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Gas-Phase Ion/Molecule Reactions of Corannulene, a Fullerene Subunit

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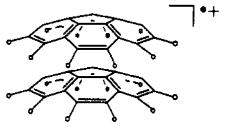
Interest in electronic features of polycyclic aromatic hydrocarbons (PAHs) originated with the concept of aromaticity first formulated by Hückel and has been reborn with the discoveries of corannulene ($C_{20}H_{10}$, dibenzofluoranthene), first synthesized in 1966,[2] and buckminsterfullerene, C_{60}.[3] Corannulene is intriguing, not only because of its highly-strained bowl-like structure,[4] but also as a subunit of C_{60} and other fullerenes. The carbon skeleton of corannulene appears several times in C_{60}, and its curvature mimics the curvature of C_{60}. Inspired by this curiosity, and having previously investigated ion/molecule reactions of C_{60} cations,[5] we began an unprecedented experimental investigation of ion/molecule reactions of corannulene. Here we report the first observations of gas-phase ion/molecule reactions with corannulene: reactions of the corannulene cation ($\text{cor}^{\bullet+}$) with C_{60} and of neutral corannulene with $\text{Ar}^{\bullet+}$, $\text{cor}^{\bullet+}$, $C_{60}^{\bullet+}$, C_{60}^{2+}, and $C_{60}^{\bullet 3+}$. Both electronic and topographical features are expected to be of consequence in many of these reactions.

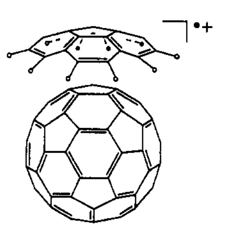
Reactions of $\text{Ar}^{\bullet+}$, $\text{cor}^{\bullet+}$, $C_{60}^{\bullet+}$, C_{60}^{2+}, and $C_{60}^{\bullet 3+}$ with corannulene and of $\text{cor}^{\bullet+}$ with C_{60} were monitored with a selected-ion flow tube (SIFT) apparatus which has been described previously,[6] operating at 294 ± 2 K and at a helium buffer gas pressure of 0.35 ± 0.01 Torr. The cations were generated by electron impact (at energies between 20 and 100 eV) of vaporized corannulene or C_{60}. The corannulene was prepared in the laboratory of Professor Scott according to a new three-step synthesis.[7] Fullerene samples (C_{60}/C_{70}, 2–12%) were obtained from Strem Chemicals Inc. and Termusa. Vapors of corannulene and C_{60} entrained in helium were introduced into the flow tube via a heated stainless-steel inlet tube which allowed the addition of variable, but not measurable, amounts of these substances.

The reaction between $\text{Ar}^{\bullet+}$ and corannulene is a straightforward electron transfer. Interestingly, the resulting $\text{cor}^{\bullet+}$ was observed to undergo an efficient dimerization to form $(\text{cor})_2^{\bullet+}$, but subsequent trimerization was inefficient. $\text{Cor}^{\bullet+}$ derived from corannulene by electron impact was observed to react with C_{60} by adduct formation and electron transfer (see Table I). The counter-reaction of $C_{60}^{\bullet+}$ with corannulene also led to the formation of an adduct ion, and electron transfer was again observed, but in this case as a minor channel (1–10%). (Observation of a second addition of corannulene was beyond the range of our mass spectrometer.) Electron transfer was also observed with C_{60}^{2+} and $C_{60}^{\bullet 3+}$, and in the latter case an unprecedented double electron transfer was observed as a competing channel (see Table I).[8]

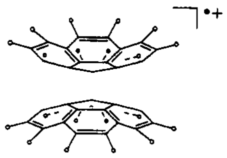
The observations of electron transfer provide insight into the electronic nature of corannulene, specifically the energy required to remove electrons from corannulene. Clearly, the observation of electron transfer in both directions between $\text{cor}^{\bullet+}$ and C_{60} implies that the ionization energies of cor and C_{60} are very close to each other. The preferred direction of electron transfer from C_{60} to $\text{cor}^{\bullet+}$ provides a lower limit for $\text{IE(cor)} \geq \text{IE}(C_{60}) = 7.61 \pm 0.02$ eV,[12] while an upper limit of 7.73 eV can be estimated by attributing the lower efficiency of electron transfer in the reverse direction to endothermicity and applying the Arrhenius expression to derive this endothermicity. As far as we know, no previous determination of IE(cor) is available for comparison. IE(cor) = 7.7 ± 0.1 eV is sufficiently low to make the electron-transfer reaction from cor to C_{60}^{2+} ($\text{IE}(C_{60}^{\bullet+}) = 11.39 \pm 0.05$ eV)[13] and $C_{60}^{\bullet 3+}$ ($\text{IE}(C_{60}^{2+}) = 15.6 \pm 0.5$ eV)[14] sufficiently exothermic (by 3.7 and 7.9 eV, respectively) to overcome the Coulombic barrier (estimated to be 1.8 and 4.5 eV, respectively)[15,16] associated with such reactions. This accounts for our observations of these reactions. The observation of double electron transfer between cor and $C_{60}^{\bullet 3+}$ suggests that less than 14.8 eV is required to remove the second electron from corannulene.



