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# Selected-Ion Flow Tube Study of Charge Transfer from Fullerene Dications: "Bracketing" the Second Ionization Energies of $C_{60}$ and $C_{70}$

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Rate coefficients are reported for charge-transfer reactions of  $C_{60}^{2+}$  and  $C_{70}^{2+}$  with various neutral molecules at  $294 \pm 2$  K. Charge transfer is not observed for molecules with ionization energy (IE)  $\geq 9.69$  eV (for  $C_{60}^{2+}$ ) and IE  $\geq 9.26$  eV (for  $C_{70}^{2+}$ ), in keeping with a recent Fourier transform-ion cyclotron resonance (FT-ICR) study. Nevertheless, our observations support a number of experimental and theoretical determinations of IE( $C_{60}^{++}$ ) for which a substantially larger value was obtained, and we propose an upper limit of IE( $C_{60}^{++}$ )  $< 11.8$  eV. The absence of charge transfer from  $C_{60}^{2+}$  to molecules having ionization energies in the range 9.7–11.8 eV is accounted for by a reaction barrier arising from the Coulombic repulsion between the two adjacent monocationic fragments of such a charge-transfer process.

## Introduction

A very large number of studies of the chemical and physical properties of fullerene molecules has followed the discovery<sup>1</sup> and synthesis<sup>2</sup> of the prototypical fullerene  $C_{60}$ , Buckminsterfullerene. Several studies have been reported which are concerned with the ionization energies of  $C_{60}$ . There is good agreement between recently reported values of the first ionization energy, IE( $C_{60}$ ) = 7.57–7.61 eV.<sup>3–6</sup> However, the second ionization energy, IE( $C_{60}^{++}$ ), has remained controversial. McElvany et al.<sup>5</sup> have reported a low value for IE( $C_{60}^{++}$ ) of  $9.7 \pm 0.2$  eV based on bracketing measurements with an FT-ICR (Fourier transform-ion cyclotron resonance) apparatus:  $C_{60}^{2+}$  was observed to charge transfer to *m*-nitrotoluene (IE = 9.48 eV) but not to hexafluorobenzene (IE = 9.91 eV) or to compounds having higher ionization energies. Lifshitz et al.<sup>7</sup> obtained a high value of  $12.25 \pm 0.5$  eV for the second ionization energy from measurements of translational energy loss in charge-stripping reactions of  $C_{60}^{++}$ . The  $\geq 1.85$  eV ( $\geq 43$  kcal mol<sup>-1</sup>) discrepancy between these extremes for IE( $C_{60}^{++}$ ) has been straddled by several other reported values. Rosén and Wästberg<sup>8</sup> have calculated IE( $C_{60}^{++}$ ) using the local density approximation, obtaining values of 10.1 and 10.8 eV by two different methods. Caldwell et al.<sup>9</sup> have recently obtained a value of  $11.9 \pm 0.5$  eV by the charge-stripping method. Yoo et al.<sup>6</sup> also determined IE( $C_{60}^{++}$ )  $\sim 11.9$  eV by photoionization of  $C_{60}$  using He I, He II, Ne I, and Ne II photoelectron spectroscopy. However, these latter authors have also commented<sup>6</sup> that extrapolation of this value from the observed spectra is contentious given the degree of curvature evident near the threshold for  $C_{60}^{2+}$  formation. An appearance potential study<sup>10</sup> cited by Cox et al.<sup>11</sup> also favors a lower value: AP( $C_{60}^{2+}$ )  $< 18$  eV, which, using IE( $C_{60}$ ) = 7.61 eV, implies IE( $C_{60}^{++}$ )  $< 10.4$  eV. A value of 11.2 eV has recently been calculated by Gallup.<sup>12</sup> Finally, a value for IE( $C_{60}^{++}$ ) =  $11.39 \pm 0.05$  eV can be derived from the direct double-ionization energy of  $19.00 \pm 0.03$  eV determined recently by Steger et al. using synchrotron radiation.<sup>13</sup>

