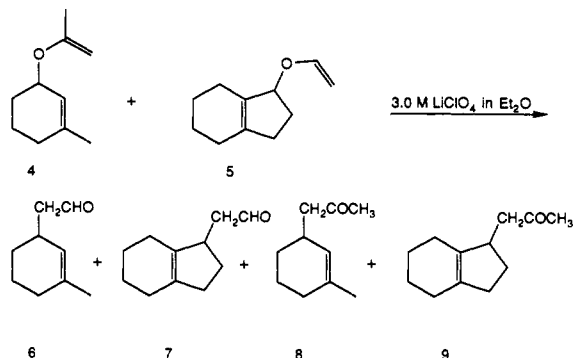
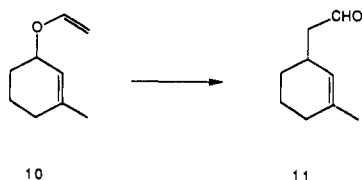


The data in Table I as well as the data for allyl vinyl ether **1** suggest that the [1,3] rearrangement products observed may arise via dissociated ions followed by recombination. Note that the vinyl ether derived from verbenol (entry **5**) gives rise to the [1,3]-rearranged product with exclusive inversion of configuration at the allylic carbon atom, suggesting that the [1,3] rearrangement is concerted. However, the formation of the observed product can also be rationalized via dissociated ions followed by recombination from the least hindered face of the molecule. In order to determine to what extent allyl vinyl ethers ionize in the presence of 3.0 M lithium perchlorate–diethyl ether, a crossover experiment was carried out employing allyl vinyl ethers **4** and **5**, each 0.1 M in 3.0 M lithium perchlorate–diethyl ether. After 1.5 h at ambient temperature, there was obtained, in excellent yield, a mixture of aldehydes **6** and **7** and ketones **8** and **9** in a ratio of 1.0:1.8:1.5:1.6, suggesting that dissociated ions are involved.



The data reported above for substrate **1** imply that the reaction rate for the [1,3] rearrangement is dependent upon the concentration of lithium ion. In order to probe this point further, allyl vinyl ether **10** was exposed to lithium perchlorate in acetone.<sup>6</sup> The rearrangement of a 0.2 M solution of **10** in 1.8 M LiClO<sub>4</sub>–acetone gave rise to a rate constant of  $8.31 \times 10^{-5} \text{ s}^{-1}$  as compared to a rate constant of  $2.05 \times 10^{-5} \text{ s}^{-1}$  in 1.0 M LiClO<sub>4</sub>–acetone. In contrast, exposure of **10** to 1.8 M tetra-*n*-butylammonium perchlorate in acetone did not give rise after 1 week to any [1,3] or [3,3] rearrangement. In 5.0 M LiClO<sub>4</sub>–acetone the rearrangement of **10** was so fast that only a lower limit for the reaction rate (ca.  $2.46 \times 10^{-2} \text{ s}^{-1}$ ) could be established. The rate accelerations observed for the [1,3] rearrangements in lithium perchlorate–acetone are in keeping with lithium ion catalysis; however, additional factors may be operational in order to account, in the case of **10**, for the greater than 1000-fold increase in reaction rate observed in going from 1.0 M to 5.0 M LiClO<sub>4</sub>–acetone.



We anticipate that the mildness and efficiency of promoting [1,3] rearrangements of allyl vinyl ethers in lithium perchlorate–diethyl ether will find considerable use in organic chemistry.

**Acknowledgment.** Generous financial support from the National Science Foundation is greatly appreciated. We thank Professor Joseph J. Gajewski for numerous helpful discussions.

(6) Acetone was employed as the solvent because in diethyl ether the reaction rates for the [1,3] rearrangement were too fast to be measured by <sup>1</sup>H NMR. In addition, tetra-*n*-butylammonium perchlorate is insoluble in ether. Reactions were carried out 0.2 M in substrate in sealed NMR tubes at 22 °C. Note that the reaction of **10** in 3.0 M LiClO<sub>4</sub>–Et<sub>2</sub>O gave rise after 1 h to an 86% isolated yield of aldehyde **11**.

