the ionization potential of the cyclic conformer to be 3.34 eV (77.0 kcal/mol), one obtains an approximate bond dissociation energy with respect to conformer tGg' of 3.9 kcal/mol for the K(g'Gg') conformer. The theoretical equilibrium bond dissociation energy is 4.8 kcal/mol. If one takes the zero-point vibrational energy correction of −1.3 kcal/mol into account, the agreement is excellent.

In this study, the upper bound of the enthalpy of K₂(en) dissociation has been determined to be 10.4 kcal/mol at 300 K. This is consistent with the theoretical dissociation energy of 7.4 kcal/mol. Approximating the upper bound of the bond dissociation energy of K₂(en) to be 10.4 kcal/mol and taking the photoionization potentials of K₂ and K₂(en) to be 4.06 eV (93.6 kcal/mol) and 3.47 eV (82.3 kcal/mol), respectively, one obtains the upper bound of the bond dissociation energy K₂⁺(en) as 21.3 kcal/mol. The theoretical equilibrium adiabatic bond dissociation energy of K₂⁺(g'Gg') is 22.3 kcal/mol. The consistency between these two values is good.

5. Conclusions

The following conclusions can be drawn from the results of the present photoionization and molecular orbital calculation studies of K(en) and K₂(en).

(a) The basic types of the conformers of K(en) can be generated in a flow reactor, and the photoionization efficiency spectrum can be resolved and interpreted. Only the most stable conformer of K₂(en) was detected by photoionization mass spectrometry at room temperature.

(b) For K(en), the nature of the bonding between the potassium atom and the two amino groups is essentially the same as that of K–NH₃ or K–CH₃NH₂, whether the potassium bond is in the bidentate (cyclic form) or monodentate form (noncyclic form). For K₂(en), the bonding energies are consistently larger than those of K(en). The charge polarization effect of K₂ by ethylenediamine contributes the additional stabilization for the dipotassium systems.

(c) The bond dissociation energies of K(en), K₂(en), K⁺(en), and K₂⁺(en) are internally consistent with each other through energy cycles, both theoretically and experimentally. For the ionization potentials of K(en) and K₂(en), the agreements between the theoretical results and the experimental values are also good.

Derivatization of the Fullerene Dications C₆₀²⁺ and C₇₀²⁺ by Ion–Molecule Reactions in the Gas Phase

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Abstract: Ion–molecule addition reactions which lead to the bonding of the fullerene dications C₆₀²⁺ and C₇₀²⁺ with various neutral molecules, most notably unsaturated hydrocarbons and amines, have been studied using a SIFT apparatus at a pressure of 0.40 ± 0.01 Torr and a temperature of 294 ± 2 K. The efficiency of adduct formation in these reactions shows a dependence upon the ionization energy, the size, and the degree of unsaturation of the molecules in question. A model is presented which relates the efficiency of adduct formation to these parameters.

Introduction

The recent discovery[1] and synthesis[2] of the fullerene series of carbon molecules has provoked a widespread and multifaceted investigation into the properties of these molecules. The ion–molecule reactivity of these species is one area of considerable interest. High-energy collision experiments, for example, have dealt with the competition between fragmentation and incorporation of small neutrals within the fullerene cage.[3–5] In the thermal energy regime, studies to date have focused both on bracketing the first three ionization energies[6–8] and the proton affinity of C₆₀ and C₇₀[9] and on the occurrence of (exohedral) adduct formation in some reactions of atomic ions with C₆₀.[10]

The unique resilience of the fullerene cage and the multiplicity of charge states of fullerenes accessible to various experimental techniques makes them a fascinating field of study. We have recently begun an extensive study of the ion–molecule reactivity of fullerenes[11] and fullerene cations and dications[8,12,13] using the Selected-Ion Flow Tube (SIFT) technique. An area of special interest is the reactivity of the dications C₆₀²⁺ and C₇₀²⁺. While several studies have been reported on the ion–molecule reactivity of atomic dications, notably the doubly-charged rare gas ions He²⁺, Ne²⁺, Ar²⁺, Kr²⁺, and Xe²⁺,[14] and while much effort has gone into characterising the second ionization energies of many molecules by techniques such as charge stripping,[15] double charge transfer,[16] electron impact[17] and photoionization,[18] very little

