Gas-phase reactions of the buckminsterfullerene cations C60•+, C602+, and C60•3+ with water, alcohols, and ethers

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Gas-Phase Reactions of the Buckminsterfullerene Cations $C_{60}^{\bullet+}$, C_{60}^{2+}, and $C_{60}^{\bullet3+}$ with Water, Alcohols, and Ethers

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Abstract: The reactions of the fullerene ions $C_{60}^{\bullet+}$, C_{60}^{2+}, and $C_{60}^{\bullet3+}$ with the neutrals H_2O, CH_3OH, CH_3CH_2OH, $CH_3CH_2CH_2OH$, $(CH_3)_2CHOH$, CH_3OCH_3, $(CH_3CH_2)_2O$, and c-C_4H_8O in helium at 0.35 ± 0.01 Torr and 294 ± 2 K have been studied using a selected-ion flow tube. Association was the most commonly encountered primary product channel seen in the reactions of C_{60}^{2+}: in keeping with earlier studies, there was a clear dependence of the efficiency of association (and of reactivity in general) upon the size of the neutral. Other product channels evident in the reactions of the dication were charge transfer (the major product channel seen in the reaction with diethyl ether) and hydroxide abstraction to form the ion $C_{60}OH^+$ (in the reactions with ethanol and 2-propanol). Charge transfer and hydroxide abstraction were seen in several reactions of the trication, $C_{60}^{\bullet3+}$: association was observed as a minor channel in the reactions with methanol, ethanol, and 1-propanol. A clear difference was observed in the reactivity of the polycationic adducts of alcohols and ethers: alcohol adducts were observed to react further by efficient proton transfer to the parent alcohol, whereas the adducts of ethers did not display subsequent proton transfer to the parent ether. This difference in reactivity is interpreted in terms of the difference in ease of proton loss from the structures ascribed to the fullerene polycation adducts of alcohols and ethers. The monocation $C_{60}^{\bullet+}$ was unreactive with all of the species studied here: monocationic product ions ($C_{60}OH^+$, $C_{60}OR^+$) were also observed to be unreactive with the neutrals from which they were produced. The implications of the non-reactivity of $C_{60}^{\bullet+}$ and the reactivity of C_{60}^{2+} for the chemical evolution of interstellar clouds and circumstellar shells are briefly discussed.

Introduction

The study of Buckminsterfullerene, C_{60}, has progressed rapidly from the original proposal of the C_{60} structure for a mass-spectrometrically detected ion.[1] Since its isolation in macroscopic quantities,[2] Buckminsterfullerene has been the subject of a large—and steadily growing—number of investigations of its chemical reactivity.[3]

Several studies of neutral fullerene chemistry have dealt with the reactions of C_{60} with oxygen or with O-containing molecules. A monooxygenated compound, $C_{60}O$, has been reported as a product of C_{60} exposure to O_2 or to air,[4] as a byproduct of fullerene synthesis (where it is expected to arise from an oxygen impurity),[5,6] from the reaction of C_{60} with dimethyldioxirane,[7] and as a product of the photooxidation of C_{60} in benzene.[8] Theoretical calculations suggest[9] that the lowest-energy isomer of $C_{60}O$ is a 1,5-oxido [9]annulene, formally arising from oxygen atom insertion into a C–C bond between a 5- and a 6-membered ring; however, ^{13}C NMR of the $C_{60}O$ product of photooxidation[8] indicates that the isomer formed has C_{2v} symmetry, suggesting either an epoxide compound (arising from O-addition across a double bond between two 6-membered rings) or a 1,6-oxido [10]annulene species (resulting from O-insertion into a single C–C bond between two 6-membered rings). The most favored structure is that of the fullerene epoxide.[8] Very recently, the crystal structure of macroscopic $C_{60}O$ has been investigated by high-resolution powder X-ray diffraction.[10] In keeping with other examples of "reversible" derivatization of fullerenes,[11,12] $C_{60}O$ is efficiently converted back to C_{60} during chromatography on neutral alumina.[8] A fullerene diketone $C_{60}O_2$ resulting from a light-induced oxygen incision has been reported.[13] Higher oxides, $C_{60}O_n$ (n = 2–5), have been produced by electrochemical oxidation[14] and photolysis[5] of C_{60}. The oxidation of C_{60} in O_2, at elevated temperatures, has been studied:[15,16] results suggest that C_{60} can take up as many as 12 oxygen atoms during oxidation at 200 °C,[15] while destructive oxidation, perhaps forming 5- or 6-membered cyclic anhydrides,[16] is increasingly rapid at higher temperatures. The total combustion of C_{60}

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(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.
(2) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffmann, D. R. *Nature* **1990**, *347*, 354.
(3) For recent reviews, see: (a) Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 293. (b) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157. (c) Wudl, F.; Hirsch, A.; Khemani, K. C.; Suzuki, T.; Allemand, P. M.; Koch, A.; Eckert, H.; Srdanov, G.; Webb, H. M. *A.C.S. Symp. Ser.* **1992**, *481*, 161. (d) Chandrasekaran, S. *Indian J. Chem. (A & B)* **1992**, *31*, F36.
(4) Vijayakrishnan, V.; Santra, A. K.; Pradeep, T.; Seshadri, R.; Nagarajan, R.; Rao, C. N. R. *J. Chem. Soc., Chem. Commun.* **1992**, 198.
(5) Wood, J. M.; Kahr, B.; Hoke, S. H., III; Dejarme, L.; Cooks, R. G.; Ben-Amotz, D. *J. Am. Chem. Soc.* **1991**, *113*, 5907.
(6) Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M.; Anz, S.; Sensharma, D.; Wudl, F.; Khemani, K. C.; Koch, A. *Science* **1991**, *252*, 548.
(7) Elemes, Y.; Silverman, S. K.; Sheu, C.; Kao, M.; Foote, C. S.; Alvarez, M. M.; Whetten, R. L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 351.
(8) Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B., III; McCauley, J. P., Jr.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 1103.
(9) Raghavachari, K. *Chem. Phys. Lett.* **1992**, *195*, 221.
(10) Vaughan, G. B. M.; Heiney, P. A.; Cox, D. E.; McGhie, A. R.; Jones, D. R.; Strongin, R. M.; Cichy, M. A.; Smith, A. B., III. *Chem. Phys.* **1992**, *168*, 185.
(11) Olah, G. A.; Bucsi, K.; Lambert, C.; Aniszfeld, R.; Trivedi, N. J.; Sensharma, D. K.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1991**, *113*, 9385.
(12) 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. N.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634.
(13) Taliani, C.; Ruani, G.; Zamboni, R.; Danieli, R.; Rossini, S.; Denisov, V. N.; Burlakov, V. M.; Negri, F.; Orlandi, G.; Zerbetto, F. *J. Chem. Soc., Chem. Commun.* **1993**, 220.
(14) Kalsbeck, W. A.; Thorp, H. H. *J. Electroanal. Chem.* **1991**, *314*, 363.
(15) Chen, H. S.; Kortan, A. R.; Haddon, R. C.; Kaplan, M. L.; Chen, C. H.; Mujsce, A. M.; Chou, H.; Fleming, D. A. *Appl. Phys. Lett.* **1991**, *59*, 2956.
(16) Vassallo, A. M.; Pang, L. S. K.; Cole-Clarke, P. A.; Wilson, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 7820.