## Gas-Phase Reactivity of Fullerene Anions

L. S. Sunderlin,\* Jose A. Paulino, Jason Chow, Bart Kahr, Dor Ben-Amotz, and Robert R. Squires\*

Department of Chemistry, Purdue University  
West Lafayette, Indiana 47907

Received March 18, 1991

Fullerenes have attracted considerable interest since 1985, when Kroto, Smalley, and co-workers first deduced their existence.<sup>1</sup> This interest has grown dramatically<sup>2</sup> since the recent report of a convenient synthesis of macroscopic quantities of C<sub>60</sub> and C<sub>70</sub>.<sup>3</sup> Very little has been published on the gas-phase reactions of fullerenes, primarily because they are exceptionally unreactive. C<sub>60</sub> and C<sub>70</sub> are unreactive with NO, CO, SO<sub>2</sub>, and NH<sub>3</sub> and react only slowly with H<sub>2</sub> and O<sub>2</sub> at partial pressures up to 120 Torr in a laser vaporization plasma.<sup>4</sup> C<sub>2n</sub><sup>+5,6</sup> and C<sub>2n</sub><sup>-7</sup> clusters (*n* > 10) have been found to be generally unreactive. This work examines the chemistry of the fullerene anions C<sub>60</sub><sup>-</sup> and C<sub>70</sub><sup>-</sup> ("fullerides") with various neutral molecules under thermal conditions in a flow reactor and gives the first examples of gas-phase reactions of fullerides, most significantly the formation of adducts with NO<sub>2</sub>.

All experiments were performed at 298 K in a flowing after-glow–triple quadrupole apparatus.<sup>8</sup> The fullerenes are synthesized by using an arcing method described previously,<sup>3</sup> extracted with refluxing benzene, and washed with diethyl ether to give a mixture of primarily C<sub>60</sub> (≈90%) and C<sub>70</sub> (≈10%). Small amounts of other carbon clusters are also seen. A solution containing ca. 1 mg of C<sub>60</sub> and C<sub>70</sub> in toluene or hexanes is applied to all exposed surfaces of an electron-impact (EI) ionization source at the upstream end of the flow tube and allowed to dry. The fullerenes sublime when the electron-emission filament is heated during operation. The electron energy is set at 20 V to minimize ionization of other species present and decomposition of the fullerenes. Electron attachment to gas-phase fullerenes or dissociative attachment to adsorbed material on the collection grid of the EI source produces the fullerides. The anions are entrained in a flow of helium or argon in the tube (*P* = 0.4 Torr) and thermalized by ca. 10<sup>5</sup> collisions with the bath gas. Ions in the flow tube are gently extracted into a region of differential pumping, mass-analyzed in the first quadrupole of an Extrel triple-quadrupole mass analyzer, and detected.<sup>8</sup>

C<sub>60</sub><sup>-</sup> and C<sub>70</sub><sup>-</sup> do not react at a significant rate with a range of acids including H<sub>2</sub>O, (CH<sub>3</sub>)<sub>2</sub>CHOH, CF<sub>3</sub>CH<sub>2</sub>OH, C<sub>2</sub>H<sub>5</sub>COOH, and CF<sub>3</sub>COOH, as shown by the lack of depletion of the parent ion signal upon addition of ≥1 mTorr of acid to the flow tube. The lack of proton transfer from trifluoroacetic acid is particularly noteworthy because of its high acidity (Δ*G*<sub>acid</sub> = 317 kcal/mol). This indicates either that C<sub>60</sub>H and C<sub>70</sub>H are extremely strong acids (Δ*G*<sub>acid</sub> ≤ 317 kcal/mol) or that there is a kinetic barrier to proton abstraction. Both explanations are consistent with the extensive charge delocalization in these ions.

C<sub>60</sub><sup>-</sup> and C<sub>70</sub><sup>-</sup> react very slowly (*k* < 10<sup>-13</sup> cm<sup>3</sup>/s) under flow-tube conditions with BF<sub>3</sub>, an extremely strong Lewis acid. Since

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162–163.

(2) For a recent listing of leading references, see: Johnson, R. D.; Meijer, G.; Salem, J. R.; Bethune, D. S. *J. Am. Chem. Soc.* **1991**, *113*, 3619–3621.

(3) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. 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, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. E.; Smalley, R. F. *J. Phys. Chem.* **1990**, *94*, 8624–8636.

(4) Zhang, Q. L.; O'Brien, S. C.; Heath, J. R.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. *J. Phys. Chem.* **1986**, *90*, 525–528.

(5) McElvaney, S. W.; Nelson, H. H.; Baronavski, A. P.; Watson, C. H.; Eyer, J. R. *Chem. Phys. Lett.* **1987**, *134*, 214–219.

(6) Weiss, F. D.; Elkind, J. L.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *J. Am. Chem. Soc.* **1988**, *110*, 4464–4465.

