ELSEVIER International Journal of Mass Spectrometry and Ion Processes 167/168 (1997) 519–524

International Journal of Mass Spectrometry and Ion Processes

The influence of surface strain on the chemical reactivity of fullerene ions: addition reactions with cyclopentadiene and 1,3-cyclohexadiene[1]

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Received 6 December 1996; accepted 29 April 1997

Abstract

Experimental results are presented which demonstrate a dependence of chemical reactivity on the strain present in a carbon lattice. Rate coefficients have been measured at room temperature by using the selected-ion flow tube (SIFT) technique for the gas-phase addition of cyclopentadiene and 1,3-cyclohexadiene to the fullerene monocations $C_{56}^{\cdot+}$, $C_{58}^{\cdot+}$, $C_{60}^{\cdot+}$ and $C_{70}^{\cdot+}$, and the cations derived from corannulene and coronene. The observed reaction efficiencies show a strong dependence on the curvature of the carbon lattice expressed in terms of the pyramidalization (POAV) angle, $\theta_{\sigma\pi} - 90$. The flat, strain-free coronene cation and the slightly strained corannulene cation do not react with a measurable rate, $k < 1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The most severely strained $C_{56}^{\cdot+}$ and $C_{58}^{\cdot+}$ fullerene ions react with a rate within a factor of about 10 of the collision limit. © 1997 Elsevier Science B.V.

Keywords: Strain; Fullerene ions; Coronene; Corannulene; Diels–Alder addition; Chemical reactivity

1. Introduction

With the discovery [1] and production [2] of fullerenes it has become possible to investigate the reactivity of curved carbonaceous surfaces *in the gas phase*. New opportunities have become available to probe the influence of the relief of strain in such surfaces on chemical reactivity and to do so in the absence of surface defects or impurities, as well as in the absence of boundary effects owing to peripheral atoms or dangling bonds which may be preferred as sites of reaction. Haddon has recently proposed that the relief of surface strain should provide a significant driving force for the chemical derivatization of fullerenes as the carbons become four-coordinate [3]. Previous results from our laboratory for addition reactions of $C_{56}^{\cdot+}$, $C_{58}^{\cdot+}$ and $C_{60}^{\cdot+}$ with ammonia, and of C_{56}^{2+}, C_{58}^{2+} and C_{608}^{2+} with acetonitrile, ethylene and n-butane, have provided early, but limited, support for this proposal for ion–molecule reactions in the gas phase [4]. The enhanced reactivities observed for the C_{56} and C_{58} cations in this earlier study were attributed to a higher *sp*^{3} character or degree of pyramidalization of the bonding carbon atoms in these cations arising

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[1] Dedicated to Chava Lifshitz on the ocassion of her 60th birthday, in part for her outstanding contibutions to the chemistry of fullerene and polycyclic aromatic hydrocarbon ions.

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PII S0168-1176(97)00097-9

from the presence of adjacent pentagons, and so to a lower coplanarity of the carbon surface. Concurrent solution studies of the osmylation of C_{70} demonstrated the influence of local curvature and strain relief on reactivity from an analysis of the $C_{70}(OsO_4py_2)_2$ product isomers [5]. Here we present direct experimental evidence for the influence of strain relief on the room-temperature rate of the gas-phase addition of cyclopentadiene and 1,3-cyclohexadiene to the fullerene monocations $C_{56}^{\cdot+}$, $C_{58}^{\cdot+}$, $C_{60}^{\cdot+}$ and $C_{70}^{\cdot+}$ according to reactions (1) and (2) with n = 56, 58, 60 and 70. We have shown previously that the

$$C_n^{\cdot+} + c - C_5H_6 \rightarrow C_nC_5H_5^{\cdot+} \quad (1)$$

$$C_n^{\cdot+} + c - C_6H_8 \rightarrow C_nC_6H_8^{\cdot+} \quad (2)$$

addition reactions with $C_{60}^{\cdot+}$ and $C_{70}^{\cdot+}$ are of the Diels–Alder type and can be compared with the corresponding reactions of neutral fullerenes in solution [6]. Also, we include reactions of the radical cations of coronene and corannulene to provide, respectively, a molecular representative of a strain-free, flat "graphitic" lattice with edges deactivated by hydrogens and a curved carbonaceous surface with intermediate strain.

