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[4+2$^+$] Diels-Alder Cycloaddition to C_{60} and C_{70} Radical Cations in the Gas Phase: A Comparison with Solution

Hansjürgen Becker,[†] Gholamreza Javahery, Simon Petrie, and Diethard K. Bohme[*]

Department of Chemistry and Centre for Research in Earth and Space Science, York University,
North York, Ontario, Canada M3J 1P3

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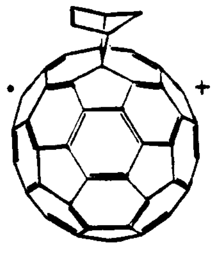
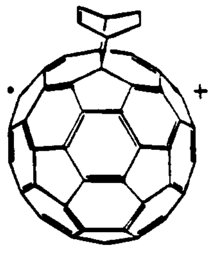
Results of an experimental study using the selected-ion flow tube (SIFT) technique are reported for ion-molecule reactions of $C_{60}^{\bullet+}$ with a variety of cycloalkenes and acyclic and cyclic dienes at 294 ± 2 K in helium gas at a pressure of 0.35 ± 0.01 Torr. Addition is observed only with 1,3-cyclopentadiene and 1,3-cyclohexadiene. Rate coefficients were measured to be 1.0 and 1.5 × 10^{-11} cm^3 molecule^{-1} s^{-1}, respectively. No reactions, $k < 3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, were observed with 1,3-butadiene, isoprene, 1,3-pentadiene, cyclopentene, cyclohexene, furan, and 1,4-cyclohexadiene. These results provide indirect evidence for the occurrence of a Diels-Alder cycloaddition with 1,3-cyclopentadiene and 1,3-cyclohexadiene. The addition reactions of these two molecules with $C_{60}^{\bullet+}$ were found to be 5 ± 1 and 6 ± 2, respectively, faster than the addition reactions with $C_{70}^{\bullet+}$ for which rate coefficients of 2.0 and 2.5 × 10^{-12} cm^3 molecule^{-1} s^{-1}, respectively, were measured. This relative reactivity, which in the case of 1,3-cyclopentadiene is remarkably similar to a reported relative reactivity of 7:1 measured in toluene solution at 293 K, has been interpreted in terms of the hybridization of the C atoms in C_{60} and C_{70}.

It is now well established that fullerene molecules undergo Diels-Alder cycloaddition reactions in *the condensed phase* with a variety of dienes, including cyclopentadiene, furan, isobenzofuran, anthracene, and 2,3-dimethylbuta-1,3-diene.[1,2] For example, up to six molecules of cyclopentadiene have been observed to add to C_{60} in benzene.[3] Very recent kinetic studies of the reactions of C_{60} and C_{70} with cyclopentadiene in excess toluene between 291 and 354 K have indicated activation energies for these two reactions and have shown that C_{60} reacts about 7 times faster than C_{70} at 293 K.[4] An analogous behavior has not yet been established for the gas phase, although it is interesting to note that a C_{60}–C_5H_6 Diels-Alder adduct produced in a low-pressure benzene flame has recently been reported.[5] Here we present results of experimental investigations of *the gas-phase* reactivity of *radical cations* of C_{60} and C_{70} toward acyclic and cyclic dienes and related compounds. (Because of their charge, cations of C_{60} and C_{70} are more easily monitored in the gas phase than their neutral counterparts.) The results reveal a remarkable selectivity of $C_{60}^{\bullet+}$ toward 1,3-cyclopentadiene and 1,3-cyclohexadiene, and so provide indirect evidence for the occurrence of gas-phase Diels-Alder cycloadditions with these two molecules to yield structures **I** and **II**, respectively.