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Table I. Reactions of C_{60}^{2+} with Various Neutral Molecules

reactant	products[a]	k_{obs}[b]	k_c[c]	$-\Delta H$[d]
H_2	none	<0.001	3.09	
CH_4	none	<0.001	1.91	
C_2H_6	none	<0.001	1.84	
C_3H_8	$C_{60}H^+ + C_3H_7^+$	0.002	1.90	62
$n\text{-}C_4H_{10}$	$C_{60}H^+ + C_4H_9^+$	<0.001	1.90	65
$i\text{-}C_4H_{10}$	$C_{60}H^+ + C_4H_9^+$	0.025	1.91	80
C_2H_2	$C_{60}\cdot C_2H_2^{2+}$	<0.001	1.78	
C_2H_4	$C_{60}\cdot C_2H_4^{2+}$	<0.001	1.86	
CH_3CCH	$C_{60}\cdot C_3H_4^{2+}$	0.5	2.27	
CH_2CCH_2	$C_{60}\cdot C_3H_4^{2+}$	0.08	1.85	
CH_3CHCH_2	$C_{60}\cdot C_3H_6^{2+}$	1.3	1.98	
$CH_2CHCHCH_2$	$C_{60}\cdot C_4H_6^{2+}$ [0.8]	1.0	1.94	
	$C_{60}^{\cdot+} + C_4H_6^{\cdot+}$ [0.2]			54
$1\text{-}C_4H_8$	$C_{60}\cdot C_4H_8^{2+}$	2.2	1.94	
$(Z)\text{-}2\text{-}C_4H_8$	$C_{60}\cdot C_4H_8^{2+}$ [0.2]	3.4	1.96	
	$C_{60}^{\cdot+} + C_4H_8^{\cdot+}$ [0.8]			53
$(CH_3)_2CCH_2$	$C_{60}\cdot C_4H_8^{2+}$ [0.9]	2.4	2.03	
	$C_{60}^{\cdot+} + C_4H_8^{\cdot+}$ [0.1]			50
C_6H_6	$C_{60}^{\cdot+} + C_6H_6^{\cdot+}$	2.3	1.81	50
NH_3	$C_{60}\cdot NH_3^{2+}$	1.2	3.37	
CH_3NH_2	$C_{60}\cdot CH_3NH_2^{2+}$ [0.9]	2.4	2.88	
	$C_{60}^{\cdot+} + CH_3NH_2^{\cdot+}$ [0.1]			54
$CH_3CH_2NH_2$	$C_{60}\cdot C_2H_5NH_2^{2+}$ [0.7]	5.0	2.68	
	$C_{60}^{\cdot+} + C_2H_5NH_2^{\cdot+}$ [0.3]			59
$(CH_3)_2NH$	$C_{60}\cdot(CH_3)_2NH^{2+}$ [0.1]	7.0	2.44	
	$C_{60}^{\cdot+} + (CH_3)_2NH^{\cdot+}$ [0.9]			73
$(CH_3)_3N$	$C_{60}^{\cdot+} + (CH_3)_3N^{\cdot+}$	5.4	2.10	83
X^e	none	<0.001		

[a] Where more than one product channel was detected, branching ratios are given in square brackets. [b] Observed effective bimolecular reaction rate coefficient at 0.40 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,[20] in units of 10^9 cm^3 molecule^{-1} s^{-1}. [d] Exothermicity of reaction in kcal mol^{-1}, calculated using values tabulated by Lias et al.[21] Thermochemical properties relevant to C_{60} are $\Delta H_f^{\circ}(C_{60}^{\cdot+}) = 720$ kcal mol^{-1}, from $\Delta H_f^{\circ}(C_{60}) = 545$ kcal mol^{-1}[22] and IE(C_{60}) = 7.61 ± 0.02 eV;[6,23] $\Delta H_f^{\circ}(C_{60}H^+) = 705$ kcal mol^{-1}, from PA(C_{60}) = 204 kcal mol^{-1};[24] $\Delta H_f^{\circ}(C_{60}^{2+}) = 983$ kcal mol^{-1}, from AP-(C_{60}^{2+}) = 19.00 ± 0.03 eV.[25] [e] No reaction was observed for X = N_2, O_2, CO, N_2O, $NO_2^{\cdot}$, CO_2, or COS.

attention has been given to the reactivity of molecular dications with neutral species. Fullerenes, having comparatively low ionization energies and exceptional stability against fragmentation, represent an ideal candidate for investigations into various aspects of dication chemistry. McElvany et al.[7] have bracketed the second ionization energy of C_{56}, C_{60}, and C_{70} by studying the reactions of C_x^{2+} with various neutrals using the FT-ICR technique. We have also investigated the second ionization energy of C_{60} and C_{70}[8] and the reactions of fullerene cations and dications with atomic and molecular hydrogen.[12]

Here we explore reactions of the fullerene dications C_{60}^{2+} and C_{70}^{2+} with a large variety of other molecules with a view to determining and understanding the efficiency with which these dications may be derivatized.