We have recently embarked upon a systematic study of the ion-molecule reactivity of the fullerene molecules  $C_{60}$  and  $C_{70}$  and the ions  $C_{60}^{++}$ ,  $C_{60}^{2+}$ ,  $C_{70}^{++}$ , and  $C_{70}^{2+}$ , using the selected-ion flow tube (SIFT) technique.<sup>14</sup> As a component of this study, we have examined the reactions of  $C_{60}^{2+}$  and  $C_{70}^{2+}$  with several neutral molecules having a wide range of ionization energies. The intent was to explore the kinetics of such reactions and also to bracket the ionization energies of  $C_{60}^{++}$  and  $C_{70}^{++}$  in a manner similar to that reported by McElvany et al.<sup>5</sup> but under quite different experimental conditions. Our results are in agreement with those of McElvany et al.,<sup>5</sup> but an analysis of a reaction barrier in the charge-transfer reactions of the doubly-charged fullerene cations arising from Coulombic repulsion between the singly-charged product ions shows support for higher values of the ionization energies of  $C_{60}^{++}$  and  $C_{70}^{++}$ .

TABLE I: Rate Coefficients and Product Distributions for Reactions of the Type  $C_{60}^{2+} + X$ , with Neutral Molecules X Having 9.0 eV  $<$  IE(X)  $<$  13.0 eV

reactants	products <sup>a</sup>	$k_{\text{obs}}^b$	$k_c^c$	IE(X) <sup>d</sup>
$C_{60}^{2+} + N_2O$	none	$< 0.001$	1.30	12.886
$C_{60}^{2+} + CH_4$	none	$< 0.001$	1.91	12.51
$C_{60}^{2+} + O_2$	none	$< 0.001$	1.06	12.071
$C_{60}^{2+} + C_2H_6$	none	$< 0.001$	1.84	11.52
$C_{60}^{2+} + C_2H_2$	$C_{60}C_2H_2^{2+}$	$< 0.001$	1.78	11.400
$C_{60}^{2+} + COS$	none	$< 0.001$	1.74	11.1736
$C_{60}^{2+} + C_2H_4$	$C_{60}C_2H_4^{2+}$	$< 0.001$	1.86	10.507
$C_{60}^{2+} + CH_3CCH$	$C_{60}C_3H_4^{2+}$	0.5	2.27	10.36
$C_{60}^{2+} + NH_3$	$C_{60}NH_3^{2+}$	1.2	3.37	10.16
$C_{60}^{2+} + NO_2^+$	none	$< 0.01$	1.35	9.75
$C_{60}^{2+} + CH_3CHCH_2$	$C_{60}C_3H_6^{2+}$	0.6	1.98	9.73
$C_{60}^{2+} + CH_2CCH_2$	$C_{60}C_3H_4^{2+}$	0.08	1.85	9.69
$C_{60}^{2+} + 1-C_4H_8$	$C_{60}C_4H_8^{2+}$	2.2	1.94	9.58
$C_{60}^{2+} + NO^+$	$C_{60}^{++} + NO^+$	0.02	1.18	9.26436
$C_{60}^{2+} + C_6H_6$	$C_{60}^{++} + C_6H_6^{++}$	2.3	1.81	9.2459
$C_{60}^{2+} + (CH_3)_2CCH_2$	$C_{60}C_4H_8^{2+}$ [0.9]	2.4	2.03	9.239
	$C_{60}^{++} + C_4H_8^{++}$ [0.1]			
$C_{60}^{2+} + (Z)-2-C_4H_8$	$C_{60}C_4H_8^{2+}$ [0.2]	3.4	1.96	9.108
	$C_{60}^{++} + C_4H_8^{++}$ [0.8]			
$C_{60}^{2+} + CH_2CHCHCH_2$	$C_{60}C_4H_8^{2+}$ [0.8]	1.0	1.94	9.07 <sup>e</sup>
	$C_{60}^{++} + C_4H_6^{++}$ [0.2]			

<sup>a</sup> Where more than one product channel was detected, product ratios are reported in square brackets. <sup>b</sup>  $k_{\text{obs}}$  is the observed reaction rate coefficient, in units of  $10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, at  $294 \pm 2$  K and a helium pressure of  $0.40 \pm 0.01$  Torr. <sup>c</sup>  $k_c$  is the ADO collision rate coefficient, in units of  $10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, calculated according to the method of Su and Bowers.<sup>16</sup> <sup>d</sup> IE(X) is the ionization energy, in electronvolts, of the neutral in question, as listed in the tabulation of Lias et al.<sup>17</sup> <sup>e</sup> IE( $CH_2CHCHCH_2$ ) obtained from ref 18.