I



II

In our gas-phase experiments, reactions of $C_{60}^{\bullet+}$ and $C_{70}^{\bullet+}$ were monitored with a selected-ion flow tube (SIFT) apparatus.[6] The fullerene cations were produced by electron impact (50 eV) from a mixture of C_{60} and C_{70} (Strem Chemicals, 2–12% C_{70}), mass selected with a quadrupole mass filter, injected into flowing helium gas at 0.35 Torr, allowed to thermalize for 4 ms (ca. 10^3 collisions with He), and then allowed to react with a neutral reagent for 13 ms downstream. The reacting mixture was sampled and mass analyzed with a second quadrupole mass filter as a function of the amount of added neutral reagent. All reagents were of commercial purity (≥95%); the 1,3-cyclopentadiene was freshly distilled just before use. Of all the reactions investigated and listed in Table 1, only those with 1,3-cyclopentadiene and 1,3-cyclohexadiene were observed to proceed by addition with measurable rate coefficients.[7] These translate into efficiencies, k_{obs}/k_c, of 1.1% and 1.5%, respectively. Here k_c is the theoretical *collision* rate coefficient calculated using the average-dipole-orientation (ADO) model of Su and Bowers.[8] A small secondary adduct was observed at the highest additions of 1,3-cyclopentadiene but not with 1,3-cyclohexadiene which has a lower vapor pressure and so could not be added in sufficient amounts.

TABLE 1: Kinetic Results for Reactions of $C_{60}^{\bullet+}$ with a Variety of Cycloalkenes and Acylic and Cyclic Dienes at 294 ± 2 K in Helium Buffer Gas at a Pressure of 0.35 ± 0.01 Torr

reactant	product	k_{obs}[a]	k_c[b]
1,3-butadiene	none	<0.001	0.97
isoprene	none	<0.0005	0.93
1,3-pentadiene	none	<0.002	0.93
cyclopentene	none	<0.002	0.91
cyclohexene	none	<0.002	0.90
1,3-cyclopentadiene	$C_{60}{\cdot}C_5H_6^{\bullet+}$	0.010	0.93
furan	none	<0.0002	1.3
1,3-cyclohexadiene	$C_{60}{\cdot}C_6H_8^{\bullet+}$	0.015	1.0
1,4-cyclohexadiene	none	<0.003	0.90

[a] Apparent bimolecular rate coefficient in units of 10^{-9} cm^3 molecule^{-1} s^{-1} with an uncertainty of less than ±30%. [b] Theoretical collision rate coefficients in units of 10^{-9} cm^3 molecule^{-1} s^{-1} based on the ADO model of Su and Bowers.[6]

Our observations do not allow a direct determination of the structure of the product ions, but they do provide indirect evidence which supports a [4+2$^+$] Diels-Alder cycloaddition reaction. The measurable formation of a stable adduct with 1,3-cyclohexadiene but not with the isomeric 1,4-cyclohexadiene suggests that covalent

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[†] On leave from the Institut für Organische Chemie, Technische Universität Berlin, Strasse des 17 Juni 135, D-1000 Berlin 12, Germany.

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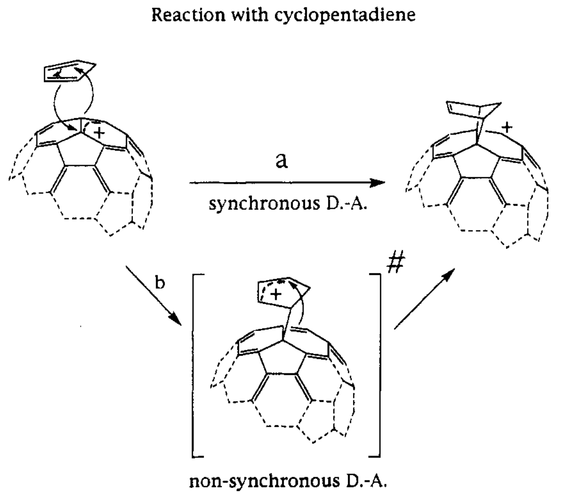

Figure 1. Proposed mechanisms for the cycloaddition of 1,3-cyclopentadiene to $C_{60}^{\bullet+}$ across a bond common to two adjacent hexagons. A parallel mechanism applies for a possible addition across a bond common to an adjacent pentagon and hexagon.

bond formation has occurred with 1,3-cyclohexadiene rather than formation of a more weakly-bound ion/molecule polarization complex.