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$$C_{60} + 60O_2 \rightarrow 60CO_2$$

has been performed in a bomb calorimeter, yielding values for $\Delta H_f°$ (C_{60}, cr, 298.15 K) of 578.9 ± 3.3 and 545.0 ± 3.2 kcal mol^{-1}.[17,18]

Reactions of C_{60} with other oxygenated substances have been studied also. A dioxolone adduct has been produced from the reaction with dimethyldioxirane.[7] The polymethoxylation of C_{60}, producing $C_{60}(OMe)_n$ ($n \leq 26$), has been reported from the action of methanol/KOH upon $C_{60}Cl_n$.[11] Multiple addition of the oxygen-containing radicals $OH^•$ and $(CH_3)_3CO^•$ to C_{60} has also been described,[19] and the preparation of polyhydroxylated fullerenes (fullerols) by aqueous acid chemistry in concentrated H_2SO_4/HNO_3 has also been reported.[20]

In the regime of ion/molecule chemistry, high-energy collisions of $O^{•+}$ with C_{60}[21] have been shown to result in a variety of processes, including charge transfer, sequential C_2 loss, and the possible formation of an endohedral complex $[CO@C_{58}]^{•+}$. The lack of reactivity of $C_{60}^{•-}$ with H_2O, i-C_3H_7OH, $(CF_3)_2CHOH$, C_2H_5COOH, and CF_3COOH suggests a surprisingly high acid strength for $C_{60}H^•$.[22] Chemical ionization of C_{60} with H_2O in a conventional CI ion source[23] has been shown to produce $C_{60}H^+$ and $C_{60}OH^+$. The ions $C_{60}H^+$, $C_{60}O^{•+}$, $C_{60}OH^+$, their C_{70} analogues, and the corresponding molecular anions have also been reported[24] to result from positive- and negative-ion fast-atom bombardment (FAB) mass spectrometry of fullerenes in 3-nitrobenzyl alcohol and 2-nitrophenyl octyl ether.

We have embarked upon an extensive study of the gas-phase ion/molecule chemistry of C_{60}.[25-40] In earlier studies we have mentioned the formation of adducts of C_{60}^{2+} with several oxygen-containing organic compounds[34] and have used the occurrence or absence of proton transfer from these adducts to their parent compounds in order to deduce thermochemical and structural information concerning the adducts.[33] We have also studied adduct formation in the reactions of $C_{60}^{•+}$, C_{60}^{2+}, and $C_{60}^{•3+}$ with amines,[28,29,35] nitriles,[34,39] and hydrocarbons.[29] A motivating factor in these studies is an interest in the possible reactivity and derivation of fullerene ions and neutrals within interstellar clouds and circumstellar shells.[30,41] In the present work, we report in detail our studies of the chemistry initiated by buckminsterfullerene cations with saturated oxygen-containing molecules.

Experimental Section

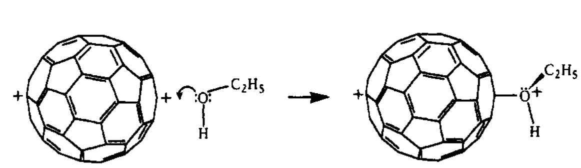
All reactions were performed at 0.35 ± 0.01 Torr and 294 ± 2 K, using helium buffer gas in a selected-ion flow tube which has been described previously.[42] $C_{60}^{•+}$, C_{60}^{2+}, and $C_{60}^{•3+}$ were produced by electron impact (50 V for $C_{60}^{•+}$ and C_{60}^{2+}, 100 V for $C_{60}^{•3+}$) upon fullerene vapor. Fullerene samples were obtained from Strem Chemicals Co. (C_{60}/C_{70}, containing 2–12% C_{70}) and from Texas Fullerenes Corp. (mixed fullerene extract, >80% C_{60}). Water was doubly distilled; all other neutral reagents were obtained commercially and were not less than 98% pure. With the exception of dimethyl ether (CH_3OCH_3) which was used as a neat gas, all reagents were additionally vacuum-distilled prior to use and were used as dilute solutions (3–50%, depending upon the neutral's vapor pressure at 294 K) in helium to facilitate their introduction into the flow tube.

Results and Discussion

Reactions of $C_{60}^{•+}$. The monocation $C_{60}^{•+}$ was not observed to react with any of the neutrals included in the present study. Upper limits of $k < 1.0 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ can be ascribed to the reactions of $C_{60}^{•+}$ with CH_3OH, C_2H_5OH, CH_3OCH_3, $C_2H_5OC_2H_5$, and c-C_4H_8O and $k < 1.0 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for the reactions with H_2O, n-C_3H_7OH, and i-C_3H_7OH. The higher upper bounds for the latter compounds reflect their lower vapor pressures: as a consequence of their low volatility, we were unable to attain such high concentrations of these species within the reaction region of the flow tube as was possible for the more volatile compounds.

This general lack of reactivity is consistent with the nonreactivity of $C_{60}^{•+}$ with most small molecules under our experimental conditions.[29,35,39] We note, however, that $C_{60}^{•+}$ is much more reactive with amines than it is with alcohols and ethers. This probably relates to the generally higher nucleophilicities of amines than those of alcohols and ethers. We have commented elsewhere that the nucleophilic addition of a molecule to $C_{60}^{•+}$ involves the formation of a product having a strongly localized charge (located, formally, upon the donor atom of the nucleophile) from a reactant ion in which the charge is presumed to be highly delocalized. For this reason, adduct formation is expected to be accompanied by a loss in the charge delocalization energy of the fullerene cation: this factor will act to disfavor association, if the reactant neutral is not a sufficiently strong nucleophile.

Reactions of C_{60}^{2+}. The observed reactivity of C_{60}^{2+} with the neutrals surveyed is summarized in Table I. Addition was the dominant reaction channel observed for the reactions of C_{60}^{2+} with the alcohols and ethers. We have proposed[29,34,35] that the addition of alcohols, ketones, nitriles, and amines to C_{60}^{2+} occurs by a process of nucleophilic addition as shown for the example of ethanol:



(1)

A clear dependence of addition efficiency upon neutral size was observed in H_2O, CH_3OH, C_2H_5OH, and n-C_3H_7OH: the rate coefficient for addition increased by at least one order of magnitude over this series. This is in keeping with the trend in increasing efficiency of addition with reactant neutral size for the reactions of C_{60}^{2+} with unsaturated hydrocarbons and with nitriles, as we have described elsewhere.[29,34,39] We have proposed