## Experimental Section

The measurements reported here were obtained by using a SIFT apparatus which has been described previously.<sup>15</sup> All were performed at  $294 \pm 2$  K in helium buffer gas at a pressure of  $0.40 \pm 0.01$  Torr. All reagents used were of C.P. grade or better. The fullerene sample used was obtained from Strem Chemicals Co. ( $C_{60}/C_{70}$ , containing 2–12%  $C_{70}$ ).  $C_{60}^{2+}$  and  $C_{70}^{2+}$  were produced in the ion source by 50-V electron bombardment of fullerene vapor entrained in argon carrier gas. The reported rate coefficients are estimated to have an uncertainty of  $\pm 40\%$ .

## Results and Discussion

Results are presented in Tables I and II for reactions of  $C_{60}^{2+}$  and  $C_{70}^{2+}$  with neutral molecules having ionization energies in the range 9.0–13.0 eV. The broader chemistry of fullerene dications will be discussed in detail elsewhere;<sup>14</sup> here we concern ourselves with the occurrence and absence of charge transfer from  $C_{60}^{2+}$  and  $C_{70}^{2+}$  as a function of the ionization energy of the neutral molecule.

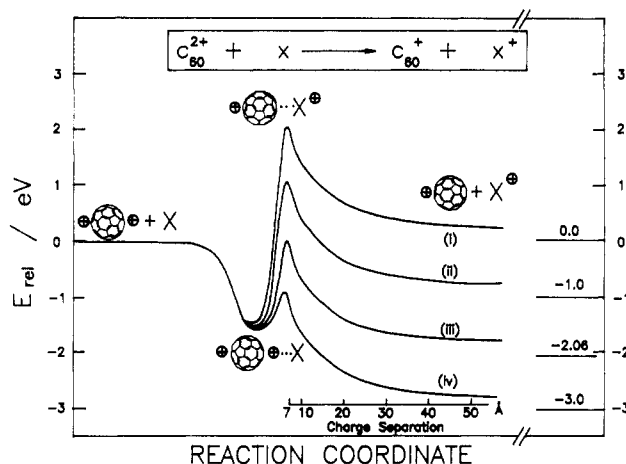
**TABLE II: Rate Coefficients and Product Distributions for Reactions of the Type  $C_{70}^{2+} + X$ , with Neutral Molecules  $X$  Having  $9.0 \text{ eV} < \text{IE}(X) < 13.0 \text{ eV}$** 

