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Selected-ion flow tube studies of reactions of C_{60}^{n+} ($n = 1, 2, 3$) with chlorinated ethylenes

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Abstract

The chlorination of singly and multiply charged C_{60} cations has been investigated using the selected-ion flow tube (SIFT) technique with chlorinated ethylenes as possible chlorinating agents. Observations are reported for the reactions of $C_{60}^{\cdot+}$, C_{60}^{2+}, and $C_{60}^{\cdot 3+}$ with $CH_2{=\!=}CHCl$, $CH_2{=\!=}CCl_2$, *trans*-$CHCl{=\!=}CHCl$, *cis*-$CHCl{=\!=}CHCl$, $CHCl{=\!=}CCl_2$ and $CCl_2{=\!=}CCl_2$ at room temperature (295 ± 2 K) in helium at a total pressure of 0.35 ± 0.02 Torr. The results generally are consistent with previous studies of the reactivities of these three ionized states of C_{60} under SIFT conditions. $C_{60}^{\cdot+}$ was observed not to react in any way and $C_{60}^{\cdot 3+}$ reacted exclusively by rapid electron transfer, $k > 1.0 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. C_{60}^{2+} was observed to be less reactive with values of k in the range from 1.5×10^{-12} to 1.6×10^{-10} cm^3 molecule^{-1} s^{-1} and exhibited three different types of reaction channels: electron transfer, adduct formation, and $(Cl)_2$ transfer. The latter channel was the only chlorination channel observed and occurred exclusively with the *cis* and *trans* isomers of 1,2-dichloroethylene, but in competition with adduct formation. The variation observed in the occurrence of these three channels with charge state is consistent with what is now known about the role of charge state in promoting bond formation with the C_{60} surface and the role of coulombic repulsion between product ions in preventing electron transfer. A bimolecular reaction of the C_{60} (*trans*-$HClC{=\!=}CHCl)^{2+}$ adduct ion with *trans*-1,2-dichloroethylene was observed leading to the elimination of acetylene or chlorine. Higher-order sequential additions to C_{60}^{2+} were seen with vinyl chloride, 1,1-dichloroethylene, and trichloroethylene and these are proposed to proceed by "ball-and-chain" polymerization. (Int J Mass Spectrom 192 (1999) 215–223) © 1999 Elsevier Science B.V.

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1. Introduction

Recent systematic experiments in our laboratory have shown that the ready production and long-term stability of singly and multiply charged C_{60} cations is well-suited for studies of ion/molecule chemistry as a function of charge state [1]. With the use of the selected-ion flow tube (SIFT) technique we have demonstrated that the room-temperature chemistry of C_{60} cations in helium bath gas at 0.35 Torr is extremely sensitive to the degree of ionization [1,2]. Briefly, we have found that monocations of C_{60} are generally unreactive under SIFT conditions. They bond only with strong nucleophiles such as ammonia and saturated amines [3] and with molecules capable of Diels-Alder additions [4]. A reaction of $C_{60}^{\cdot+}$ with iron pentacarbonyl, first observed by Freiser and

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co-workers [5], produces derivatized $C_{60}Fe(CO)_4^{\cdot+}$ [6] and is the only example of a *bimolecular* derivatization reaction with $C_{60}^{\cdot+}$ that we have observed to date. Covalent bonding to $C_{60}^{\cdot+}$ is difficult because it is necessary to distort the C_{60} carbon cage at the C site of bond formation with the substituent so as to achieve the required sp^3 hybridization. This energy barrier is more readily overcome with the higher charge states of C_{60} as the electrostatic interaction between the reactants increases [7]. For example, we have previously found C_{60}^{2+} to be very reactive toward many molecules and to exhibit a rich addition chemistry, although electron transfer becomes an important competitive reaction channel. With $C_{60}^{\cdot 3+}$, also a very reactive cation, this competition often favours electron transfer or even dissociative electron transfer, but addition is still observed [8]. However, electron transfer is delayed by an energy barrier arising from coulombic repulsion between the two product ions [9].