(17) Steele, W. V.; Chirico, R. D.; Smith, N. K.; Billups, W. E.; Elmore, P. R.; Wheeler, A. E. J. Phys. Chem. 1992, 96, 4731.
(18) Beckhaus, H. D.; Ruchardt, C.; Kao, M.; Diederich, F.; Foote, C. S. Angew. Chem., Int. Ed. Engl. 1992, 31, 63.
(19) Krusic, P. J.; Wasserman, E.; Parkinson, B. A.; Malone, B.; Holler, E. R., Jr.; Keizer, P. N.; Morton, J. R.; Preson, K. F. J. Am. Chem. Soc. 1991, 113, 6274.
(20) Chiang, L. Y.; Swirczewski, J. W.; Hsu, C. S.; Chowdhury, S. K.; Cameron, S.; Creegan, K. J. Chem. Soc., Chem. Commun. 1992, 1791.
(21) Christian, J. F.; Wan, Z.; Anderson, S. L. Chem. Phys. Lett. 1992, 199, 373.
(22) Sunderlin, L. S.; Paulino, J. A.; Chow, J.; Kahr, B.; Ben-Amotz, D.; Squires, R. R. J. Am. Chem. Soc. 1991, 113, 5489.
(23) Schröder, D.; Bohme, D. K.; Weiske, T.; Schwarz, H. Int. J. Mass Spectrom. Ion Processes 1992, 116, R13.
(24) Miller, J. M.; Chen, L.-Z. Rapid Commun. Mass Spectrom. 1992, 6, 184.
(25) Petrie, S.; Javahery, G.; Wang, J.; Bohme, D. K. J. Phys. Chem. 1992, 96, 6121.
(26) Javahery, G.; Petrie, S.; Wang, J.; Bohme, D. K. Chem. Phys. Lett. 1992, 195, 7.
(27) Petrie, S.; Javahery, G.; Wang, J.; Bohme, D. K. J. Am. Chem. Soc. 1992, 114, 6268.
(28) Javahery, G.; Petrie, S.; Ketvirtis, A.; Wang, J.; Bohme, D. K. Int. J. Mass Spectrom. Ion Processes 1992, 116, R7.
(29) Petrie, S.; Javahery, G.; Wang, J.; Bohme, D. K. J. Am. Chem. Soc. 1992, 114, 9177.
(30) Petrie, S.; Javahery, G.; Bohme, D. K. Astron. Astrophys. 1993, 271, 662.
(31) Javahery, G.; Petrie, S.; Wang, J.; Bohme, D. K. Int. J. Mass Spectrom. Ion Processes 1992, 120, R5.
(32) Wang, J.; Javahery, G.; Petrie, S.; Bohme, D. K. J. Am. Chem. Soc. 1992, 114, 9665.
(33) Petrie, S.; Javahery, G.; Bohme, D. K. Int. J. Mass Spectrom. Ion Processes 1993, 124, 145.
(34) Petrie, S.; Javahery, G.; Bohme, D. K. J. Am. Chem. Soc. 1993, 115, 1445.
(35) Javahery, G.; Petrie, S.; Wincel, H.; Wang, J.; Bohme, D. K. J. Am. Chem. Soc., in press.
(36) Petrie, S.; Wang, J.; Bohme, D. K. Chem. Phys. Lett. 1993, 204, 473.
(37) Javahery, G.; Wincel, H.; Petrie, S.; Bohme, D. K. Chem. Phys. Lett. 1993, 204, 467.
(38) Petrie, S.; Javahery, G.; Wincel, H.; Bohme, D. K. J. Am. Chem. Soc., in press.
(39) Javahery, G.; Petrie, S.; Wincel, H.; Wang, J.; Bohme, D. K. J. Am. Chem. Soc., submitted for publication.
(40) Bohme, D. K., et al., in preparation.

Table I: Reactions of C_{60}^{2+} with ROR′

reactant	products[a]		k_{obs}[b]	k_c[c]	$-\Delta H°$[d]
H_2O	none		<0.01[e]	3.36	
CH_3OH	$C_{60}{\cdot}CH_3OH^{2+}$		0.007[e]	2.92	
C_2H_5OH	$C_{60}{\cdot}C_2H_5OH^{2+}$	[0.9]	0.037[e]	2.77	
	$C_{60}OH^+ + C_2H_5^+$	[0.1]			>29[f]
n-C_3H_7OH	$C_{60}{\cdot}C_3H_7OH^{2+}$	[0.6]	0.10	2.52	
	$C_{60}OH^+ + C_3H_7^+$	[0.4]			>29[f,g]
i-C_3H_7OH	$C_{60}OH^+ + C_3H_7^+$		0.23	2.56	>44[f,h]
CH_3OCH_3	$C_{60}{\cdot}C_2H_6O^{2+}$		0.003	2.46	
$(CH_3CH_2)_2O$	$C_{60}{\cdot}C_4H_{10}O^{2+}$	[0.1]	0.91	2.30	
	$C_{60}^{\cdot+} + (C_2H_5)_2O^{\cdot+}$	[0.9]			44
c-C_4H_8O	$C_{60}{\cdot}C_4H_8O^{2+}$	[0.6]	1.9	2.50	
	$C_{60}^{\cdot+} + c$-$C_4H_8O^{\cdot+}$	[0.4]			46

[a] Where more than one product channel was detected, the branching ratio for each channel is reported in square brackets. [b] Observed effective bimolecular rate coefficient (at 0.35 ± 0.01 Torr) in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [c] ADO collision rate coefficient, calculated according to the method of Su and Bowers,[43] in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [d] Reaction exothermicity in kcal mol^{-1}, calculated according to thermochemical data tabulated in the compilation of Lias et al.,[44] and using also $\Delta H_f°(C_{60}^{\cdot+}) = 810.5 \pm 0.5$ kcal mol^{-1} and $\Delta H_f°(C_{60}^{2+}) = 1073.2 \pm 0.7$ kcal mol^{-1} expressed relative to $\Delta H_f°(C_{60}) = 635$ kcal mol^{-1} as discussed in ref 38. [e] Rate coefficient and products previously reported in ref 29. [f] Calculated on the basis of $\Delta H_f°(C_{60}OH^+) \leq 773$ kcal mol^{-1} as discussed in the text. [g] Assuming the initial structure $CH_3CH_2CH_2^+$ for the alkyl cation product of this reaction. [h] Assuming the initial structure $(CH_3)_2CH^+$ for the alkyl cation product of this reaction.

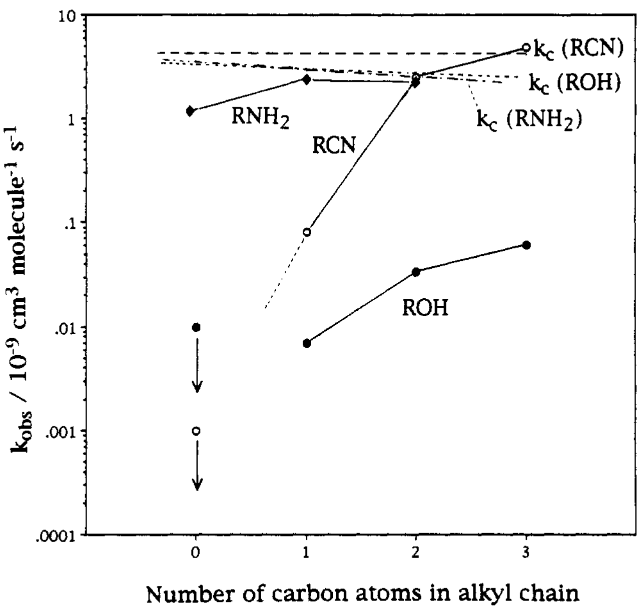
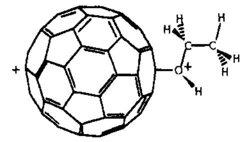
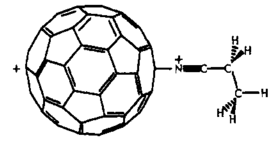