Experimental Section

The measurements reported here were obtained using a SIFT apparatus which has been described previously.[19] All measurements were obtained at a temperature of 294 ± 2 K in helium buffer gas at a pressure of 0.40 ± 0.01 Torr unless otherwise indicated. The fullerene sample used was obtained from Strem Chemicals Inc. (C_{60}/C_{70}, containing 2-12% C_{70}). Fullerene ions were produced in the ion source by a 50-V electron impact upon fullerene vapor entrained in argon carrier gas. All reagents used were of research grade (99.5 mol % or better). All rate coefficients reported here are expressed as effective bimolecular rate

Table II. Reactions of C_{70}^{2+} with Various Neutrals

reactant	products[a]	k_{obs}[b]	k_c[c]	$-\Delta H$[d]
H_2	none	<0.001	3.09	
CH_4	none	<0.001	1.90	
C_2H_6	none	<0.001	1.84	
C_3H_8	none	<0.001	1.89	
$n\text{-}C_4H_{10}$	none	<0.001	1.89	
$i\text{-}C_4H_{10}$	none	<0.001	1.90	
C_2H_2	$C_{70}\cdot C_2H_2^{2+}$	<0.001	1.78	
C_2H_4	$C_{70}\cdot C_2H_4^{2+}$	<0.001	1.85	
CH_3CCH	$C_{70}\cdot C_3H_4^{2+}$	0.03	2.26	
CH_2CCH_2	$C_{70}\cdot C_3H_4^{2+}$	0.009	1.84	
CH_3CHCH_2	$C_{70}\cdot C_3H_6^{2+}$	>0.4	1.97	
$CH_2CHCHCH_2$	$C_{70}\cdot C_4H_6^{2+}$	1.0	1.93	
	$C_{70}^{\cdot+} + C_4H_6^{\cdot+}$			<51
$1\text{-}C_4H_8$	$C_{70}\cdot C_4H_8^{2+}$	1.8	1.93	
$(Z)\text{-}2\text{-}C_4H_8$	$C_{70}\cdot C_4H_8^{2+}$	2.0	1.95	
	$C_{70}^{\cdot+} + C_4H_8^{\cdot+}$			<51
$(CH_3)_2CCH_2$	$C_{70}\cdot C_4H_8^{2+}$	0.4	2.01	
C_6H_6	$C_{70}^{\cdot+} + C_6H_6^{\cdot+}$	0.14	1.80	<47
NH_3	$C_{70}\cdot NH_3^{2+}$	1.2	3.36	
X^e	none	<0.001		

[a] Due to the low ion signals of C_{70}^{2+} obtainable, branching ratios for these reactions could not be assigned with confidence. [b] Observed effective bimolecular reaction rate coefficient at 0.40 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,[20] in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [d] Exothermicity of reaction in kcal mol^{-1}, calculated using values tabulated by Lias et al.,[21] and IE($C_{70}^{\cdot+}$) <11.3 eV.[8] [e] No reaction was observed for X = N_2, O_2, CO, N_2O, $NO_2^{\cdot}$, CO_2, or COS.

coefficients at a pressure of 0.40 Torr and have an estimated uncertainty of ±40%.

Results and Discussion

Rate coefficients and product distributions for the reactions of C_{60}^{2+} and C_{70}^{2+} with neutral molecules are presented in Tables I and II. The results listed in Table I indicate that adduct formation is much more efficient for the unsaturated hydrocarbons C_2H_2, C_2H_4, C_3H_4, C_3H_6, C_4H_6 and C_4H_8 than it is for H_2 and the saturated hydrocarbons CH_4, C_2H_6, C_3H_8, and C_4H_{10}. Adduct formation is also efficient in the reactions with NH_3 and the amines, except when charge transfer is particularly exothermic. Adduct formation is not seen with the other compounds surveyed. Another observation from Table I is that adduct formation is noticeably much more efficient with the C_3 unsaturated hydrocarbons allene, propyne, and propene than with the analogous C_2 compounds acetylene and ethylene. Why should this be so?