2. Experimental

The addition reactions with cyclopentadiene and 1,3-cyclohexadiene were achieved in the reaction region of a selected-ion flow tube (SIFT) mass spectrometer in helium buffer gas at 294 ± 2 K and 0.35 ± 0.01 torr [7]. The C_{60}, C_{70}, corannulene and coronene cations were generated by electron impact of the vapours of the parent compounds, while $C_{56}^{\cdot+}$ and $C_{58}^{\cdot+}$ appeared to be produced by the dissociative ionization of C_{60} in the ion source. The reactant ions were selected with a quadrupole mass filter, injected into the flow tube and then allowed to thermalize by collision with helium buffer gas atoms (ca. 10^5 collisions) before entering the reaction region further downstream. The data were analyzed in the usual manner [7]. The rate coefficients for primary reactions reported here are estimated to have an uncertainty of ± 30%. Cyclopentadiene and 1,3-cyclohexadiene were added into the reaction region as vapours diluted with helium. Both were freshly distilled before use. The fullerene sample (~90% C_{60}, ~9% C_{70}) was obtained from Termusa Inc. and was introduced into the ion source without further purification. Corannulene was prepared according to a new three-step synthesis [8a] (for an earlier synthesis of corannulene see [8b]).

3. Results and discussion

The data obtained for the observed addition reactions with cyclopentadiene and 1,3-cyclohexadiene are shown in Fig. 1. Table 1 summarizes the

Table 1
Kinetic results for reactions of a variety of carbonaceous ions with cyclopentadiene and 1,3-cyclohexadiene at 294 ± 2 K in helium buffer gas at 0.35 ± 0.01 torr

Reactant ion	POAV angle[a]	Product	k_{obs}^{b}
$C_{56}^{\cdot+}$	> 12[c], < 16.71[c]	$C_{56}C_5H_6^{\cdot+}$	1.1×10^{-10}
		$C_{56}C_6H_8^{\cdot+}$	1.1×10^{-10}
$C_{58}^{\cdot+}$	> 12[c], < 16.71[c]	$C_{58}C_5H_6^{\cdot+}$	1.2×10^{-10}
		$C_{58}C_6H_8^{\cdot+}$	1.2×10^{-10}
$C_{60}^{\cdot+}$	$\theta_1 = 11.64$[d]	$C_{60}C_5H_6^{\cdot+}$	1.0×10^{-11}
		$C_{60}C_6H_8^{\cdot+}$	1.5×10^{-11}
$C_{70}^{\cdot+}$	$\theta_1 = \theta_2 = 11.96$[e]	$C_{70}C_5H_6^{\cdot+}$	2.0×10^{-12}
	$\theta_3 = 11.46$	$C_{70}C_6H_8^{\cdot+}$	2.5×10^{-12}
	$\theta_4 = 10.06$		
	$\theta_5 = 8.78$		
Corannulene$^{\cdot+}$	$\theta_1 = 7.7(8.2)$[f]	none	$< 1 \times 10^{-13}$
	$\theta_2 = 3.0(3.8)$	none	$< 1 \times 10^{-13}$
	$\theta_3 = 0$		
Coronene$^{\cdot+}$	$\theta_1 = \theta_2 = \theta_3 = 0$	none	$< 1 \times 10^{-13}$
		none	$< 1 \times 10^{-13}$

[a] The POAV angle (in deg) for the positions indicated in Scheme 1.

[b] Apparent bimolecular rate coefficient in units of cm^3 molecule^{-1} s^{-1} with an uncertainty estimated to be less than 30%.

[c] Estimated, see text.

[d] From [9].

[e] From [3,10].

[f] Calculated values from [11] and experimental values from [12]. Experimental values are in parentheses.