Figure 1. Comparison of the observed effective bimolecular rate coefficients, at 294 ± 2 K and 0.35 ± 0.01 Torr, for the association of C_{60}^{2+} with amines (RNH$_2$, filled diamonds), with nitriles (RCN, open circles), and with alcohols (ROH, filled circles) featuring the unbranched alkyl substituents R = C_nH_{2n+1} (n = 0–3). The calculated ADO collision rate coefficients for the reactions are also shown. Rate coefficients shown at n = 0 for HCN and H_2O are upper limits, since these substances did not react detectably with C_{60}^{2+} under our experimental conditions.

that this trend reflects the increase in the number of rotational and bending vibrational modes available for energy dispersal within the collision complex. In this respect, it is interesting to compare the relative rate coefficients for the addition reactions $C_{60}^{2+} + C_nH_{2n+1}X$ (n = 0–3, X = OH, CN; n = 0–2, X = NH$_2$), as is depicted in Figure 1. This figure shows that the efficiency of association with primary amines is comparatively insensitive to the size of the alkyl substituent, while the efficiency of association with nitriles and with alcohols shows a clear size dependence. It seems evident that the increase in association efficiency with increasingly alkyl substituent size is much greater for nitriles than for alcohols, even with consideration for the existence of a competing reaction channel (which does not approach the collision rate) in the reactions of C_{60}^{2+} with alcohols. The proposed mechanism shown in (1) of nucleophilic addition is the same in both cases. One possible rationale for the observed trends in reaction efficiency is that nonbonding interactions between the alkyl substituent and the fullerene cage surface will be more destabilizing for the alcohol adducts than the nitrile adducts, given the relative orientations of these substituents in the product ions **I** and **II**. Rotation about the O–C axis in the



I



II

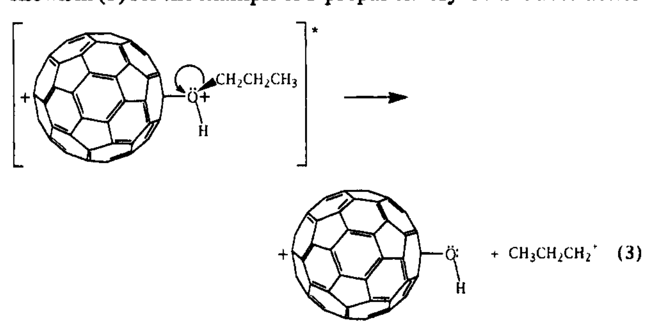
ethanol moiety in **I** is especially likely to be hindered by nonbonding interactions between the methyl pendant and the fullerene cage, while all C–C rotations within the propanenitrile functionality of **II** are essentially unhindered by proximity to the fullerene surface.

Another product channel observed in the reactions with C_2H_5OH, n-C_3H_7OH, and i-C_3H_7OH was the hydroxide abstraction channel

$$C_{60}^{2+} + C_nH_{2n+1}OH \rightarrow C_{60}OH^+ + C_nH_{2n+1}^+ \quad (2)$$

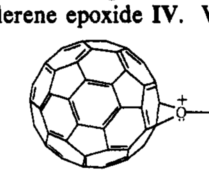
As with association, this channel increased in efficiency with increasing reactant size and was the sole product observed in the reaction with i-C_3H_7OH as shown in Figure 2.

We propose that this channel occurs in competition with stabilization of the collision complex, by a mechanism such as is shown in (3) for the example of 1-propanol. Hydroxide abstraction



III

is most efficient in the reaction with 2-propanol: the 2-propyl cation (as a secondary carbocation) is the best leaving group of the possible alkyl groups included in the reactants surveyed. The relative efficiency of this channel in the reactions with 1-propanol and 2-propanol thus suggests that dissociation occurs prior to any possible rearrangement of the alkyl cation. Two main possibilities exist for the structure of the fullerene product ion $C_{60}OH^+$: the reaction as shown leads initially to a hydroxylated fullerene cation **III**, but rearrangement may permit the formation of a protonated fullerene epoxide **IV**. We have noted several



IV

(41) Millar, T. J. *Mon. Not. R. Astron. Soc.* **1992**, *259*, 35P.

(42) (a) Mackay, G. I.; Vlachos, G. D.; Bohme, D. K.; Schiff, H. I. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 259. (b) Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1983/1984**, *55*, 69.

(43) Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347.

(44) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1.

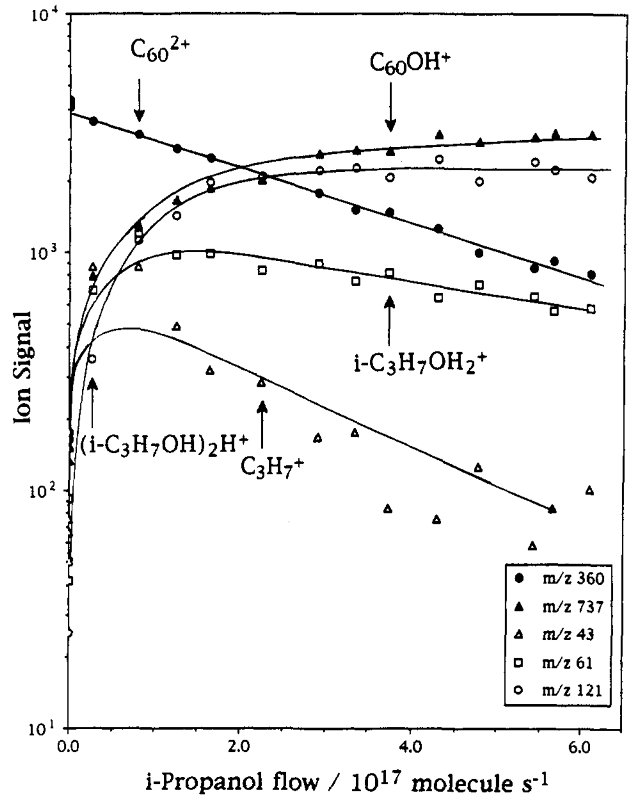


Figure 2. Experimental data for the reaction of C_{60}^{2+} with 2-propanol, $(CH_3)_2CHOH$, at 294 ± 2 K and 0.352 Torr of helium. The sole product channel observed is hydroxide abstraction, yielding the product ions $C_{60}OH^+$ and $C_3H_7^+$. A secondary product, i-$C_3H_7OH_2^+$, is formed by proton transfer from $C_3H_7^+$ (PA(C_3H_6) = 179.8 kcal mol^{-1}) to i-C_3H_7OH (PA = 191.2 kcal mol^{-1}).[44] Subsequent formation of a proton-bound dimer of i-C_3H_7OH is also noted.

instances, in the reaction chemistry initiated by reactions of fullerene cations with ammonia and amines[35] and with nitriles,[39] which suggest that fullerene cations derivatized with nitrogen-containing substituents tend to rearrange to result in charge localization upon the nitrogen atom. Analogous rearrangement would, in this instance, yield structure IV with the charge formally localized upon the oxygen atom. The absence of observable proton transfer from $C_{60}OH^+$ to i-C_3H_7OH suggests PA($C_{60}O$) > PA(i-C_3H_7OH) (191.2 kcal mol^{-1}),[45] which is reasonable given the high proton affinity which has been determined for C_{60} itself (PA = 205.5 ± 1.5 kcal mol^{-1}).[46]