We have used many of the reactions listed in Table I to "bracket" the second ionization energy of C_{60}.[8] During this study, we realized that charge transfer from a dication to a neutral would generally be inhibited by a substantial activation energy barrier arising from the Coulombic repulsion between the two monocation products, which are initially formed in close proximity to each other. The potential energy curve for such a process is shown in Figure 1. The relevance of this curve to the present work is that the activation energy barrier is expected to be preceded by a potential energy well arising from the attractive ion-induced dipole interaction between the reactants. The interaction is likely to be strengthened by the two charges on the dication: the magnitude of the induced dipole on the neutral will be larger for the dication than for the equivalent monocation. The existence of such a potential well (which may be comparatively deep), occurring upon the reaction coordinate before any barriers or constrictions are encountered, favors adduct formation in competition with bimolecular product channels (especially those involving production

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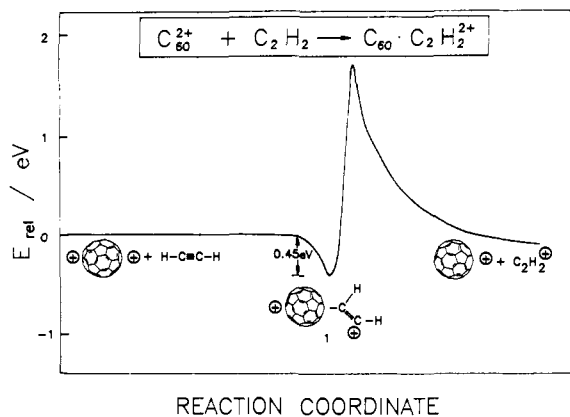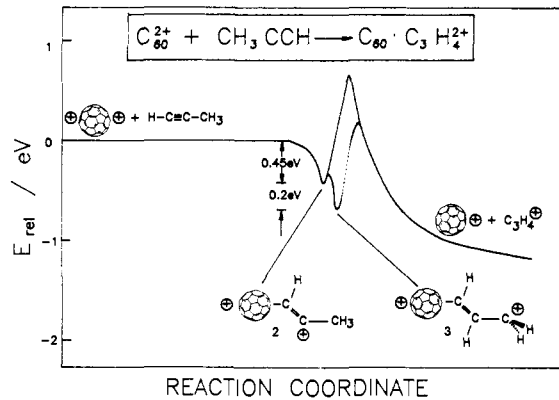
Figure 1. Schematic potential energy curve for association of C_{60}^{2+} with HC≡CH. The well depth of 0.45 eV represents the stabilization arising from the change in charge separation from 7.0 Å (in C_{60}^{2+}) to approximately 9.0 Å (in $C_{60} \cdot C_2H_2^{2+}$); other factors influencing the depth of this potential well, such as the loss of resonance energy associated with charge delocalization in the reactant dication and the formation of a new chemical bond between C_{60}^{2+} and C_2H_2, are not represented in this figure for simplicity. Charge transfer is essentially thermoneutral ($IE(C_{60}^{\bullet+})$ = 11.39 ± 0.05 eV;[8,25] $IE(C_2H_2)$ = 11.40 eV[21]) but is inhibited by a sizeable activation energy barrier.[8]

Figure 2. Schematic potential energy curve for association of C_{60}^{2+} with HC≡CCH₃. The depth of the first minimum on the potential energy surface is likely to be very similar to that for C_2H_2 (see Figure 1) on chemical and electrostatic grounds; the second minimum is expected to be approximately 0.2 eV lower in potential energy due to an increase in charge separation resulting from a 1,2-hydride transfer. Charge transfer is exothermic but, as with C_2H_2, is not observed due to the presence of an activation energy barrier.

of two monocations). While the second ionization potential of C₆₀ is still somewhat uncertain, the exothermicity of bimolecular product channels for the reactions listed in Table I cannot be reliably determined, but it appears that adduct formation can compete very effectively with, for example, charge transfer, as can be seen in the reaction with butadiene, for which the barrier to charge transfer is expected to lie at least 0.4 eV *below* the initial energy of the reactants.[8]

