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ADDITION OF AMINES AND HALOGENS TO FULLERENES C_{60} AND C_{70}

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Abstract: In solution phase, aliphatic amines add on to fullerenes; vapourization of graphite in presence of methylamine gives nitrogeneous C_{60} derivatives. Reactions of C_{60} with $SbCl_5$ and liquid Br_2 yield halogen adducts.

Since the availability of a method to prepare C_{60} and C_{70} in macroscopic quantities[1], there has been intense interest in exploring the reactions of these fullerenes. C_{60} has been hydrogenated[2], methylated[3] and fluorinated[4]. We have been interested in examining addition reactions of C_{60} and C_{70} especially with nucleophiles such as aliphatic amines. We present some of the results along with those on the addition of halogens.

Reaction of C_{60} with excess methylamine in toluene solution at 298K is nearly instantaneous, giving a yellow product containing a mixture of adducts. The mass spectrum of the product shows that upto 14 amine units add to C_{60}. The UV-visible spectrum of the product is distinct from that of C_{60}, showing bands only below 325 nm. Of the different adducts, those corresponding to the addition of 1, 2 and 6 amine units are prominent as seen from the molecular ion and fragmentation features in the mass spectra. Addition of a secondary amine such as dimethylamine to C_{60} under similar conditions also gives a yellow product mainly containing adducts corresponding to the addition of 1, 2 and 6 amines units. The IR spectrum of the methylamine addition product shows the N-H stretching band at 3390 cm^{-1}, absent in the spectrum of the product of dimethylamine addition[5]. The product containing the mixture of adducts of CH_3NH_2 gave three bands in TLC which gave the following analysis from mass spectra: band 1, R_F = 0.61, $n \leq 6$ (n = number of CH_3NH_2 units added); 2, R_F = 0.73, n = 6-8 and 3, R_F = 0.94, n = 10-18. A unique feature of the amine adducts is that they exhibit fluorescence (λ_{max} 326 nm, excitation λ_{max} 290 nm) in methanol solution unlike C_{60}.

We have obtained an essentially pure 1:1 amine adduct[6] by refluxing C_{60} with n-butylamine (1:2 molar ratio) in toluene solution for 30 hrs. We are able to study second harmonic generation with such a mono-adduct and explore the possibility of synthesizing polymers containing C_{60}. C_{70} also undergoes the addition reaction with amines; with excess methylamine, adducts with 1, 2 and 6 amine units are prominent.

Contact vapourization of graphite in an atmosphere of He + CH_3NH_2 gives a yellow product with a mass spectrum similar to that obtained with NH_3 which can be interpreted as due to the addition of (N_a) and substitution by (N_s) nitrogen atoms. Main peaks found at m/z 764, 728 and 724 are due to $C_{59}N_6$ with $5N_a + 1N_s$ (or $C_{52}N_{10}$ with $2N_a + 8N_s$), $C_{56}N_4$ ($4N_s$) and $C_{58}N_2$ ($2N_s$) respectively.

Reaction of C_{60} with excess $SbCl_5$ in CCl_4 solution gave a brown precipitate, due to the chlorine adduct. The adduct shows a C-Cl stretching band in the IR spectrum around 812 cm^{-1} and a UV absorption maximum at 250 nm. C_{60} reacts with liquid bromine to give an orange product containing the dibromo-adduct[7] (C-Br stretching, 515-575 cm^{-1}; UV λ_{max} 282 and 330 nm). Reaction of C_{60} with I_2 vapour in a sealed tube at temperatures upto 530K yielded no product.

References

1. Kratschmer, W.; Lamb, L.D.; Fostiropoulos, K.; Huffman, D.R. *Nature*, 1990, *347*, 354

2. Haufler, R.E.; Conceicao, J.; Chibante, L.P.F.; Chai, Y.; Byrne, N.E.; Flanagan, S.; Haley, M.M.; O'Brien, S.C.; Pan, C.; Xiao, Z.; Billups, R.F.; Smalley, R.E. *J. Phys. Chem.* 1990, *94*, 8634

3. Bausch, J.W.; Prakash, G.K.S.; Olah, G.A.; Tse, D.S.; Lorents, D.C.; Bae, Y.K.; Malhotra, R. *J. Am. Chem. Soc*, 1991, *113*, 3205

4. Selig, H.; Lifshitz, C.; Peres, T.; Fischer, J.E.; McGhie, A.R.; Romanow, J.W.; McCauley, J.P., Jr.; Smith, A.B., III. *J. Am. Chem. Soc.*, 1991, *113*, 5475; Holloway, J.H.; Hope, E.G.; Taylor, R.; Langley, G.J.; Aven, A.G.; Dennis, T.J.; Hare, J.P.; Kroto, H.W.; Walton, D.R.M. *J. Chem. Soc. Chem. Commun.*, 1991, 966

5. Bands due to the stretching and deformation modes of the CH_3 groups were found in the spectra of both the adducts

6. The IR spectrum, besides bands due to C_{60} shows those due to CH_2 and CH_3. UV-visible spectrum shows peaks at 328, 286, 271, 265, 257 nm in THF solution. Fluorescence maximum is at 394 nm (excitation λ_{max} 330 nm)

7. Since completing this work, we have noticed a paper reporting the bromine adduct by G.A. Olah and coworkers (*J. Am. Chem. Soc.* 1991, *113*, 9385)

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