reactants	products <sup>a</sup>	$k_{\text{obs}}^b$	$k_c^c$	$\text{IE}(X)^d$
$C_{70}^{2+} + N_2O$	none	<0.001	1.30	12.886
$C_{70}^{2+} + CH_4$	none	<0.001	1.90	12.51
$C_{70}^{2+} + O_2$	none	<0.001	1.06	12.071
$C_{70}^{2+} + C_2H_6$	none	<0.001	1.84	11.52
$C_{70}^{2+} + C_2H_2$	$C_{70}C_2H_2^{2+}$	<0.001	1.78	11.400
$C_{70}^{2+} + COS$	none	<0.001	1.73	11.1736
$C_{70}^{2+} + C_2H_4$	$C_{70}C_2H_4^{2+}$	<0.001	1.85	10.507
$C_{70}^{2+} + CH_3CCH$	$C_{70}C_3H_3^{2+}$	0.03	2.26	10.36
$C_{70}^{2+} + NH_3$	$C_{70}NH_3^{2+}$	0.7	3.36	10.16
$C_{70}^{2+} + NO_2$	none	<0.01	1.35	9.75
$C_{70}^{2+} + CH_3CHCH_2$	$C_{70}C_3H_6^{2+}$	>0.4	1.97	9.73
$C_{70}^{2+} + CH_3CCH_2$	$C_{70}C_3H_5^{2+}$	0.009	1.84	9.69
$C_{70}^{2+} + 1-C_4H_8$	$C_{70}C_4H_8^{2+}$	1.8	1.93	9.58
$C_{70}^{2+} + NO^+$	none	<0.001	1.18	9.26436
$C_{70}^{2+} + C_6H_6$	$C_{70}^{++} + C_6H_6^{++}$	0.14	1.80	9.2459
$C_{70}^{2+} + (CH_3)_2CCH_2$	$C_{70}C_4H_8^{2+}$	0.3	2.01	9.239
$C_{70}^{2+} + (Z)-2-C_4H_8$	$C_{70}C_4H_8^{2+}$	2.0	1.95	9.108
$C_{70}^{2+} + CH_2CHCHCH_2$	$C_{70}^{++} + C_4H_8^{++}$			
	$C_{70}^{++} + C_4H_6^{++}$	1.0	1.93	9.07 <sup>e</sup>

<sup>a</sup> Because the ion signal  $m/z$  420 ( $C_{70}^{2+}$ ) was low, product signal intensities were too low to allow the confident assignment of product ratios. <sup>b</sup>  $k_{\text{obs}}$  is the observed reaction rate coefficient, in units of  $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , at  $294 \pm 2 \text{ K}$  and a helium pressure of  $0.40 \pm 0.01 \text{ Torr}$ . <sup>c</sup>  $k_c$  is the ADO collision rate coefficient, in units of  $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , calculated according to the method of Su and Bowers.<sup>16</sup> <sup>d</sup>  $\text{IE}(X)$  is the ionization potential, in electronvolts, of the neutral in question, as listed in the tabulation of Lias et al.<sup>17</sup> <sup>e</sup>  $\text{IE}(\text{CH}_2\text{CHCHCH}_2)$  obtained from ref 18.

As can be seen from Table I, our results are entirely consistent with the findings of McElvany et al.<sup>5</sup> who have reported charge transfer from  $C_{60}^{2+}$  to *m*-nitrotoluene ( $\text{IE} = 9.48 \text{ eV}$ ) but not to perfluorobenzene ( $\text{IE} = 9.91 \text{ eV}$ ) in an FT-ICR study. In fact, the absence of charge transfer to allene ( $\text{IE} = 9.69 \text{ eV}$ ) observed in our experiments suggests a lower ionization energy for  $C_{60}^{++}$  than the bracketed value  $\text{IE}(C_{60}^{++}) = 9.7 \pm 0.2 \text{ eV}$  from the FT-ICR study.<sup>5</sup> In our study, charge transfer was also not evident in the reaction of  $C_{60}^{2+}$  with 1-butene ( $\text{IE} = 9.58 \text{ eV}$ ), although the efficient occurrence of adduct formation in this reaction makes it less favorable as an upper limit to a bracketed value for  $\text{IE}(C_{60}^{++})$ . However, although our findings corroborate and support those of McElvany et al. with regard to the reactivity of  $C_{60}^{2+}$ , we feel that considerable care must be taken in deriving the ionization energy of  $C_{60}^{++}$ . This ionization energy cannot simply be bracketed by the observed occurrence or absence of charge transfer to a neutral ion IE, because the electrostatic interaction between two monocations separated by a few angstroms is considerable and repulsive: hence the heat of formation of a pair of monocations separated by a few angstroms does not correspond to the sum of the monocations' standard heats of formation at infinite separation. Figure 1 illustrates in a schematic fashion the expected potential energy curve for charge transfer from a dication to a neutral molecule  $X$ . The Coulombic repulsion between the two monocations produced by such a reaction can constitute a barrier to the reaction unless the reaction is substantially exothermic or unless the two monocations are produced at a sufficiently large distance that electrostatic repulsion is negligible. We consider that charge transfer is most likely to occur when the reactants are in close proximity, since at large separation there will be negligible interaction between the reactants. A substantially similar model has been used to account for the observed kinetics of charge-transfer and hydride-abstraction reactions involving alkaline-earth<sup>19</sup> and transition-metal containing<sup>20,21</sup> dications.