We have only very recently explored the ease of chlorination of charged C_{60} as a function of the degree of ionization in reactions with chlorine gas and the four chlorinated methanes CH_nCl_{4-n} ($n = 0-4$) [10]. $C_{60}^{\cdot+}$ and C_{60}^{2+} were observed not to chlorinate, or react in any other way. Chlorine also did not react with $C_{60}^{\cdot 3+}$, but bimolecular chloride transfer and electron transfer reactions, reactions that result in charge reduction / charge separation, were observed to occur between $C_{60}^{\cdot 3+}$ and CCl_4, $CDCl_3$, CH_2Cl_2, and CH_3Cl. Chloride transfer was the predominant channel seen with CCl_4, $CDCl_3$, and CH_2Cl_2 and electron transfer dominates the reaction with CH_3Cl. These results were observed to be consistent with trends in chloride affinity and ionization energy. The reluctant chlorination of the first two charge states of C_{60} was attributed to the energy required to distort the carbon cage upon bond formation, and the observed chloride transfer to $C_{60}^{\cdot 3+}$ was attributed to the greater attractive electrostatic interactions with this ion [10].

Here we investigate the chlorination of C_{60} cations further, this time with the chlorinated ethylenes $CH_2{=\!=}CHCl$, $CH_2{=\!=}CCl_2$, *trans*-$CHCl{=\!=}CHCl$, *cis*-$CHCl{=\!=}CHCl$, $CHCl{=\!=}CCl_2$, and $CCl_2{=\!=}CCl_2$. We continue to assess the role of charge state on the chemical reactivity of C_{60}^{n+}. The competitions between addition, electron transfer, and chloride transfer are also investigated further. A new competitive channel corresponding to $(Cl)_2$ transfer is identified for the reactions of C_{60}^{2+} with 1,2-dichloroethylenes and its competition with adduct formation is investigated. Also, observations of higher-order chemistry initiated by C_{60}^{2+} provide a further opportunity to investigate chemical reactions of derivatized C_{60}^{2+} ions.

2. Experimental

The ion/molecule reactions of the fullerene cations C_{60}^{x+} ($x = 1,2,3$) with the selected chlorinated molecules were achieved within the reaction region of a SIFT mass spectrometer in helium carrier gas at 0.35 ± 0.02 Torr and 295 ± 2 K [11,12]. The fullerene cations were produced in an ion source by electron impact ionization of the vapour from a sample of fullerene powder (~99.5+% C_{60}, SES Research, Inc.): $C_{60}^{\cdot+}$ at ~50 eV, C_{60}^{2+} at ~ 80 eV and $C_{60}^{\cdot 3+}$ at ~100 eV. The desired C_{60} cation was selected with a quadrupole mass filter, injected into the flow tube containing He and then allowed to thermalize by collisions with He ($\sim 4 \times 10^5$ collisions) prior to entering the reaction region further downstream.

Vinyl chloride (99.9%) was obtained from Matheson and was used pure. The remaining neutral reagents were obtained as liquids from Aldrich with the following purities: 1,1-dichloroethylene (99%), *trans*-1,2-dichloroethylene (98%), *cis*-1,2-dichloroethylene (98%), trichloroethylene (99.5%), and tetrachloroethylene (99.9+%). They were introduced into the reaction region as vapours diluted in helium to levels of between 2.4% and 24.6% in the studies of reactions with $C_{60}^{\cdot+}$ and C_{60}^{2+} and between 2.4% and 5.5% in studies of reactions with $C_{60}^{\cdot 3+}$. Rate coefficients were measured in the usual manner [11,12] and have an uncertainity estimated to be less than ±30%.

3. Results and discussion

The kinetic results obtained for the reactions investigated in this study are summarized in Table 1.

Table 1
Product distributions and rate coefficients measured for the primary reactions of C_{60}^{n+} ($n = 1, 2, 3$) with chlorinated ethylenes at 295 ± 2 K in He at 0.35 ± 0.02 Torr