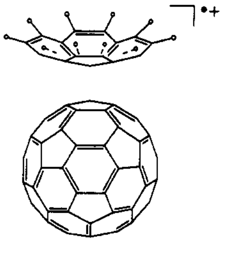
I



III



II



IV

The unprecedented observation of the *rapid* formation of adducts of corannulene with $\text{cor}^{\bullet+}$ and $C_{60}^{\bullet+}$ raises fascinating

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Table I. Branching Ratios and Collision Rate Coefficients for Reactions of the Corannulene Cation with C_{60} and Various C_{60} Cations with Corannulene at 294 ± 2 K in Helium Buffer Gas at a Pressure of 0.35 ± 0.01 Torr

reaction[a]							BR[b]	k_c
$cor^{\bullet+}$	+	C_{60}	→	$cor^{\bullet+}{\cdot}C_{60}$			0.6	1.4
			→	$C_{60}{}^{\bullet+}$	+	cor	0.4	
$C_{60}{}^{\bullet+}$	+	cor	→	$C_{60}{}^{\bullet+}{\cdot}cor$			≥0.9	0.90
			→	$cor^{\bullet+}$	+	C_{60}	≤0.1	
$C_{60}{}^{2+}$	+	cor	→	$C_{60}{}^{\bullet+}$	+	$cor^{\bullet+}$	1.0	1.8
$C_{60}{}^{\bullet 3+}$	+	cor	→	$C_{60}{}^{2+}$	+	$cor^{\bullet+}$	≤0.99	2.7
			→	$C_{60}{}^{\bullet+}$	+	cor^{2+}	≥0.01	

[a] Branching ratio with an estimated uncertainty of ±30%. [b] Collision rate constant in units of 10^{-9} cm^3 molecule^{-1} s^{-1} calculated according to the Langevin or ADO theory.[9] μ_D(cor) = 0.60 D;[10] α(cor) = 25.5 Å^3 and $\alpha(C_{60})$ = 63.9 Å^3.[11]

questions about their stability and structure, particularly given that corannulene is bowl-shaped and that a polar form containing two concentric conjugated systems (an inner cyclopentadienyl anion and a peripheral cyclopentadecaheptaenyl cation) is postulated to contribute significantly to the π electron distribution within this molecule.[3b] **I–IV** depict possible structures for the $(cor)_2{}^{\bullet+}$ and $C_{60}{}^{\bullet+}{\cdot}cor$ adduct ions which were observed. The bonding in these adduct ions is probably dominated by electrostatic interaction in analogy with flat $PAH^{\bullet+}{\cdot}PAH$ dimers.[17,18] If so, the "stacked umbrella" structure **I** of $(cor)_2{}^{\bullet+}$ is expected to be more stable than the "opposing umbrella" structure **II** on the basis of more favorable electrostatic interaction between the negative center of neutral corannulene and the positive charge which is expected to be delocalized primarily in the rim of $cor^{\bullet+}$.[19] If the positive charge on the $C_{60}{}^{\bullet+}{\cdot}cor$ adduct ion is preferentially localized on C_{60} because of its slightly lower IE, the "inverted umbrella" structure **IV** could be more stable than the "umbrella" structure **III** since it minimizes the Coulombic repulsion between the charge on $C_{60}{}^{\bullet+}$ and the delocalized positive charge on the perimeter of corannulene.[20] A relatively strong attractive interaction is expected between the site of positive charge on $C_{60}{}^{\bullet+}$ and the negative charge on the pentagon in corannulene. Finally, it should be noted that the formation of adducts of $C_{60}{}^{\bullet+}$ with benzene, naphthalene, and C_{60} itself is much less efficient,[21,22] presumably because of differences in binding energies arising from differences in electrostatic interactions. Calculations now seem warranted for all five of these adduct ions: $(cor)_2{}^{\bullet+}$, $C_{60}{}^{\bullet+}{\cdot}cor$, $C_{60}{}^{\bullet+}{\cdot}C_6H_6$, $C_{60}{}^{\bullet+}{\cdot}C_{10}H_8$, and $(C_{60})_2{}^{\bullet+}$.

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(17) Meot-Ner, M. *J. Phys. Chem.* **1980**, *84*, 2724. The binding energies of dimer ions involving identical flat PAHs have been measured to be 20 ± 5 kcal mol^{-1}. For different PAHs the binding energies range from 10 to 20 kcal mol^{-1}. These values may be reasonable first approximations to the binding energies of $cor^{\bullet+}{\cdot}cor$ and $C_{60}{}^{\bullet+}{\cdot}cor$, respectively.

(18) The possibility of a Diels–Alder reaction may be ruled out since an anthracene subunit is not available. See: Biermann, D.; Schmidt, W. *J. Am. Chem. Soc.* **1980**, *102*, 3163.

(19) There may also be a significant attractive interaction between the electron-deficient edge of $cor^{\bullet+}$ and the π cloud on corannulene. It is interesting to speculate about the possibility of rotation, in the same or opposite direction, of the two corannulene molecules in structures **I** and **II** and the possibility of a synchronous inversion.

(20) A significant attractive interaction between the electron deficient edge of cor and the π cloud on $C_{60}{}^{\bullet+}$ might invert the expected relative stability of **III** and **IV** and would influence the rotation of C_{60} which can be imagined to occur below the corannulene umbrella in **III** or below the inverted umbrella in **IV**.

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