As estimate can be made of the thermochemistry relating to hydroxide abstraction. If (as seems reasonable) OH^- abstraction occurs only at a close separation of the reactants, for example by the mechanism shown in (3), then there will exist a reverse activation barrier δ arising from the Coulombic repulsion between the initially-adjacent monocationic product ions. The expected features of the energy profile are shown in Figure 3. The exothermicity must exceed the reverse activation barrier height δ *if the reaction is to proceed efficiently. In the reaction of* C_{60}^{2+} with ethanol, the rate coefficient for hydroxide abstraction is 3.7 × 10^{-12} cm^3 molecule^{-1} s^{-1}, compared with a collision rate coefficient of 2.8 × 10^{-9} cm^3 molecule^{-1} s^{-1}. The ratio k_{obs}/k_c yields an upper limit to the forward activation energy barrier E_a, via the Arrhenius expression

$$k_{obs} \le k_c \exp(-E_a/RT) \qquad (4)$$

This expression yields E_a < 4 kcal mol^{-1}; if it is assumed that the initial charge separation of the monocationic products does not

(45) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.
(46) McElvany, S. W.; Callahan, J. H. *J. Phys. Chem.* **1991**, *95*, 6187.

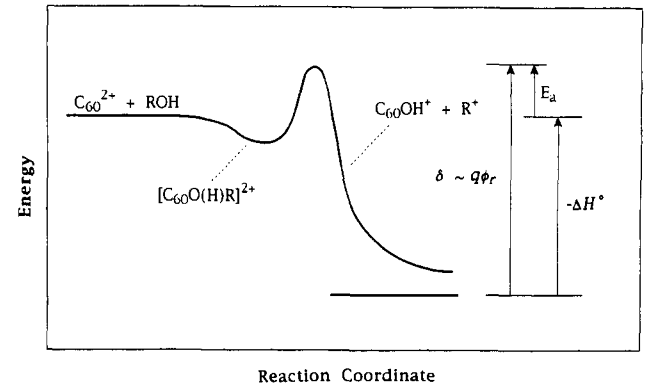
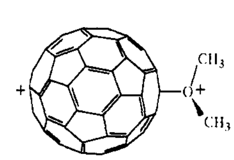


Figure 3. Reaction profile expected for the hydroxide-abstraction reaction of C_{60}^{2+} with ROH. The profile shown assumes that the exothermicity, $-\Delta H°$, is slightly less than the reverse activation barrier, δ, resulting in a slight forward activation barrier E_a. In making the approximation $\delta \sim q\phi_r$ ($q\phi_r$ is the Coulombic repulsion energy between two cations at a charge separation r), we assume also that ion–dipole and ion–induced dipole attractive interactions between the cations are substantially less significant than the ion–ion repulsive interaction at this separation. It is also possible that other factors act to raise the activation energy; for example, the occurrence of hydroxide abstraction may require additional energy for the generation of a transition state or intermediate. In support of this possibility, we note that most hydride transfer reactions of C_{60}^{2+} are observed to be inefficient even when the exothermicity substantially outweighs the calculated Coulombic repulsion between the product ions.

exceed 10 Å, then the Coulombic repulsion $q\phi_r$ > 1.44 eV or 33 kcal mol^{-1}. The approximation $\delta = q\phi_r$, then indicates a reaction exothermicity $-\Delta H°$ > 29 kcal mol^{-1}, yielding as an upper limit $\Delta H_f°(C_{60}OH^+)$ < 773 kcal mol^{-1} and as a lower limit $D(C_{60}^{\bullet +}$–OH) > 47 kcal mol^{-1}.

The association reactions of dimethyl and diethyl ether with C_{60}^{2+} are inefficient in comparison to the reactions with alcohols. In the case of $C_2H_5OC_2H_5$, a competing charge transfer channel is evident, but the overall observed rate coefficient is reproducibly below the calculated collision rate coefficient, suggesting that charge transfer is marginally impeded by an activation barrier. We note that the ionization potential of $C_2H_5OC_2H_5$ (IE = 9.51 ± 0.03 eV) is very close to that of *m*-nitrotoluene (IE = 9.48 ± 0.02 eV), to which charge transfer from C_{60}^{2+} was reported in an ion cyclotron resonance (ICR) study,[47] and is lower than that of allene (IE = 9.69 ± 0.01 eV) and other neutrals, to which charge transfer is not observed.[25,47] If charge transfer from C_{60}^{2+} to diethyl ether is impeded by a small barrier, then only those collisions featuring sufficient energy to overcome the barrier will result in charge transfer: collision complexes from such "high-energy-tail" collisions would be expected to have a shorter lifetime anyway, impeding stabilization to form the adduct, and so the occurrence of charge transfer from these collisions may not seriously affect the incidence of association. No such analysis is required for the reaction of dimethyl ether (IE = 10.025 ± 0.025 eV), for which association is the only product channel evident and which is more than an order of magnitude slower than the association reaction of its isomer C_2H_5OH. It is possible that free rotation about both O–C axes in structure V is hindered by



V

(47) McElvany, S. W.; Bach, S. B. H. *A.S.M.S. Conf. Mass Spectrom. Allied Top.* **1991**, *39*, 422.
(48) *CRC Handbook of Chemistry and Physics*, 67th ed.; Weast, R. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1987.

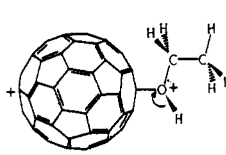
proximity to the fullerene surface: this would then reduce the number of modes available for effective dispersal of excess energy within the complex $[C_{60}O(CH_3)_2^{2+}]^*$, decreasing its lifetime. This explanation, however, does not appear to account satisfactorily for the high efficiency of adduct formation in the reaction of C_{60}^{2+} with tetrahydrofuran, c-C_4H_8O. In this reaction, which occurs at the collision rate within the uncertainty of the experimental technique, association is efficient despite competition from charge transfer (IE(c-C_4H_8O) = 9.41 ± 0.02 eV). In the reactions of nitriles[39] and of ketones[40] which we have studied, unsaturation is clearly seen to reduce the efficiency of association reactions, and it seems reasonable that cyclic reactants (which, like unsaturated reactants, possess fewer internal degrees of freedom than their saturated, acyclic counterparts) might also undergo addition with comparatively low efficiency. A factor in favor of a higher association efficiency for c-C_4H_8O is the higher dipole moment of this compound (μ(c-C_4H_8O) = 1.63 D; $\mu(C_2H_5OC_2H_5)$ = 1.15 D):[48] the larger the dipole moment, the stronger the ion–dipole interaction will be between the reactants, enhancing the depth of the potential well. Another factor in favor of the addition of tetrahydrofuran is the less sterically demanding nature of this reactant than diethyl ether.

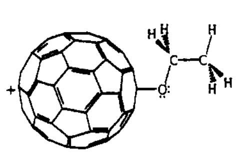
While hydroxide transfer from the ethers is obviously not accessible without considerable rearrangement, it might be anticipated that alkoxide transfer could occur by a mechanism analogous to reaction 3, viz.:

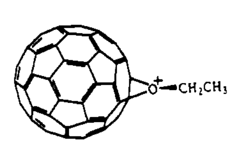
$$C_{60}^{2+} + ROR \rightarrow C_{60}OR^+ + R^+ \qquad (5)$$

It is probable that this channel was not detected for diethyl ether and tetrahydrofuran because of competition with charge transfer (additionally, in the case of THF, two O–C or C–C bonds would need to be broken in order to lose R^+), while its absence in the case of dimethyl ether can be comprehended since the methyl cation is a considerably poorer leaving group than the larger alkyl cations.