Reactant neutral/ion	Products	B.R.[a]	k_{obs}[b]	k_c[c]
$CH_2{=}CHCl$				
$C_{60}^{\cdot+}$	Not observed		$<2.1 \times 10^{-13}$	1.3×10^{-9}
C_{60}^{2+}	$C_{60}C_2H_3Cl^{2+}$	1.0	1.5×10^{-12}	2.5×10^{-9}
$C_{60}^{\cdot 3+}$	$C_{60}^{2+} + C_2H_3Cl^{+\cdot}$	1.0	3.9×10^{-9}	3.7×10^{-9}
$CH_2{=}CCl_2$				
$C_{60}^{\cdot+}$	Not observed		$<5.3 \times 10^{-13}$	1.1×10^{-9}
C_{60}^{2+}	$C_{60}C_2H_2Cl_2^{2+}$	1.0	2.2×10^{-11}	2.2×10^{-9}
$C_{60}^{\cdot 3+}$	$C_{60}^{2+} + C_2H_2Cl_2^{+\cdot}$	1.0	1.9×10^{-9}	3.3×10^{-9}
trans-$CHCl{=}CHCl$				
$C_{60}^{\cdot+}$	Not observed		$<3.2 \times 10^{-13}$	7.7×10^{-10}
C_{60}^{2+}	$C_{60}C_2H_2Cl^{2+}$	0.16	1.0×10^{-11}	1.5×10^{-9}
	$C_{60}Cl_2^{2+} + C_2H_2$	0.84		
$C_{60}^{\cdot 3+}$	$C_{60}^{2+} + C_2H_2Cl_2^{+\cdot}$	1.0	2.5×10^{-9}	2.3×10^{-9}
cis-$CHCl{=}CHCl$				
$C_{60}^{\cdot+}$	Not observed		$<1.5 \times 10^{-13}$	1.3×10^{-9}
C_{60}^{2+}	$C_{60}C_2H_2Cl_2^{2+}$	0.34	9.1×10^{-12}	2.5×10^{-9}
	$C_{60}Cl_2^{2+} + C_2H_2$	0.66		
$C_{60}^{\cdot 3+}$	$C_{60}^{2+} + C_2H_2Cl_2^{+\cdot}$	1.0	2.8×10^{-9}	3.8×10^{-9}
$ClCH{=}CCl_2$				
$C_{60}^{\cdot+}$	Not observed		$<1.8 \times 10^{-13}$	8.6×10^{-10}
C_{60}^{2+}	$C_{60}C_2H_2Cl_3^{2+}$	0.80	1.7×10^{-11}	1.7×10^{-9}
	$C_{60}^{+\cdot} + C_2HCl_3^{+\cdot}$	0.20		
$C_{60}^{\cdot 3+}$	$C_{60}^{2+} + C_2HCl_3^{+\cdot}$	1.0	2.3×10^{-9}	2.6×10^{-9}
$CCl_2{=}CCl_2$				
$C_{60}^{\cdot+}$	Not observed		$<1.3 \times 10^{-12}$	7.5×10^{-10}
C_{60}^{2+}	$C_{60}C_2Cl_4^{2+}$	0.05	1.6×10^{-10}	1.5×10^{-9}
	$C_{60}^{+\cdot} + C_2Cl_4^{+\cdot}$	0.95		
$C_{60}^{\cdot 3+}$	$C_{60}^{2+} + C_2Cl_4^{+\cdot}$	1.0	1.6×10^{-9}	2.3×10^{-9}

[a] Reaction branching ratio.

[b] Observed apparent bimolecular rate coefficient in units of cm^3 $molecule^{-1}$ s^{-1} with an uncertainty of ±30%.

[c] Theoretical collision-rate coefficients in units of cm^3 $molecule^{-1}$ s^{-1} calculated with the variational transition state theory [13].

Included in Table 1 are values for collision rate coefficients calculated with the variational transition state theory of Su and Chesnavich [13]. Use is made in these calculations of the dipole moments [14,15] and polarizabilities [16] given in Table 2 which also lists values for the ionization energies of the chlorinated ethylenes investigated. The ratio of the measured reaction-rate coefficient to the calculated collision-rate coefficient, k_{obs}/k_c, provides a measure of reaction efficiency.

3.1. Reactions with $C_{60}^{\cdot+}$

Not one of the six chlorinated ethylenes reacted with $C_{60}^{\cdot+}$, $k < 5.3 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. Electron transfer is endothermic in all cases because

Table 2
Ionization energies, dipole moments and polarizabilities for the chlorinated ethylenes used in this work