The trend in increasing efficiency of adduct formation with increasing neutral size (best seen, as discussed above, with the unsaturated C₂ and C₃ hydrocarbons but evident also to some extent in a comparison of C₃ and C₄ hydrocarbon reactivity) suggests a correlation between the efficiency of adduct formation and the size of the neutral. While such an effect would be anticipated in accordance with the increase in the lifetime of the collision complex with increasing reactant size or degrees of freedom, the magnitude of the increase in efficiency seems too large to be explained upon these grounds alone. We note that in the case of C₂H₂ and C₂H₄ fewer than one collision in 10³ results in the formation of an adduct, while adduct formation occurs at least 100 times more frequently in the reactions of the unsaturated C₄ hydrocarbons (also involving a competing accessible channel of charge transfer, which should serve to *decrease* the efficiency of adduct formation). These two cases do not differ substantially in the size of the collision complex: $C_{60} \cdot C_2H_4^{2+}$ contains 66 atoms, $C_{60} \cdot C_4H_8^{2+}$ contains 72 atoms. We propose that this trend in observed association rates depends only indirectly upon the size of the reactant neutral, insofar as it mirrors the extent to which adduct formation can provide "Coulombic relaxation" by increased separation of the two charges. For example, if addition of C₂H₂ to C_{60}^{2+} occurs "radially" to form the structure shown in Figure 1, one charge becomes localized upon the β carbon and the other charge is constrained by Coulombic repulsion to reside more or less diametrically opposed to this charge on the other side of the fullerene sphere. Some delocalization (i.e., resonance) energy is therefore lost, which is compensated for by the binding energy of the fullerene–C₂H₂ interaction and by the reduction in Coulombic repulsion between the two, now more distant, charges. If an initial charge separation in C_{60}^{2+} of 7.0 Å (the fullerene cage diameter)[26] is assumed and if the mean charge separation in the $C_{60} \cdot C_2H_2^{2+}$ product ion (**1**) is 9.0 Å, then the decrease in the electrostatic repulsion between the charges is approximately 0.45 eV. In the reaction of C_{60}^{2+} with CH₃CCH shown in Figure 2,

radial addition produces the initial structure shown, with one charge localized upon the β carbon. The energies of interaction for this structure should be very similar to those applicable to structure **1**, but **2** can undergo a 1,2-hydride shift to localize the charge upon the γ carbon atom, forming **3**. The increased charge separation reduces the Coulombic repulsion, and this is likely to stabilize **3** relative to **2** and to **1**. If the mean charge separation in **3** is 10.3 Å, then the electrostatic repulsion in structure **3** is approximately 0.2 eV less than that present in structures **1** and **2**. This should correspond to a clear increase in the potential well depth for $C_{60}^{2+} \cdots C_3H_4$ as against $C_{60}^{2+} \cdots C_2H_2$. Such considerations can account for the consistent trend seen in increasing association reaction rates for the various hydrocarbon series increasing in size from two to four carbons. In this context, it is worth noting that while the association reaction of C_{60}^{2+} + C_2H_2 was observed to occur very slowly at 0.4 Torr, the association reaction of $C_{60}^{\bullet3+}$ + C_2H_2 was noted in an FT-ICR operating at a substantially lower pressure.[7] This can be interpreted in view of the greater "charge crowding" in the trication and the greater exothermicity of the Coulombic relaxation resulting from its association reaction.

The extent of adduct formation is influenced, as is expected, by the existence of competing bimolecular product channels. This is best seen in the reactions of the three isomeric butenes listed in Table I. Adduct formation is the only channel seen in the reaction of C_{60}^{2+} with 1-butene (IE = 9.58 eV), whereas adduct formation accounts for 90% of the products seen for reaction with methylpropene (IE = 9.24 eV) and only 20% of the products of (Z)-2-butene (IE = 9.11 eV). The reaction with (E)-2-butene (IE = 9.10 eV) was not studied, but we would anticipate the reaction rate and product channels to be very similar to those observed for (Z)-2-butene. Charge transfer dominates as the reaction becomes substantially exothermic. It should be noted, however, that geometric factors also favor the exothermicity of adduct formation with 1-butene. Addition to the terminal unsaturated C atom, followed by hydride transfer, can propagate the charge up to four C atoms distant from the fullerene surface, while addition to 2-butene or methylpropene can only lead, at most, to a maximum separation of the charge on the third C atom distant from the fullerene surface.