Differences are apparent in the subsequent reactivity of the addition products of C_{60}^{2+} with alcohols and with ethers. Efficient proton transfer is seen in the reactions of $C_{60}{\cdot}O(H)CH_3^{2+}$ with CH_3OH, $C_{60}{\cdot}O(H)C_2H_5^{2+}$ with C_2H_5OH, and $C_{60}{\cdot}O(H)C_3H_7^{2+}$ with n-C_3H_7OH. In contrast, proton transfer does not occur in the reactions of $C_{60}{\cdot}O(CH_3)_2^{2+}$ with CH_3OCH_3, $C_{60}{\cdot}O(C_2H_5)_2^{2+}$ with $C_2H_5OC_2H_5$, and $C_{60}{\cdot}OC_4H_8^{2+}$ with c-C_4H_8O: the only product channels evident in these instances are adduct formation, at a rate not exceeding that observed for the primary association reaction. The proton affinities of ethers are generally higher than those of the corresponding alcohols:[45] the observed proton-transfer reactivity therefore indicates that the gas-phase acidity (GA) of the addition products with ethers is, in general, substantially higher than the GA of addition products with alcohols. This can be comprehended in terms of the different consequences of deprotonation from our proposed structures for these adducts. Deprotonation of an alcohol adduct **VI** results in the formation of structure **VII**, which may undergo isomerization


VI


VII


VIII

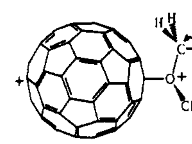
to an alkylated epoxide cation **VIII**. In contrast, deprotonation

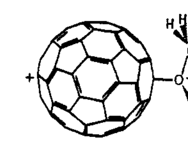
Table II: Reactions of $C_{60}^{\cdot 3+}$ with ROR′

reactant	products[a]		k_{obs}[b]	k_c[c]	$-\Delta H°$[d]
H_2O	$C_{60}H^{2+} + OH^+$		0.20	4.54	24
CH_3OH	$C_{60}^{2+} + CH_3OH^{\cdot +}$	[0.8]	2.5[e]	4.38	110
	$C_{60}{\cdot}CH_3OH^{\cdot 3+}$	[0.2]			
CH_3CH_2OH	$C_{60}OH^{\cdot 2+} + C_2H_5^+$	[0.7]	2.4	4.16	>66[f]
	$C_{60}^{2+} + C_2H_5OH^{\cdot +}$	[0.2]			118
	$C_{60}{\cdot}C_2H_5OH^{\cdot 3+}$	[0.1]			
$CH_3CH_2CH_2OH$	$C_{60}^{2+} + C_3H_7OH^{\cdot +}$	[0.5]	3.9	3.78	124
	$C_{60}OH^{\cdot 2+} + C_3H_7^+$	[0.4]			>66[f,g]
	$C_{60}{\cdot}C_3H_7OH^{\cdot 3+}$	[0.1]			
$(CH_3)_2CHOH$	$C_{60}OH^{\cdot 2+} + C_3H_7^+$	[0.7]	4.1	3.84	>82[f,h]
	$C_{60}^{2+} + C_3H_7OH^{\cdot +}$	[0.3]			127
CH_3OCH_3	$C_{60}^{2+} + CH_3OCH_3^{\cdot +}$		3.0	3.69	129
$(CH_3CH_2)_2O$	$C_{60}^{2+} + (CH_3CH_2)_2O^{\cdot +}$		3.3	3.45	141
c-C_4H_8O	C_{60}^{2+} + *c*-$C_4H_8O^{\cdot +}$		3.3	3.76	143

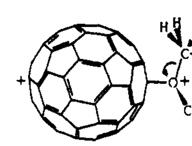
[a] Where more than one product channel was detected, the branching ratio for each channel is reported in square brackets. [b] Observed effective bimolecular rate coefficient (at 0.35 ± 0.01 Torr) in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [c] ADO collision rate coefficient, calculated according to the method of Su and Bowers,[43] in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [d] Reaction exothermicity in kcal mol^{-1}, calculated according to thermochemical data tabulated in the compilation of Lias *et al.*,[44] and using also $\Delta H_f°(C_{60}^{2+})$ = 1073.2 ± 0.7 kcal mol^{-1}, $\Delta H_f°(C_{60}H^{\cdot 2+})$ = 1042 ± 9 kcal mol^{-1}, and $\Delta H_f°(C_{60}^{\cdot 3+})$ = 1433 kcal mol^{-1} expressed relative to $\Delta H_f°(C_{60})$ = 635 kcal mol^{-1} as discussed in ref 38. [e] Rate coefficient and products previously reported in ref 37. [f] Calculated on the basis of $\Delta H_f°(C_{60}OH^{\cdot 2+}) \leq 1108$ kcal mol^{-1} as discussed in the text. [g] Assuming the initial structure $CH_3CH_2CH_2^+$ for the alkyl cation product of this reaction. [h] Assuming the initial structure $(CH_3)_2CH^+$ for the alkyl cation product of this reaction.

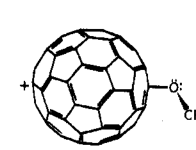
of an ether adduct **IX** requires substantial rearrangement to yield a feasible monocationic product ion: the integrity of the bond


IX


X

between the fullerene surface and the O atom requires that this oxygen atom remains trivalent and hence positively charged during proton loss, yielding a zwitterion-like structure **X** which is expected to be highly unstable. Alternatively, deprotonation might occur if accompanied by CH_2 loss as in **XI** → **XII**: this channel amounts to methyl cation loss from the dicationic adduct, which also was not observed. Neither of these possibilities is at all likely to be


XI


XII

as favorable, kinetically or thermodynamically, as proton loss from an alcohol adduct. The observed secondary chemistry of the alcohol and ether adducts of C_{60}^{2+} is thus entirely consistent with the products expected from the nucleophilic addition mechanism proposed.