The requirement for charge transfer from a dication to a neutral molecule, producing two monocations initially in close proximity, is that the reaction exothermicity must exceed  $q\phi_r$ , the electrostatic potential which denotes the Coulombic repulsion between the monocations at the moment of charge transfer. The Coulombic



**Figure 1.** Schematic diagram of the potential energy surface for charge transfer from the dication  $C_{60}^{2+}$  to a neutral  $X$ .  $E_{\text{rel}}$  is the potential energy relative to the standard enthalpies of formation of the reactants at infinite separation. The diagram assumes that charge transfer occurs at the point of closest approach and that the binding energy of the products is negligible in comparison to the electrostatic repulsion between them. The Coulomb repulsion term  $q\phi_r$  is set at  $2.06 \text{ eV}$ , corresponding to an interchange separation, at the point of charge transfer, of  $7.0 \text{ Å}$ . The curves shown are for the following cases: (i),  $\text{IE}(X) = \text{IE}(C_{60}^{++})$ ; (ii),  $\text{IE}(X) = \text{IE}(C_{60}^{++}) - 1.0 \text{ eV}$ ; (iii),  $\text{IE}(X) = \text{IE}(C_{60}^{++}) - q\phi_r$ ; (iv),  $\text{IE}(X) = \text{IE}(C_{60}^{++}) - 3.0 \text{ eV}$ .

repulsion depends upon the distance separating the two charges. If it is assumed that the charge separation  $r$  at charge transfer is equal to or greater than the diameter of the fullerene cage ( $d(C_{60}) \sim 7.0 \text{ Å}$ ),<sup>22</sup> then  $q\phi_r < 2.06 \text{ eV}$ . This assumption seems warranted—while the structure of  $C_{60}^{2+}$  has not been determined rigorously, the most likely model for such a structure involves two fully delocalized positive charges which are constrained by Coulombic forces to constantly remain more-or-less opposite each other.

The rapid occurrence of charge transfer from  $C_{60}^{2+}$  requires that  $\text{IE}(C_{60}^{++}) - \text{IE}(X) \geq q\phi_r$ . The results detailed in Table I imply that this criterion is met for charge transfer to benzene ( $\text{IE} = 9.246 \text{ eV}$ ) but not, apparently, for nitric oxide ( $\text{IE} = 9.264 \text{ eV}$ ), suggesting that the charge separation at the point of charge transfer is greater in benzene than is possible in the case of most collisions with  $NO^+$ . Because the Coulombic interaction which can impede the reaction efficiency is distance dependent, reactivity experiments (such as the present study) cannot yield reliable thermochemical information unless the charge separation at the point of charge transfer is known. We can surmise, however, that the charge transfer most probably occurs when  $C_{60}^{2+}$  and  $X$  are in reasonable proximity—between zero and three angstroms in separation—and that the ion-induced dipole interaction favors localization of one positive charge at the point of collision of  $C_{60}^{2+}$  and  $X$ , with the other charge diametrically opposed on the fullerene surface. In this scenario, the reaction cannot occur efficiently unless charge transfer is exothermic by  $\sim 1.4$ – $2.0 \text{ eV}$ , with the lower value corresponding to a charge separation of  $10 \text{ Å}$ —that is, when the reactant neutral  $X$  is  $3 \text{ Å}$  from the surface of the  $C_{60}$  dication. We have no direct evidence that charge transfer does not occur at greater charge separations via a harpoon mechanism, but, as stated earlier, at large distances there is little interaction between the reactants and thus there is very little opportunity or incentive for the polarization of charge on the fullerene and a consequent reaction to occur. We note that, in the reactions studied here, the calculated ADO (average dipole orientation) collision rate coefficient (the calculation of which assumes a relatively close interaction) appears to serve as a good upper limit to the observed reaction rates for charge transfer. We conclude that charge transfer from  $C_{60}^{2+}$  to a neutral occurs via a close interaction between the reactants.