Association of C_{60}^{2+} is also seen to be efficient with ammonia and amines from the data in Table I, although again, charge transfer becomes dominant for the amines with low ionization energies. Adduct production in these reactions implies the formation of alkylammonium functionalities, wherein the fullerene becomes one of the groups attached to the nitrogen atom; again, Coulombic relaxation plays some part in the stabilization of the adduct. In contrast to the hydrocarbon series studied, there is no clear size dependence for these association reactions. The reaction with the smallest species, NH₃, already occurs at a high

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9180　*J. Am. Chem. Soc., Vol. 114, No. 23, 1992*

Petrie et al.

fraction of the bimolecular collision rate coefficient, and the adduct structure for all the amines is expected to be very similar. The charge is always localized upon the nitrogen atom, one atom "up" from the fullerene surface, so there is little scope for a trend in increasing Coulombic relaxation with increasing amine size.

The further chemistry of several of these adducts is interesting and will be discussed in detail elsewhere.[13]

The association chemistry of C_{70}^{2+}, as detailed by the reactions listed in Table II, is very similar to that of C_{60}^{2+}—as is to be expected given the similarities in structure of these two ions. Two differences are apparent. Firstly, in keeping with the lower second ionization energy of C_{70}, some association reactions are less hindered by competition with charge transfer, as can be seen in the reaction with $(CH_3)_2CCH_2$. Secondly, reaction rates for the association reactions of C_{70}^{2+} are often substantially lower than the corresponding values for C_{60}^{2+}. This latter observation provides support for our proposal that most dication association reactions are driven by a tendency to isolate the two charges: a higher rate of association for C_{70}^{2+} than C_{60}^{2+} would be expected upon the basis of the lifetime of the collision complex in the absence of other factors, while a lower rate is consistent with the greater mean charge separation in the egg-shaped C_{70}^{2+} than in the presumably spherical C_{60}^{2+} since the stabilization gained by Coulombic relaxation (in adding a neutral to the larger dication) is lower. This factor would tend to offset the slight increase in the lifetime of the collision complex otherwise expected for an addition reaction involving C_{70}^{2+}.

The model which we have proposed assumes that the height of the barrier to charge transfer from C_{60}^{2+} to X will depend on the separation between the two positive charges at the instant of charge transfer. Note that this barrier relates only to formation of the products $C_{60}^{\bullet+}$ and $X^{\bullet+}$ and does not in any way impinge upon the migration of charge within the collision complex or adduct—although if the collision complex or adduct *does* dissociate into monocationic fragments, the height of the Coulombic repulsion barrier to this process will be less if charge migration to a greater-than-initial separation has already occurred. We have suggested[8] that such a phenomenon may influence the relative rates of charge transfer from C_{60}^{2+} to $NO^{\bullet}$ and to C_6H_6. The ionization energies of these two neutrals are virtually identical (IE($NO^{\bullet}$) = 9.264 eV, IE(C_6H_6) = 9.246 eV),[21] and yet the observed rate coefficients for charge transfer differ by more than 2 orders of magnitude. This difference in reaction rates is substantially greater than that expected if the reaction efficiency could be determined by a purely Arrhenius-type expression ($k = Ae^{-\Delta E/RT}$), with the preexponential factor A being equivalent for $C_{60}^{2+} + NO^{\bullet}$ and $C_{60}^{2+} + C_6H_6$, but is consistent with a model in which the initial charge separation at the point of charge transfer is somewhat larger for the larger benzene molecular ion than for NO^+.