Reactions of $C_{60}^{\cdot 3+}$. The reactivity of $C_{60}^{\cdot 3+}$ with the neutrals surveyed is summarized in Table II. Previous studies of $C_{60}^{\cdot 3+}$ reactivity[35,37,47] have indicated that $C_{60}^{\cdot 3+}$ displays efficient charge transfer to neutrals having ionization energy IE < 11.09 ± 0.09 eV. Since all of the neutrals in the present work, with the exception of H_2O, have IE < 11 eV, it is not surprising that $C_{60}^{\cdot 3+}$ displays rapid reactivity with these neutrals and that charge transfer is a commonly-detected product channel. Hydroxide abstraction

$$C_{60}^{\cdot 3+} + ROH \rightarrow C_{60}OH^{\cdot 2+} + R^+ \qquad (6)$$

competes with efficient charge transfer in the reactions of ethanol,

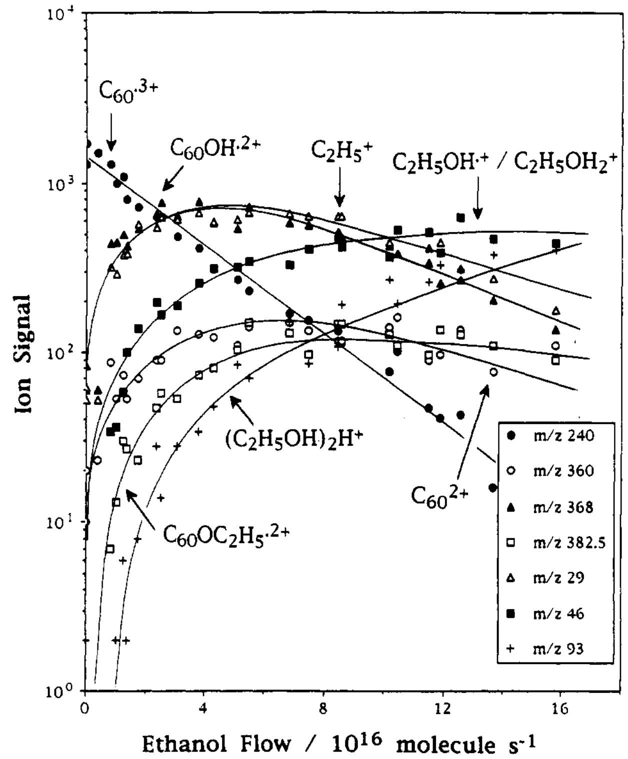


Figure 4. Plot of experimental data for the reaction of $C_{60}^{\bullet 3+}$ with ethanol, at 294 ± 2 K and 0.341 Torr of helium. Primary product channels observed are the following: charge transfer, yielding C_{60}^{2+} and $C_2H_5OH^{\bullet +}$; hydroxide abstraction, producing $C_{60}OH^{\bullet 2+}$ and $C_2H_5^+$; and addition, yielding $C_{60}{}^{\bullet}C_2H_5OH^{\bullet 3+}$ (*m/z* 255.3, not monitored in this data set). Protonated ethanol, $C_2H_5OH_2^+$, arises as a secondary product via proton transfer from $C_2H_5OH^{\bullet +}$, $C_{60}OH^{\bullet 2+}$, and $C_2H_5^+$. A subsequent proton-bound dimer of ethanol is seen also. The data shown were obtained with the downstream (detection) quadrupole mass spectrometer in the high mass setting: this mode did not permit unit mass resolution and so the signal at *m/z* 46 also contains a contribution from *m/z* 47, $C_2H_5OH_2^+$. The other secondary product ion shown, $C_{60}OC_2H_5^{\bullet 2+}$, arises via proton transfer from the primary adduct to C_2H_5OH: this ion is observed to react only slowly to form an adduct $C_{60}{\cdot}OC_2H_5{\cdot}C_2H_5OH^{\bullet 2+}$ (*m/z* 405.5, not monitored). Also not shown on this figure are the signals due to $C_{60}O^{\bullet +}$, arising from proton transfer from $C_{60}OH^{\bullet 2+}$, and the product ions arising from the reaction of C_{60}^{2+} with ethanol.

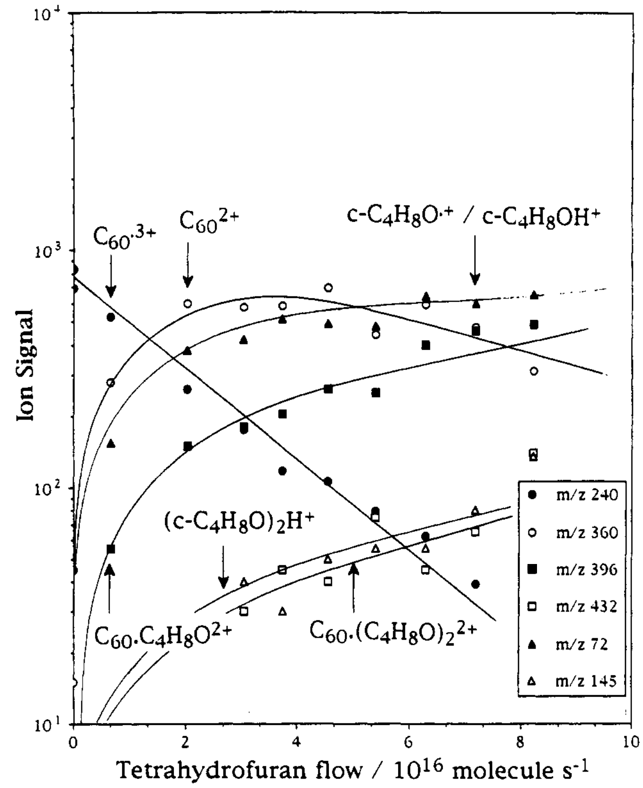


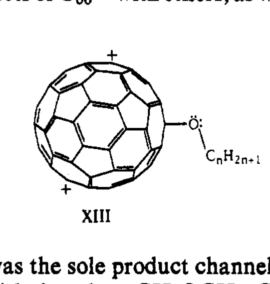
Figure 5. Experimental data for the reaction of $C_{60}^{\bullet 3+}$ with tetrahydrofuran, at 294 ± 2 K and 0.351 Torr of helium. The sole primary product channel seen is charge transfer. Subsequent product ions, $C_{60}{}^{\bullet}(C_4H_8O)_n{}^{2+}$ (n = 1, 2), arising from addition of $c\text{-}C_4H_8O$ to C_{60}^{2+}, are shown also: the monocation $C_{60}^{\bullet +}$, which arises from charge transfer from C_{60}^{2+} to $c\text{-}C_4H_8O$, is not shown.

1-propanol, and 2-propanol: an example is shown in Figure 4, for the reaction with $C_{60}^{\bullet 3+}$ with C_2H_5OH.

The ion $C_{60}OH^{\bullet 2+}$ formed by hydroxide abstraction in reaction 6 was observed to react further by proton transfer to the parent alcohol:

$$C_{60}OH^{\bullet 2+} + ROH \rightarrow C_{60}O^{\bullet +} + ROH_2^+ \qquad (7)$$