Reactants	IE[a] (eV)	Dipole moment[b] (D)	Polarizability[b] (10^{-24} cm^3)
Vinyl chloride $CH_2{=\!=}CHCl$	9.99 ± 0.02	1.45	6.41
1,1-Dichloroethylene $CH_2{=\!=}CCl_2$	9.79 ± 0.04	1.34	10.03
trans-1,2-dichloroethylene trans-$CHCl{=\!=}CHCl$	9.66 ± 0.01	0	9.28
cis-1,2-dichloroethylene cis-$CHCl{=\!=}CHCl$	9.65 ± 0.02	1.90	9.19
Trichloroethylene $CHCl{=\!=}CCl_2$	9.47 ± 0.01	0.75[c]	~12.0[d]
Tetrachloroethylene $CCl_2{=\!=}CCl_2$	9.32	0	~14.0[d]

[a] From [14].
[b] From [15].
[c] From [16].
[d] Value estimated from a linear extrapolation of the polarizabilities of vinyl chloride and *cis*-1,2-dichloroethylene as a function of number of Cl atoms.

of the low electron-recombination energy of $C_{60}^{\cdot+}$, $RE(C_{60}^{\cdot+}) = 7.64 \pm 0.02$ eV [17]. The ionization energies of the six molecules investigated all exceed 9.3 eV (see Table 2). There was no evidence for H atom, hydride, Cl atom, or chloride abstraction. The occurrence of H-atom transfer was difficult to rule out experimentally due to insufficient resolution of the detection quadrupole. There is insufficient information to determine the overall thermochemistry of any of these abstraction reactions. In any case, these reactions can be expected to be kinetically controlled in the sense that a barrier is expected to be associated with C–H or C–Cl bond formation with $C_{60}^{\cdot+}$. This is because of the rehybridization from largely sp^2 to largely sp^3 that is required at the C atom on the C_{60} surface should bond formation occur [7].

3.2. Reactions with C_{60}^{2+}

C_{60}^{2+} was observed to react with all six chlorinated ethylenes. Representative results are shown in Figs. 1 and 2. Three types of reactions were observed: electron transfer, addition, and $(Cl)_2$ transfer. The latter two of these channels involve chemical-bond formation with C atoms on the C_{60} surface. We have previously suggested that bond formation with C_{60}^{2+} is generally more favourable than with $C_{60}^{\cdot+}$ because of the stronger electrostatic interaction between reactants that results from the higher charge on C_{60}^{2+} [7].

Electron transfer was not observed with vinyl chloride and 1,1-dichloroethylene, which, of the six molecules studied, have the two highest ionization energies (see Table 2), even though the electron-recombination energy of C_{60}^{2+}, $RE(C_{60}^{2+}) = 11.36 \pm 0.05$ eV [8], is much larger than the ionization energies of these two molecules, IE $\leq$ 9.99 eV. This result is consistent with our previous measurements that have demonstrated an onset for electron transfer with molecules having IE $\leq$ 9.51 eV [8]. Vinyl chloride and 1,1-dichloroethylene have ionization energies $\geq$9.79 eV. The low onset for electron transfer previously has been attributed to the barrier arising from coulombic repulsion in the resulting charge separation [9].

Vinyl chloride and 1,1-dichloroethylene were observed to react with C_{60}^{2+} by addition only,

$$C_{60}^{2+} + CH_2{=\!=}CHCl \rightarrow C_{60}(CH_2{=\!=}CHCl)^{2+} \qquad (1)$$

$$C_{60}^{2+} + CH_2{=\!=}CCl_2 \rightarrow C_{60}(CH_2{=\!=}CCl_2)^{2+} \qquad (2)$$

The effective bimolecular rate coefficients for these two reactions were measured to be 1.5×10^{-12} and 2.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively. Fig. 1 shows that up to two sequential additions were observed with vinyl chloride and three with 1,1-dichloroethylene. The structures of these adduct ions are uncertain and could not be probed using our multicollision induced dissociation technique [18] because of their low ion intensities. It is not clear whether the derivatization occurs directly on