While a systematic study of the pressure dependence of these association reactions is beyond the scope of this paper, we have performed measurements which indicate that the reaction rate coefficient for association of C_{60}^{2+} with allene does indeed display a dependence upon pressure as shown in Figure 3. We selected allene for this purpose because it has a measurable association rate coefficient which is, however, substantially less than the calculated collision rate coefficient and is thus unlikely to be saturated at our standard operating pressure of 0.4 Torr. The observed results verify this expectation and indicate that termolecular association (collisional stabilization) is the dominant channel at this pressure. There appears, nevertheless, to be a significant channel due to bimolecular (radiative) association: extrapolation of the observed data yields an effective bimolecular rate coefficient at zero pressure of $(2.6 \pm 1.3) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. The possible occurrence of radiative association in this and similar fullerene association reactions is of considerable significance for interstellar cloud chemistry, since fullerenes and highly-unsaturated hydrocarbon species are expected to be significant components of dense interstellar clouds. We thus suggest that many of the association reactions we have reported here should also be viable (albeit perhaps with reduced efficiencies)
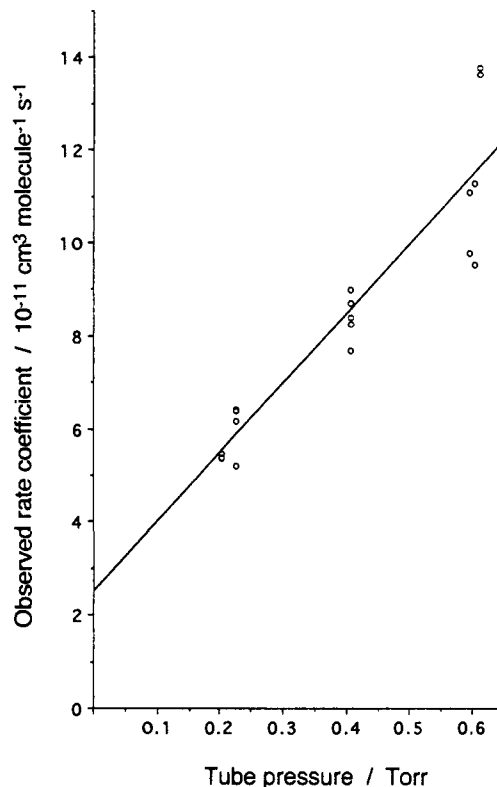

Figure 3. Pressure dependence of the rate coefficient measured for the reaction of C_{60}^{2+} with allene (CH_2CCH_2). The effective bimolecular rate coefficient for this reaction was determined by repeated measurements at helium buffer gas pressures of 0.2, 0.4, and 0.6 Torr. The solid line represents a least-squares fit to the data. $T = 294 \pm 2$ K.

Table III. Reactions of $C_{60}^{\bullet+}$ with Various Neutrals

reactant	products	$k_{obs}{}^a$	$k_c{}^b$
X^c	none	<0.001	
NH_3	$C_{60}{\bullet}NH_3{}^{\bullet+}$	<0.001	1.69
CH_3NH_2	$C_{60}{\bullet}CH_3NH_2{}^{\bullet+}$	0.09	1.44
$CH_3CH_2NH_2$	$C_{60}{\bullet}C_2H_5NH_2{}^{\bullet+}$	0.72	1.34
$(CH_3)_2NH$	$C_{60}{\bullet}(CH_3)_2NH^{\bullet+}$	2.0	1.22
$(CH_3)_3N$	$C_{60}{\bullet}(CH_3)_3N^{\bullet+}$	2.5	1.05

^{a} Observed effective bimolecular reaction rate coefficient at 0.40 Torr, in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}. ^{b} ADO collision rate coefficient, calculated according to the method of Su and Bowers,[20] in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}. ^{c} No reaction was detected for X = H_2, CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10}, C_2H_2, C_2H_4, CH_3CCH, CH_2CC-H_2, CH_3CHCH_2, $CH_2CHCHCH_2$, 1-C_4H_8, (Z)-2-C_4H_8, $(CH_3)_2CC$-H_2, C_6H_6, N_2, O_2, CO, N_2O, $NO_2{}^{\bullet}$, CO_2, or COS.

at much lower pressures than we are able to attain. To this end, a study using FT-ICR or some other "low-pressure" ion–molecule technique would seem to be warranted.

Finally, we note that while C_{60}^{2+} and C_{70}^{2+} are observed to add reasonably readily to several species, the fullerene monocations $C_{60}^{\bullet+}$ and $C_{70}^{\bullet+}$ are seen to be much less reactive. In experiments which we have performed involving these monocations and the neutrals listed in Table I, adduct formation was only observed in the reactions of $C_{60}^{\bullet+}$ and $C_{70}^{\bullet+}$ with NH_3, CH_3NH_2, C_2H_5-NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$. The lower incidence of adduct formation in the reactions of these monocations is consistent with the lesser ion-induced dipole interactions expected for these ions, the very high degree of charge delocalization on the fullerene cation's surface, and the absence of any gain in stability through Coulombic relaxation in these reactions. This last point is illustrated quite clearly by the observation that $C_{60}^{\bullet+}$ adds to amines but not to any of the hydrocarbons studied (see Table III). Adduct stability in the reactions with amines is largely by virtue of the formation of alkylammonium ions, whereas a major component of the stability of hydrocarbon ion adducts (with the dications C_{60}^{2+} and C_{70}^{2+}) arises through the increased charge