We expect that, as with the occurrence of hydroxide abstraction in the reactions of C_{60}^{2+} + ROH, reaction 6 occurs during rearrangement of the collision complex: stabilization of this collision complex (prior to rearrangement or charge transfer) would be expected to yield the adduct $C_{60}O(H)R^{\bullet 3+}$. Adduct formation was noted only with methanol and with 1-propanol and was a minor channel in each instance. The lower incidence of adduct formation from $C_{60}^{\bullet 3+}$ than from C_{60}^{2+} is similar to the trend seen in the reactions of C_{60}^{n+} (n = 1, 2, 3) with the amines $(CH_3)_nNH_{3-n}$ (n = 1, 2, 3) and $CH_3CH_2NH_2$:[34] adduct formation was the sole channel seen in the reactions of $C_{60}^{\bullet +}$, was observed to occur in competition with charge transfer in the reactions of C_{60}^{2+}, and did not occur in the reactions of $C_{60}^{\bullet 3+}$ (from which charge transfer is highly exothermic). The ionization energies of small alcohols and ethers are typically ~1.5–2 eV higher than the IEs of the corresponding amines, and so charge transfer is less exothermic from $C_{60}^{\bullet 3+}$ to ROH or ROR than from $C_{60}^{\bullet 3+}$ to amines: however, the inefficiency of adduct formation in the reactions of $C_{60}^{\bullet 3+}$ with alcohols and ethers is in keeping with the relatively poor nucleophilic character of these species. In those reactions ($C_{60}^{\bullet 3+}$ with methanol, ethanol, 1-propanol) in which adduct formation was observed, the adduct ions $C_{60}O(H)R^{\bullet 3+}$ were observed to react further by proton transfer. We have previously recorded examples of proton transfer from the adducts of $C_{60}^{\bullet 3+}$ with NH_3 and with HCN.[35,39] The deprotonated adducts $C_{60}OR^{\bullet 2+}$ appeared to be substantially less reactive than the addition products $C_{60}O(H)R^{2+}$ formed by association of C_{60}^{2+} + ROH: the absence of proton transfer from $C_{60}OR^{\bullet 2+}$ to ROH suggests either that neither charge in the dication is significantly localized upon the substituent (as in **XIII**) or that the dication cannot donate a proton without undergoing substantial rearrangement—for reasons analogous to those applicable to the reactivity of the adducts of C_{60}^{2+} with ethers, as we have discussed above.



XIII

Charge transfer was the sole product channel observed in the reactions of $C_{60}^{\bullet 3+}$ with the ethers CH_3OCH_3, $C_2H_5OC_2H_5$, and $c\text{-}C_4H_8O$. A typical reaction profile, for the reaction with tetrahydrofuran, is shown in Figure 5.

A slow hydride abstraction channel was evident in the reaction of $C_{60}^{\bullet 3+}$ with water:

$$C_{60}^{\bullet 3+} + H_2O \rightarrow C_{60}H^{\bullet 2+} + OH^+ \qquad (8)$$

We have noted several other examples of slow hydride transfer to fullerene polycations.[25,40] In a study on the reactivity of the ion $C_{60}H^{\bullet 2+}$,[38] we found that proton transfer

$$C_{60}H^{\bullet 2+} + X \rightarrow C_{60}^{\bullet +} + XH^{+} \quad (9)$$

did not occur for neutrals X having a gas-phase basicity GB(X) < 163 kcal mol^{-1}. This is consistent with the lack of reactivity seen for the product ion $C_{60}H^{\bullet 2+}$ with H_2O (GB = 159.0 kcal mol^{-1})[45] in the present system. It is interesting to note that addition of H_2O to $C_{60}^{\bullet 3+}$ is not observed—yet addition of NH_3 to $C_{60}^{\bullet 3+}$ is efficient despite competition with charge transfer (for which the exothermicity is expected to exceed the reverse activation barrier height δ by approximately 20 kcal mol^{-1}).[35,37] As with the tendency for addition of amines to $C_{60}^{\bullet +}$ (while alcohols and ethers fail to do so), this difference in reactivity is in keeping with the greater nucleophilic character of ammonia and the amines.

Implications for Space Chemistry

We have previously suggested[26,30] that the reaction

$$He^{\bullet +} + C_{60} \rightarrow C_{60}^{\bullet +} + He \quad [<0.9] \quad (10a)$$

$$\rightarrow C_{60}^{2+} + He + e \quad [>0.1] \quad (10b)$$

is a source for fullerene mono- and dications within interstellar clouds and circumstellar envelopes. In other studies,[27,35] we have explored the possible reactions of these ions with atomic hydrogen and with ammonia and amines. The low reactivity of these two ions with water, methanol, ethanol, and dimethyl ether (which are all known interstellar molecules)[49] in the present study suggests that reactions with these neutrals are unlikely to constitute substantial sinks for these ions within interstellar environments. In particular, the lack of detectable reactivity of the singly-charged $C_{60}^{\bullet +}$ with any of the neutrals included in the present study suggests that the derivatization of fullerene ions with oxygen-containing substituents is likely to be much less significant than the corresponding derivatization with nitrogen-containing groups. The reactions of double-charged $C_{60}^{\bullet 2+}$ with the larger alcohols do indicate a pathway to formation of $C_{60}OH^+$ and, therefore, by dissociative recombination or by proton transfer, to $C_{60}O$:

$$C_{60}^{2+} + R\text{—}OH \rightarrow C_{60}OH^{+} + R^{+} \quad (11)$$

$$C_{60}OH^{+} + e(M) \rightarrow C_{60}O + H^{\bullet}\,(MH^{+}) \quad (12a)$$

$$\rightarrow C_{60} + OH^{\bullet} \quad (12b)$$

However, several factors mitigate against derivatization, within interstellar clouds or circumstellar envelopes, by this mechanism. Firstly, the apparent unreactivity of all singly-charged fullerene ions with the neutrals surveyed in the present work indicates that neutralization of $C_{60}OH^+$ and other derivatived ions $C_{60}OR^+$ by proton transfer is likely to occur only with neutrals having a high proton affinity: such neutrals are comparatively scarce within interstellar environments, and so neutralization by dissociative recombination (a less "gentle" neutralization method) is likely to dominate. The products of dissociative recombination are difficult to predict: we have proposed previously that fragmentation of the fullerene skeleton by electron–ion recombination is unlikely given its rigidity.[26,30] It is entirely possible that dissociation of pendant groups from the fullerene cage—i.e., breaking the bond between the fullerene surface and the next atom out (in this case, an oxygen atom as in channel 12b)—is the major channel for dissociative recombination. Secondly, it appears that the efficiency of reaction 11 increases with increasing size of the alcohol ROH. Alcohols larger than ethanol have not yet been identified within any interstellar cloud or circumstellar envelope, and it seems probable that propanols and larger alcohols will have low abundances within these objects. For these reasons, we anticipate that the prospects for detection of interstellar or circumstellar oxygenated fullerenes (resulting from reactions with water, alcohols, and ethers) are considerably poorer than the opportunities for detection of the nitrogen analogues of these species, arising from the reactions of fullerene ions with ammonia and amines.

(49) Turner, B. E. *Space Sci. Rev.* **1989**, *51*, 235.

Conclusion

The reactivity of the fullerene ions $C_{60}^{\bullet +}$, C_{60}^{2+}, and $C_{60}^{\bullet 3+}$ with water, alcohols, and ethers has been assessed. $C_{60}^{\bullet +}$ did not react measurably with any of the reactants. Addition was observed in most of the reactions of C_{60}^{2+}, with a clear dependence of addition efficiency upon the size of the neutral reactant. Charge transfer occurred in most reactions of $C_{60}^{\bullet 3+}$, and the reactions of both C_{60}^{2+} and $C_{60}^{\bullet 3+}$ exhibited hydroxide abstraction from all of the alcohols except methanol. Proton transfer from the dicationic adducts of alcohols (but not of ethers) provides support for proposed adduct structures featuring a bond between the fullerene surface and the oxygen atom of the reactant. Proton transfer from the tricationic adducts of alcohols was also evident: the derivatized dications resulting from this deprotonation did not undergo further proton-transfer reactions. The occurrence of addition and hydroxide transfer reactions can be accounted for by a mechanism of nucleophilic attack of the fullerene cation by ROR′. This is in keeping with previous studies in our laboratory of the reactions of C_{60}^{n+} with other classes of compounds.

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