(7) O'Brien, S. C.; Heath, J. R.; Kroto, H. W.; Curl, R. F.; Smalley, R. E. *Chem. Phys. Lett.* **1986**, *132*, 99–102.

(8) Graul, S. T.; Squires, R. R. *Mass Spectrom. Rev.* **1988**, *7*, 263.

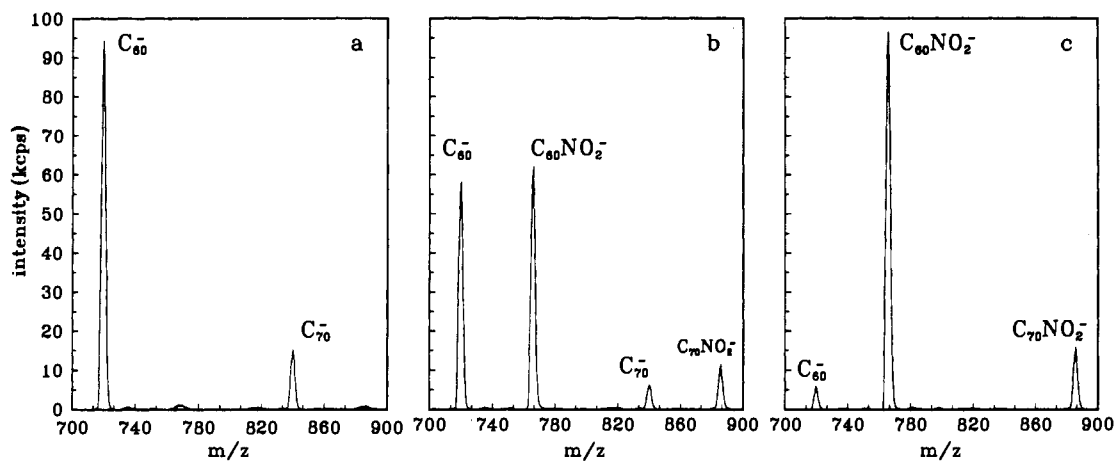


Figure 1. Mass spectra showing reactions of  $C_{60}^-$  and  $C_{70}^-$  with  $NO_2$  at  $NO_2$  flow rates (STP  $cm^3/min$ ) of (a) 0.04, (b) 0.56, and (c) 2.6.

the 0.4 Torr of buffer gas in the flow tube can stabilize adducts through collisional cooling, this indicates that  $C_{60}^-$  and  $C_{70}^-$  do not form stable adducts with  $BF_3$  and are therefore not Lewis bases.

$C_{60}^-$  and  $C_{70}^-$  readily add  $NO_2$  to form  $C_{60}NO_2^-$  and  $C_{70}NO_2^-$ . Mass spectra for these reactions are shown in Figure 1.  $C_{60}^-$  is slightly less reactive than  $C_{70}^-$ . The rate constants measured in argon by using standard methods<sup>8</sup> are  $1.2 \times 10^{-10} cm^3/s$  and  $2.1 \times 10^{-10} cm^3/s$ , respectively, with error limits of  $\pm 40\%$ . The relative error limits are much smaller, ca. 10%, so the ordering of reactivity is clear. For comparison, the collision rates for both reactions are estimated to be  $6.4 \times 10^{-10} cm^3/s$ .<sup>9</sup> The reactions are therefore 19% and 33% efficient, respectively. The structures of the adducts are unknown, with the nitro form ( $C_nNO_2^-$ ) probably more stable and the nitrite form ( $C_nONO^-$ ) possibly favored kinetically.<sup>10</sup> Further addition of  $NO_2$  is at most very slow, with an apparent bimolecular rate constant of  $\leq 10^{-13} cm^3/s$ . This shows that the first  $NO_2$  addition deactivates the fullerenes, at least with respect to further addition of  $NO_2$ . This suggests that the doublet character of the fullerenes enhances reaction with  $NO_2$ , while  $C_{60}NO_2^-$  and  $C_{70}NO_2^-$ , presumably singlets, are unreactive.

The apparent bimolecular rate constant for reaction with  $NO_2$  is only weakly dependent on flow-tube pressure, with apparent rate constants for both fullerenes at  $P = 0.5$  Torr only slightly larger (ca. 50%) than the rate at 0.1 Torr. We interpret this to mean that adduct formation by termolecular association is nearly saturated at these flow-tube pressures.