Derivatization of Fullerenes C_{60}^{2+} and C_{70}^{2+}

J. Am. Chem. Soc., Vol. 114, No. 23, 1992 9181

separation resulting from adduct formation. (There is clearly no avenue for increasing charge separation in the adducts of the monocation $C_{60}^{•+}$!). The formation of a formal chemical bond in association, for example, in the production of $C_{60}-NH_3^{•+}$, necessitates a transition from a reactant ion with extreme charge delocalization (each carbon atom carries $1/_{60}$ of the total charge) to a product ion possessing an extreme localization of charge (upon the nitrogen atom). The consequent loss of this charge delocalization energy is almost certainly a factor contributing to the apparent unwillingness of $C_{60}^{•+}$ to form addition products. The trend in association rates with amines (increasing amine substitution leads to an increase in the reaction rate) can be accounted for by the relative Lewis base strengths—the willingness to donate an electron pair—of the series of amines. With increasing alkyl substitution, the Lewis base strength increases due to the inductive electron donation tendency of the alkyl groups.[27] Also, it is interesting to note that this trend is *not* consistent with changes in the polarizabilities or dipole moments of the neutral reagents. For NH_3, CH_3NH_2, $CH_3CH_2NH_2$, $(CH_3)_2NH$, and $(CH_3)N$, the polarizabilities have values of 2.18, 4.35, 7.10, 6.37, and 8.15 Å³ and the dipole moments have decreasing values of 1.47, 1.31, 1.22, 1.03, and 0.61 D.[28] Similar comments apply to the reactions of these molecules with C_{60}^{2+} in Table I. The apparent bimolecular rate coefficients for the association reactions of $C_{60}^{•+}$ with dimethyl- and trimethylamine and a number of the reactions of C_{60}^{2+} in Table I are unusually large, easily exceeding the calculated values for the collision rate constant predicted by the ADO theory.[20] This is perhaps not too surprising. The ADO theory cannot be expected to provide an adequate measure of the collision rate constant for these reactions since the fundamental assumption of a point charge for the reactant ion fails badly in the case of the large hollow fullerene cage cations and is likely to lead to an underestimation of the collision rate constant. Furthermore, the likelihood that $C_{60}^{•+}$ and C_{60}^{2+} have high polarizabilities will lead to a relatively larger importance of the secondary dipole/induced dipole interaction between the polar neutral molecule and the polarizable fullerene cation, again resulting in a larger collision rate constant.

Conclusions

Association has been observed to occur efficiently in several reactions of C_{60}^{2+} and C_{70}^{2+} with alkenes, alkynes, and amines.

Association with hydrocarbons shows a clear size dependence, which is interpreted by way of the greater increase in charge separation (Coulombic relaxation) possible with larger hydrocarbons. Association with amines does not show such a size dependence, which is consistent with the roughly equivalent Coulombic relaxation expected for all of these adducts. Association reactions of C_{60}^{2+} are generally more rapid than those of C_{70}^{2+}, which is consistent with the greater degree of charge crowding upon the smaller fullerene's surface.

Association reactions of the dications with unsaturated hydrocarbons are much more efficient than the association reactions of the monocations with these species ($C_{60}^{•+}$ has not been seen to add to any such species). Association reactions of $C_{60}^{•+}$ with NH_3 and amines have been detected. It appears, therefore, that the driving force for amine adduct formation is largely chemical (the interaction between the positively-charged ion and the basic nitrogen atom), whereas a significant component of the driving force for hydrocarbon adduct formation, in the reactions of the dications, is electrostatic (the greater stability of the dication product due to the increase in charge separation and consequent decrease in Coulombic repulsion).

Based on our observations of monocation and dication reactivity and the notion of Coulombic relaxation, we expect that the trications $C_{60}^{•3+}$ and $C_{70}^{•3+}$ will have a greater tendency to form adducts with small unsaturated compounds, as has already been reported in an FT-ICR study[7] which included the association reaction of $C_{60}^{•3+}$ with C_2H_2. We anticipate, however, that most reactions of fullerene trications with larger species will exhibit bimolecular product channels (such as charge transfer, hydride abstraction, etc.) in preference to adduct formation, owing to the high third ionization energy of fullerenes. This expectation mirrors our observation that adduct formation of fullerene dications becomes less efficient as it competes with substantially exothermic charge transfer.

(27) See, for example: Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry*; W. A. Benjamin, Inc: New York, 1965; p 517.

(28) *CRC Handbook of Chemistry and Physics*, 67th ed. Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1986.