the 44 amu peak on heating a sample of $C_{60}O$ (without matrix).

[9], the structure agreeing with prediction [10]. The present Letter indicates that a second mechanism of C_{119} formation exists that does not require the presence of C_{60} itself.

The sharp single lines in the spectra arise from restriction of the molecular motions of the matrix-trapped molecules, which could be expected to be greater than in the material deposited on a NaCl surface, and consequently ν_2 appears at a lower frequency. This shift is not due to the different matrix material since if NaCl is used instead of KBr, the CO_2 band again appears at 2330 cm^{-1}. The amazing effectiveness of the KBr matrix as a trap for fullerene-produced CO_2 is shown by the spectra being completely unchanged after 10 months storage of the KBr discs at room temperature. They are also completely unchanged by heating the discs at 225°C for 26 h.

Fullerenes (especially the higher ones) produce insoluble material on storage. Most notable in this respect is the C_{2v}(II) isomer of C_{78}. Within 6 weeks of HPLC purification, ~30% of the material was totally insoluble in all solvents. After a further 14 weeks, none of it would dissolve, and we find that other higher fullerenes (e.g., C_{84}) behave similarly, though with lower degradation rates (e.g., 70% in 4 years for C_{84}). Our provisional conjecture [11] that the insoluble material might be due to graphitisation was disproved in two ways: (1) no graphitic planes could be detected by X-ray powder diffraction; and (2) on heating of a KBr disc as described, it produced the intense sharp band at 2330 cm^{-1} (Fig. 4a) showing that it is an oxidised material. The insoluble degradation products of the other higher fullerenes all give the same band. Heating a KBr matrix of graphite does not produce the CO_2 band, nor does one of single wall nanotubes that had been hydrothermally purified from amorphous material.

It should be noted that C_{60} (a pure sample stored for 7 years) also produces the CO_2 band on heating as described, albeit of lower intensity (freshly purified material does not). Though we reported previously that allowing thin films of C_{60} to stand in air for a few days, caused them to become harder to redissolve (the resultant solutions having a pinkish hue) [12], and also that solutions of C_{60} in benzene, stored in light for ~2 years become either partly or completely (there is a sample dependence) converted

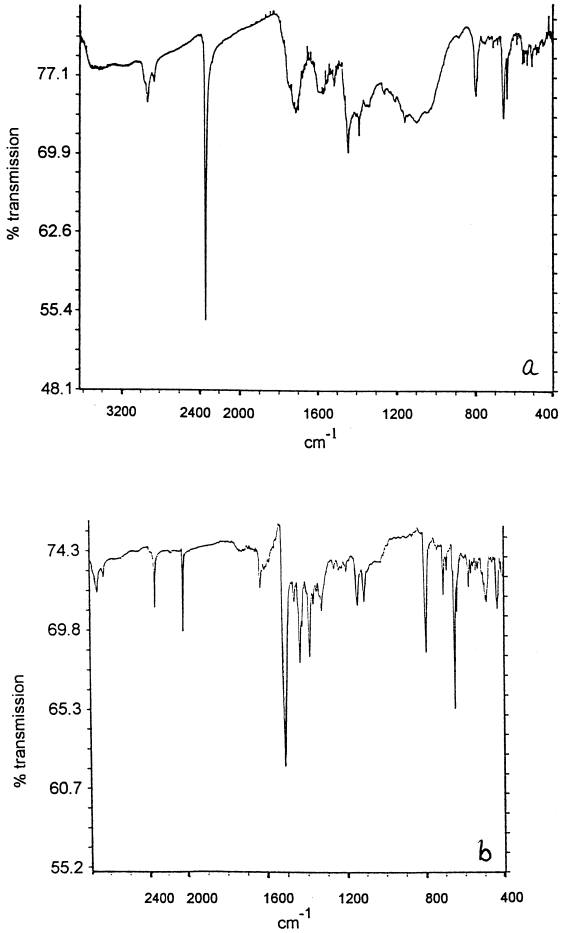

Fig. 4. (a) IR spectrum (KBr disc) of degraded C_{2v}(II)-C_{78} after heating at 225°C for 2 h. (b) IR spectrum (KBr disc) of degraded C_{84} after heating at 225°C for 2 h.

to water-soluble derivatives [11], these previous observations concerned highly dispersed material.