As a result of the reaction studies performed here, we recommend an upper limit for  $\text{IE}(C_{60}^{++}) \leq 11.8 \text{ eV}$ . This value is based on the absence of charge transfer to allene ( $\text{IE} = 9.69 \text{ eV}$ ) or to

any compound having a higher IE and on the expected maximum Coulombic repulsion of 2.06 eV between the product ions if the initial charge separation is equal to the  $C_{60}^{2+}$  cage diameter. We also expect that the true value for this ionization energy must be at least 10.9 eV based on the observation, by McElvany et al.,<sup>5</sup> of charge transfer to *m*-nitrotoluene (IE = 9.48 eV) and on the electrostatic repulsion of 1.44 eV for a charge separation of 10 Å at the point of charge transfer.

The observation of reasonably efficient adduct formation in many of the reactions studied here is consistent with our model for charge transfer in which a potential well precedes the transition state to charge transfer. The existence of such a potential well would favor the occurrence of addition processes, especially insofar as they present an opportunity for "coulombic relaxation"—that is, to reduce the repulsive force between the positive charges by increasing the charge separation in the adduct. This topic will be discussed in more detail elsewhere.<sup>14</sup>

The charge-transfer reactivity of  $C_{70}^{2+}$  (see Table II) is analogous to that of  $C_{60}^{2+}$ , and similar energetic constraints are expected to apply for charge transfer from  $C_{70}^{2+}$  to a neutral molecule. If the minimum charge separation at the point of charge transfer is again taken as 7 Å, then our failure to detect charge transfer from  $C_{70}^{2+}$  to  $NO^+$  (IE = 9.264 eV) implies an upper limit of  $IE(C_{70}^{++}) \leq 11.3$  eV. In fact, the slightly larger long axis of the  $C_{70}$  fullerene cage implies that the charge separation  $r$  at the point of charge transfer is larger than for processes involving  $C_{60}^{2+}$ , so the Coulombic repulsion in the case of  $C_{70}^{2+}$  is likely to be less than for reactions of  $C_{60}^{2+}$ .

### Conclusions

The reactivity of the fullerene dications  $C_{60}^{2+}$  and  $C_{70}^{2+}$ , in the present work, is compatible with the findings of McElvany et al.<sup>5</sup> who studied several charge-transfer processes involving these ions in an FT-ICR experiment. The magnitude of the apparent discrepancy between the earlier FT-ICR bracketed  $IE(C_{60}^{++})$  and the other experimental determinations of  $IE(C_{60}^{++})$ <sup>6,7,9,13</sup> is consistent with the expected electrostatic repulsion between two like charges separated by a distance equal to, or not substantially greater than, the diameter of the  $C_{60}$  fullerene cage. As a result of our studies, we recommend an upper limit of  $IE(C_{60}^{++}) \leq 11.8$  eV and of  $IE(C_{70}^{++}) \leq 11.3$  eV.

The existence of substantial energetic barriers to near-thermoneutral charge-transfer processes in the interactions of dications with neutral molecules raises an interesting point with respect to the stability of molecular dications. The coulombic repulsion between charges in such a dication would seem, intuitively, to be a destabilizing influence on these species: however, since this repulsion cannot be greatly lessened (at close separation) by the occurrence of charge transfer, molecular dications are more stable with regard to a charge-exchanging reaction with neutral molecules than their high enthalpies of formation would indicate. This consideration should apply not only to charge transfer from dications but to hydride abstraction, proton transfer, and other reactions of dications which involve transfer or abstraction of a charged moiety.<sup>21</sup> While exothermic monocation/neutral reactions generally occur with high efficiency, it appears that exothermic dication/neutral reactions often will not be efficient because of

the existence of very substantial barriers to reaction. For this reason, we anticipate that dication thermochemistry will not prove such a useful tool in comprehending dication reactivity as is the case for monocations: conversely, the derivation of thermochemical information from studies of dication reactivity will not be as facile or as reliable as has been the case, for example, in determining proton affinity values from proton-transfer reactions involving monocations.

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