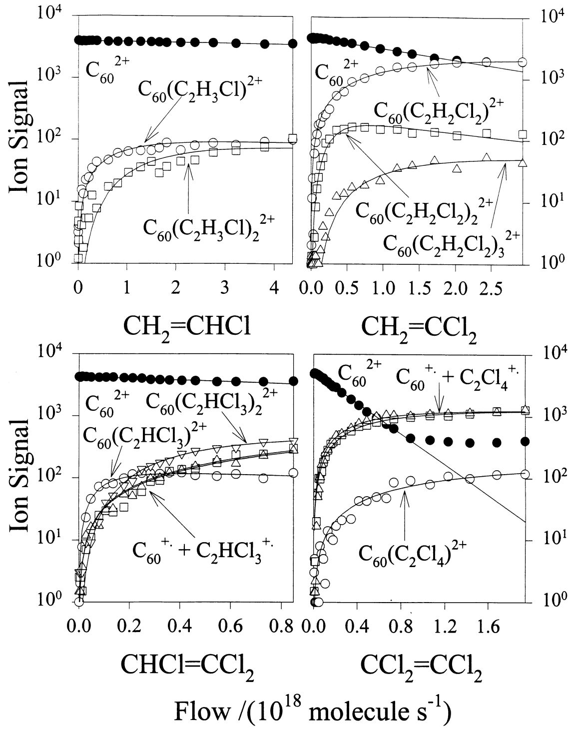


Fig. 1. Experimental data for the chemistry initiated by the reaction of C_{60}^{2+} with $CH_2{=}CHCl$ (left top), $CH_2{=}CCl_2$ (right top), $CHCl{=}CCl_2$ (left bottom), and $CCl_2{=}CCl_2$ (right bottom). C_{60}^{2+} was produced in a low pressure ion source by electron impact at 100 eV with C_{60} vapor derived from a fullerene powder. The measurements were performed at 295 ± 2 K and at a helium buffer gas pressure of 0.35 ± 0.02 Torr.

the surface or in a "ball-and-chain" fashion [2]. The latter appears more likely in analogy with the ball-and-chain derivatization that we have previously proposed with ethylene [19].

Surprisingly, the *cis* and *trans* isomers of CHCl═CHCl reacted in a manner quite different from the $CH_2{=}CCl_2$ isomer. Although addition was still observed, the major reaction channel that was recorded involves the unexpected simultaneous transfer of two Cl atoms. This is illustrated in

$$C_{60}^{2+} + CHCl{=}CHCl \rightarrow C_{60}Cl_2^{2+} + C_2H_2 \quad (3a)$$

$$\rightarrow C_{60}(CHCl{=}CHCl)^{2+} \quad (3b)$$

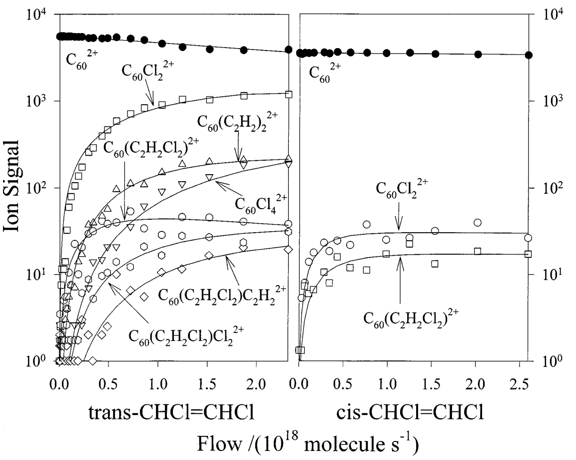


Fig. 2. Experimental data for the chemistry initiated by the reaction of C_{60}^{2+} with *cis*-CHCl═CHCl (left) and *trans*-CHCl═CHCl (right). C_{60}^{2+} was produced in a low-pressure ion source by electron impact at 100 eV with C_{60} vapor derived from a fullerene powder. The measurements were performed at 295 ± 2 K and at a helium buffer gas pressure of 0.35 ± 0.02 Torr.

and the data are shown in Fig. 2. Both isomers reacted slowly with C_{60}^{2+} at about 1/20 of the collision rate (see Table 1). Channel (3a) was the predominant channel with both the *cis* and the *trans* isomer; the measured branching ratios were 0.66 and 0.84, respectively. Higher-order reactions were seen only with the *trans* isomer in the flow range investigated. A second $(Cl)_2$ transfer reaction was recorded for $C_{60}Cl_2^{2+}$,

$$C_{60}Cl_2^{2+} + CHCl{=}CHCl \rightarrow C_{60}Cl_4^{2+} + C_2H_2 \quad (4)$$

and the adduct $C_{60}(CHCl{=}CHCl)^{2+}$ ion reacted further with a second molecule of *trans*-CHCl═CHCl primarily to eliminate $2Cl_2$ [reaction (5a)], and to a lesser extent (≤10%) to eliminate C_2H_2 or Cl_2 [reactions (5b) and (5b,c)], respectively].