2.2. Evidence for matrix isolation of C_3

Our results have an even more remarkable aspect indicated in the spectrum of heated 'insoluble' C_{84} (Fig. 4b). This shows not only the CO_2 band (at 2327 cm^{-1} in this case) but also a second sharp band at 2035 cm^{-1} and this is unchanged after 10 months storage. This was also reproduced from samples of different origin, and from one sample of $C_{60}O_2$; like the CO_2 band, it is removed by dissolving the disc and reforming, indicating that it is produced by a gas. Given the starting materials, it appears that the only species that could give this band in this IR region is C_3 (see below) due to cage fragmentation, and although this (CO_2-isostructural dicarbene) should be reactive, the extraordinary effectiveness of the KBr matrix as a trap may prevent it from undergoing further reaction. Since the yield of [84]fullerene from graphite is only ~ 0.03%, confirmation of the identity of this band through isotopic enrichment is precluded at present by financial considerations.

There have been numerous studies of the IR spectra of matrix-isolated carbon species (C_2–C_9) in inert gases, at ~ 4–10 K, during recent years (leading references are to be found in Ref. [13]). C_3 has been of particular interest because it is the major species present in carbon vapour [14], and nature of the coalescence products on annealing have been given particular attention, e.g. Ref. [15]. In the gas phase C_3 gives a sharp ν_3 band at 2040 cm^{-1}, and this becomes 2039 and 2035 cm^{-1} in Ar and Kr matrices, respectively [16]. The band we observe cannot be attributed to bonding of CO to the cage (values in this region are obtained for some σ-bonded inorganic complexes) because it is absent in a [60]fullerene matrix-isolated spectrum of CO (introduced under ~ 10 kbar pressure) [17].

2.3. Matrix isolation of CO

We are also able to produce a matrix-isolated spectrum of CO by heating a KBr disc of pure $C_{70}F_{38}O$ [18]. Meier and co-workers have described a fullerene matrix-isolated spectrum of CO which consists at 298 K of a broad band at 2120 cm^{-1} [17]. We obtain a broad CO band at 2108, 2107, 2105 and 2104 cm^{-1} after the following respective heating regimes: 3 h at 100°C, then 2 h at 150°C, 1 h at 200°C, and a further 1.5 h at 200°C. $C_{70}F_{38}O$ is also extremely effective at producing the CO_2 band, at 2340, 2338, 2336 and 2335 cm^{-1} (with increasing intensities) after the above heating/times; ν_2 here appears at 659 cm^{-1}; none of these bands are present in the pure material. The frequency shifts are attributable to the loss of fluorine from the fullerene precursor in the matrix on heating. The CO-containing matrix does not have the same stability of the

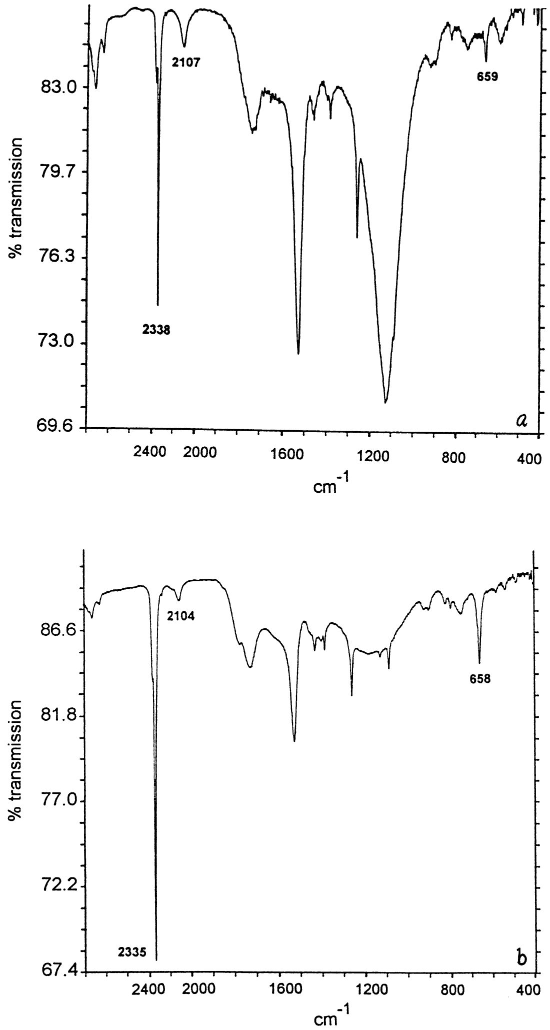

Fig. 5. (a) IR spectrum (KBr disc) of $C_{70}F_{38}O$ after heating for a total of 3 h at 100°C followed by 1.5 h at 150°C. (b) The KBr disc from Fig. 4b, heated for a further 2.5 h at 200°C.