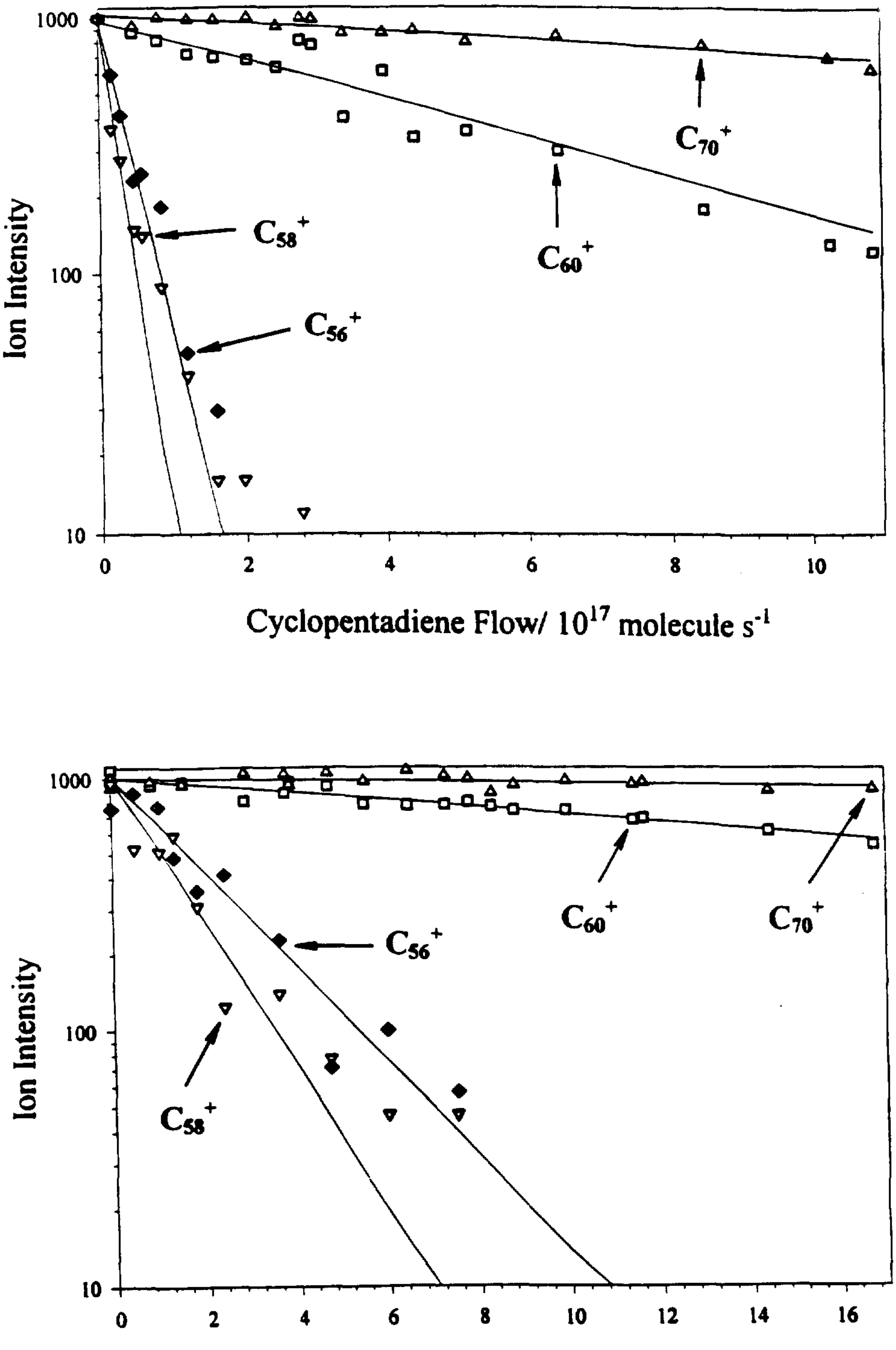


Fig. 1. Data obtained for the addition reactions of fullerene cations with cyclopentadiene and 1,3-cyclohexadiene in helium buffer gas at 0.35 ± 0.01 torr and 294 ± 2 K. The observed decays have been normalized.

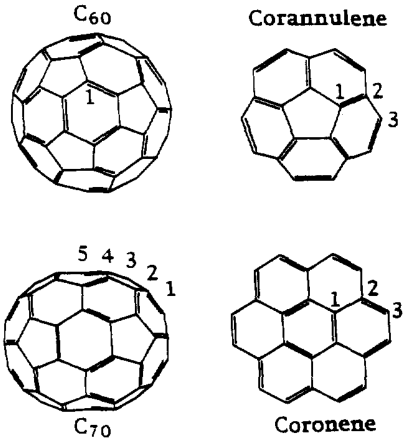
effective bimolecular rate coefficients which were determined. The reaction efficiencies, k_{obs}/k_c, have been estimated by using a collision rate coefficient k_c of 10^{-9} cm^3 molecule^{-1} s^{-1} which is typical for ion/molecule reactions in the gas phase. These results clearly show that fullerene cations are distinctly more reactive than either the corannulene or the coronene cations and that there is a trend in reactivity with the curvature of, and therefore the strain within, the carbon skeleton of the fullerene cations.

We adopt here an index of strain based on the π-orbital axis vector (POAV) analysis of nonplanar conjugated organic molecules [13] that has been applied to neutral fullerenes previously [3]. Strain is expressed in terms of the pyramidalization (POAV) angle, $\theta_{\sigma\pi} - 90$, where $\theta_{\sigma\pi}$ is the angle between the π-orbital axis vector and one of the σ bonds at a conjugated carbon atom [3]. Table 1 provides the theoretical and experimental POAV angles for bonding at the various positions on the fullerenes and on coronene and corannulene that are depicted in Scheme 1. The POAV angle of a cation has been assumed to be equal to that for the corresponding neutral molecule. The POAV angle is 0° for the flat coronene molecule and can exceed 12° for the more strained fullerene cations $C_{56}^{\cdot+}$ and $C_{58}^{\cdot+}$. The upper bound to the POAV angle for the latter has been taken to be equal to the POAV angle of a carbon atom in an ideal [5-5-6] ring which is 16.71° [14]. The strain energy (SE) at a given carbon atom in kcal mol^{-1} can be estimated from Eq. (3), where the angles are expressed in radians [15]

$$SE = 196(\theta_{\sigma\pi} - \pi/2)^2 \qquad (3)$$

For an extreme POAV angle of 16.71°, this amounts to a strain energy per carbon atom of 16.6 kcal mol^{-1}.