$NO_2$  does not extract an electron from  $C_{60}^-$  or  $C_{70}^-$ , indicating that the vertical electron affinities of the corresponding fullerenes are greater than 2.27 eV,<sup>11</sup> the electron affinity (EA) of  $NO_2$ .<sup>12</sup> This is consistent with the work of Smalley and co-workers, who estimated EA( $C_{60}$ ) to be 2.6–2.8 eV from photoelectron measurements.<sup>13</sup> It is much greater than the EAs of polyaromatic hydrocarbons, which are typically in the range 0.5–1 eV. The high EAs for the fullerenes result from both their large size and the known effects of double-bond pyramidalization on electron binding energies (LUMO energies).<sup>14</sup>

$C_{60}^-$  and  $C_{70}^-$  react with  $O_2$  and  $NO$  in the flow tube slowly if at all, with effective bimolecular reaction rate coefficients of  $< 10^{-13} cm^3/s$ . By contrast, significant formation of neutral fullerene oxides in solution has been reported.<sup>15</sup> Since  $O_2$  is a triplet and  $NO$  is a doublet, it is clear that simply having an unpaired electron is not sufficient to induce reactivity with gas-phase fullerenes.

**Acknowledgment.** This work was supported by the National Science Foundation (CHE-8815502) and the Department of Energy, Office of Basic Energy Science. We thank Prof. R. G. Cooks for helpful comments.

(14) Stoziar, R. W.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 1340–1343. Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N.; Jordan, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 1143. Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095–1109. Chou, P. K.; Kass, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 697–698.

(15) Wood, J. M.; Kahr, B.; Hoke, S. H.; Dejarne, L.; Cooks, R. G.; Ben-Amotz, D. *J. Am. Chem. Soc.*, in press.

### Empirical Correlation between Protein Backbone Conformation and $C\alpha$ and $C\beta$ $^{13}C$ Nuclear Magnetic Resonance Chemical Shifts

Silvia Spera<sup>†</sup> and Ad Bax\*

Laboratory of Chemical Physics, National Institute of Diabetes and Digestive and Kidney Diseases  
National Institutes of Health, Bethesda, Maryland 20892

Received February 27, 1991

For unstructured "random coil" peptides it has long been recognized that the chemical shift of the  $C\alpha$  and side-chain carbons of a given residue is largely independent of the nature of neighboring residues in the peptide, and "random coil"  $^{13}C$  shifts have been reported for all amino acids.<sup>1</sup> In proteins, in contrast, widely different chemical shifts can be observed for a given type of amino acid. For example, Torchia et al.<sup>2</sup> reported a chemical shift distribution of over 8 ppm for the alanyl methyl carbons in staphylococcal nuclease (S.Nase). Previous solid-state NMR work suggested a strong correlation between peptide backbone conformation and  $^{13}C$  chemical shifts. For a review, see Saito<sup>3</sup> and references therein. Theoretical FPT INDO calculations also predict different  $C\alpha$  and  $C\beta$  chemical shifts for helical and ex-

(9) Calculated by using ADO theory: Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. I, Chapter 3.  $\mu_D(NO_2) = 0.316$  D taken from the following: Nelson, R. D.; Lide, D. R.; Maryott, A. A. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1967**, NSRDS-NBS 10.  $\alpha(NO_2) = 3.02 \text{ \AA}^3$  taken from the following: Maryott, A. A.; Buckley, F. *Natl. Bur. Stand. Circ. (U.S.)* **1953**, No. 537.

(10) For examples of radical-ONO coupling, see: Bandow, H.; Akimoto, H.; Akiyama, S.; Tezuka, T. *Chem. Phys. Lett.* **1984**, *111*, 496–500 and references therein.

(11) Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Phys. Chem.* **1988**, *92*, 5405.

(12) The observation of both adduct formation and electron transfer in the analogous reaction of  $C_2H_4^-$  with  $NO_2$  suggests that competition from adduct formation does not prevent charge transfer. See: McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491–6498.

(13) Yang, S. H.; Pettiette, C. L.; Conceicao, J.; Chesnovsky, O.; Smalley, R. E. *Chem. Phys. Lett.* **1987**, *139*, 233–238.

<sup>†</sup> On leave from Istituto Guido Donegani, Novara, Italy.

(1) Howarth, O. W.; Lilley, D. M. *J. Prog. NMR Spectrosc.* **1978**, *12*, 1–40.

(2) Torchia, D. A.; Sparks, S. W.; Bax, A. *Biochemistry* **1988**, *27*, 5135–5141.

(3) Saito, H. *Magn. Reson. Chem.* **1986**, *24*, 835–852.