CO_2-containing matrix (the difference being attributed to the smaller molecular size) and the CO band is eventually lost on heating under vacuum at 225°C. Fig. 5a shows the spectrum after heating for 3 h at 100°C followed by 2 h at 150°C, and Fig. 5b shows the same sample after further heating for a total of 2.5 h at 200°C. The development in intensities of the ν_2 and ν_3 bands for CO_2 is accompanied by a shift to lower wavenumbers as the fluorine (C–F stretch at 1125 cm^{-1}) is lost. In Fig. 5b the band for CO has decreased in intensity relative to that in Fig. 5a, because of the lower stability of the CO/KBr matrix and the extended heating.

2.4. The nature of the matrix

The similarity of the band positions when using either KBr or NaCl appears to indicate that the matrix is simply the fullerene embedded in the salt. This would seem to be supported by the slightly different band positions obtained with different fullerene precursors. However, this is a simplification, because as described above, heating the solids in the absence of the salt results in release of CO_2 gas. Moreover, heating to 225°C a KBr matrix of 2,4-dihydroxybenzoic acid (well known to produce CO_2 on heating) also gives an intense stable CO_2 band, centred at 2337 cm^{-1}. However, this is 2–3 times broader than the bands obtained from fullerene precursors (and has a major shoulder at 2360 cm^{-1}), indicating that a significant proportion of the CO_2 is able to rotate here. Overall, it seems that it is the combination of the fullerene and salt (compounded by the pressure involved in forming the matrix) which gives rise to the spectra we observe.

Further investigations on the matrix isolation of other fullerene-derived species is in hand.

Acknowledgements

We thank Dr. T. Drewello and Mr. M. Barrow (Warwick University) for the MALDI-TOF mass spectra of $C_{60}O$ and $C_{60}O_2$, and Mr. R. Loutfy (MER) for the sample of nanotubes.

References

[1] E. Knoezinger, P. Beichert, J. Phys. Chem. 99 (1995) 4906.
[2] M. Falk, J. Chem. Phys. 86 (1987) 560.
[3] M.J. Irvine, J.G. Mathieson, A. David, E. Pullin, Aust. J. Chem. 35 (1982) 1971.
[4] M.J. Irvine, A. David, E. Pullin, Aust. J. Chem. 35 (1982) 1961.
[5] J. Heidberg, S. Zehme, C.F. Chen, H. Hartmann, Ber. Bunsenges. Phys. Chem. 75 (1971) 1009.
[6] S. Lebedkin, S. Ballenweg, J. Gross, R. Taylor, W. Krätschmer, Tetrahedron Lett. 36 (1995) 4971.

[7] R. Taylor, J. Chem. Soc., Chem. Commun. (1994) 1629.
[8] E. Albertazzi, F. Zerbetto, J. Am. Chem. Soc. 118 (1996) 2734.
[9] A. Gromov, S. Ballenweg, S. Geisa, S. Lebedkin, W.E. Hull, W. Krätschmer, Chem. Phys. Lett. 267 (1997) 460.
[10] G.B. Adams, J.B. Page, M. O'Keefe, O. Sankey, Chem. Phys. Lett. 228 (1994) 485.
[11] R. Taylor, in: H. Kuzmany (Ed.), Molecular Nanostructures (Proc. Int. Winterschool on Electronic Properties of Novel Materials), World Scientific, Singapore, 1998, p. 136.
[12] R. Taylor, Interdiscip. Sci. Rev. 17 (1992) 161.
[13] S. Tam, M. Macier, M.E. Fajardo, J. Chem. Phys. 106 (1997) 8955.
[14] W. Weltner, P.N. Walsh, C.L. Angell, J. Chem. Phys. 40 (1964) 1299.
[15] J. Sczcepanski, M. Vala, J. Phys. Chem. 95 (1991) 2792.
[16] J. Sczcepanski, M. Vala, J. Chem. Phys. 99 (1993) 7371.
[17] I. Holleman, G. von Helden, E.H.T. Olthof, P.J.M. van Bentum, R. Engeln, G.H. Nachtegaal, A.P.M. Kentgens, B.H. Meier, A. van der Avoird, G.J.N. Meijer, Phys. Rev. Lett. 79 (1997) 1138.
[18] O.V. Boltalina, J.M. Street, R. Taylor (to be published).