Also, it is arguable that the additional observation of the failure of $C_{60}^{\bullet+}$ to react with isoprene and 1,3-*trans*-pentadiene within the dynamic range of the technique (see Table 1) provides indirect evidence for the occurrence of cycloaddition with 1,3-cyclopentadiene and 1,3-cyclohexadiene. The collision complex formed with the two acyclic dienes, which have at least the same number of vibrational modes as 1,3-cyclopentadiene, is expected to have a similar or greater lifetime but the wrong configuration for cycloaddition. Isoprene and 1,3-pentadiene are predominantly in their trans rather than cis configuration at room temperature.[9] (The nonreactivity of the acyclic 1,3-butadiene is also readily understood in terms of its preferred trans configuration at room temperature.) Furthermore, given the observed reactivities of 1,3-cyclopentadiene and 1,3-cyclohexadiene and the nonreactivities of cyclopentene and cyclohexene, these results suggest a $[4+2^+]$ rather than a $[2+2^+]$ cycloaddition. The slightly higher reaction efficiency of 1,3-cyclohexadiene compared to the 1,3-cyclopentadiene may reflect the higher flexibility in this molecule which facilitates the matching of the reacting π-orbitals.

The observed nonreactivity with furan is of special interest, particularly given the reported reactivity of furan toward neutral C_{60} in solution.[1a] This gas-phase result is likely to reflect the role of the charge on $C_{60}^{\bullet+}$. Furan is dipolar (μ = 0.66 D)[10] and aromatic, and both of these features are likely to disfavor Diels–Alder cycloaddition to $C_{60}^{\bullet+}$; dipolar alignment will prefer an orientation in which the O atom interacts with the charge and so displaces the interaction with a double bond on furan. Furthermore, electrophilic addition, if it does become allowed by a side-on orientation, will destroy the aromaticity of furan and so should be unfavorable for this orientation as well.

The mechanism which we propose for the addition reactions observed in this study is illustrated in Figure 1. In this mechanism the attack by the diene occurs at the site of positive charge at a 6–6 ring junction[1e] on the C_{60}.[11] We cannot distinguish between synchronous and nonsynchronous σ-bond formation (paths a and b in Figure 1).[12] The end product in this mechanism is Diels–Alder-like, and the charge is expected once again to be delocalized on the C_{60} surface. In a sense then *the charge "catalyzes"* the formation of the Diels–Alder adduct. Our observation of a second adduct indicates that this mechanism repeats itself. Cation-radical-catalyzed Diels–Alder reactions are known in solution[13] and are currently of considerable interest.[14]

Turning now to the relative reactivity of C_{60} and C_{70}, we have found that $C_{60}^{\bullet+}$ reacts 5 ± 1 times faster than $C_{70}^{\bullet+}$ with 1,3-cyclopentadiene at 294 ± 2 K ($k(C_{70}^{\bullet+}) = 2.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}). This result is remarkably similar to the 7:1 ratio measured for the neutral Diels–Alder reaction in toluene solution at 293 K.[4] Should this latter ratio be a measure of the relative *intrinsic* reactivity, this agreement provides further evidence for the occurrence of a Diels–Alder reaction in our gas-phase experiments. We have measured the relative reactivity of $C_{60}^{\bullet+}$ and $C_{70}^{\bullet+}$ with 1,3-cyclohexadiene to be 6 ± 2 ($k(C_{70}^{\bullet+}) = (2.5 \pm 0.8) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}). These latter reactions have not yet been carried out in solution.

We propose that the relatively slow reactions of C_{70} and $C_{70}^{\bullet+}$ can be attributed to the higher degree of π-delocalization around the equatorial belt of C_{70} due to the higher sp^2 character of equatorial carbon atoms.[15] This favors the formation of a π-complex but opposes σ-bond formation and therefore Diels–Alder addition.

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