Fig. 2 plots the estimated reaction efficiencies for the Diels–Alder addition reactions with cyclopentadiene against $(\theta_{\sigma\pi} - 90)^2$, which is proportional to the strain energy. The behaviour obseved for the reactions with 1,3-cyclohexadiene is essentially identical. The observed reactivity is seen to increase with increasing strain energy. The flat, strain-free coronene cation and even



Scheme 1.

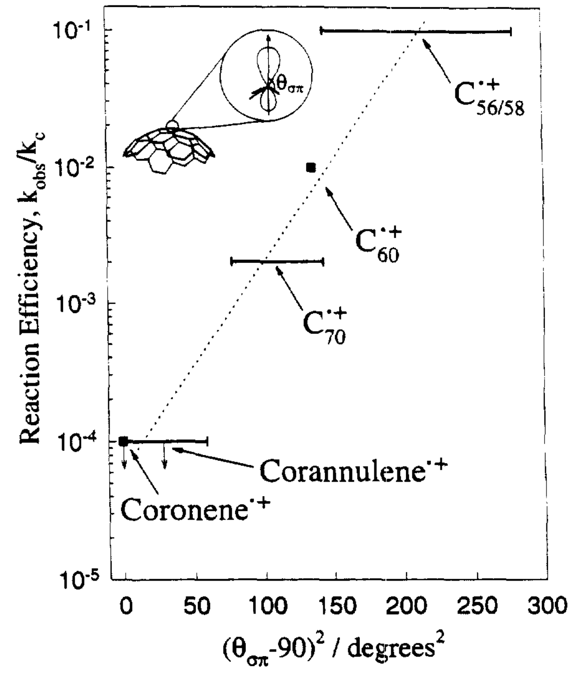


Fig. 2. A correlation of reaction efficiency with the square of the POAV angle, $(\theta_{\sigma\pi} - 90)^2$, for reactions of coronene, corannulene and fullerene cations with cyclopentadiene at room temperature in helium buffer gas at 0.35 torr. The solid bars indicate the range in the POAV angle given in Table 1 for the various carbon positions within these cations. The collision rate coefficient, k_{theor}, has been estimated to be 10^{-9} cm^3 molecule^{-1} s^{-1}.

the slightly strained corannulene cation do not react with a measurable rate, $k < 1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The most severely strained fullerene ions react with a rate within a factor of about 10 of the collision limit. The correlation presented in Fig. 2 leads to the following relationship

$$k_{\mathrm{obs}} = 6.0 \times 10^{-14}\, e^{0.59\mathrm{SE}} \qquad (4)$$

for the dependence of the reaction rate coefficient on strain energy (in kcal mol^{-1}) over the range in POAV angle explored. Unfortunately, we were not able to measure the activation energies for the individual Diels–Alder addition reactions in order to compare them with the computed strain energies.

The trend identified in Fig. 2 suggests a preference in reactivity for carbon atoms with the highest strain energy (or the bond with the highest local curvature) in those cations with more than one site of different strain as is the case, for example, with $C_{70}^{\cdot+}$ and corannulene$^{\cdot+}$ (see Table 1 and Scheme 1). Such regioselectivity was identified in the earlier solution studies of the osmylation of C_{70} [5]. Since then, Hermann et al. [16] have proposed a simple model for the qualitative evaluation of the local curvature on fullerene surfaces and used it to predict the sites of addition in higher fullerenes. These authors have compared their predictions with experimental results on the Diels–Alder reactions of C_{70} and C_{76} with an *ortho*-quinodimethane intermediate generated in situ. Furthermore, they have made comparisons with predictions resulting from π-bond-order considerations and from calculated pyramidalization angles. The experimental results were found to correlate well with the calculated pyramidalization angles.

4. Conclusions

The observations reported here provide a clear demonstration of the driving force of strain relief in ion–molecule reactions leading to the derivatization of curved, carbonaceous molecular ''surfaces'' by Diels–Alder addition in the gas phase. Current models of strain in such carbonaceous environments have been applied to provide a qualitative correlation of reaction efficieny with strain energy. The gas-phase results obtained in this study augment earlier results obtained for similar reactions involving neutral fullerenes in solution.

Acknowledgements

D.K.B. thanks the Natural Sciences and Engineering Research Council of Canada for the financial support of this research. H.B. thanks Professor H. Schwarz and the Fonds der Chemischen Industrie for financial support. L.T.S. is pleased to acknowledge financial support from the US Department of Energy Office of Basic Energy Sciences.

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