$$C_{60}(CHCl{=}CHCl)^{2+} + CHCl{=}CHCl$$

$$\rightarrow C_{60}(C_2H_2)_2^{2+} + 2Cl_2 \quad (5a)$$

$$\rightarrow C_{60}(C_2H_2Cl_2)Cl_2^{2+} + C_2H_2 \quad (5b)$$

$$\rightarrow C_{60}(C_2H_2Cl_2)C_2H_2^{2+} + Cl_2 \quad (5c)$$

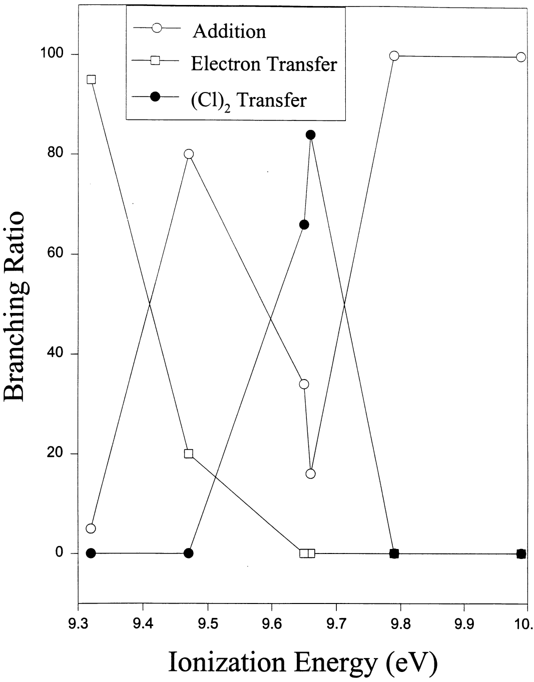
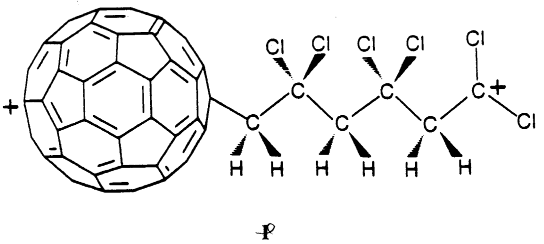


Fig. 3. Branching ratio of product ions as a function of the ionization energy in the reactions of C_{60}^{2+} with various chlorinated ethylene molecules (see Table 2 for the ionization energies of the chlorinated ethylenes).

There was again no evidence for H atom, hydride, Cl atom, or chloride abstraction. Hydride and chloride abstraction would lead to charge separation and therefore involve a barrier arising from coulombic repulsion between the product ions [9].

The competition between the three reaction channels observed with C_{60}^{2+} was found to be very sensitive to the ionization energy of the chlorinated ethylene. Fig. 3 summarizes the experimental results obtained for the reactions between C_{60}^{2+} and the six chloroethylenes investigated in this study in terms of a plot of reaction branching ratio as a function of ionization energy. It is seen that the electron transfer channel diminishes and disappears as the ionization energy increases and is replaced by addition and (Cl)$_2$ transfer. (Cl)$_2$ transfer was observed only with the *cis* and *trans* isomers of dichloroethylene (IE = 9.65 and 9.66 eV, respectively) and addition is the only channel observed with vinyl chloride (IE = 9.99 eV) and vinylidene chloride (9.79 eV). Electron transfer with these latter four molecules is not expected, and does not occur, since their ionization energies lie above the empirical upper limit of IE = 9.51 eV established from previous extensive investigations of electron transfer between C_{60}^{2+} and many other molecules [8]. The predominance of the chlorine transfer channel observed exclusively with the *cis* and *trans* isomers of dichloroethylene is striking but may be accounted for in terms of thermodynamics. Available standard enthalpies of formation [14,20] indicate standard enthalpies of (Cl)$_2$ abstraction for $CH_2{=}CCl_2$, *trans*-$CHCl{=}CHCl$, *cis*-$CHCl{=}CHCl$, $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$ of 98.5, 53.5, 53.5, 65.5, and 53.0 kcal mol^{-1}, respectively. Clearly, (Cl)$_2$ transfer is energetically much more favourable with the *cis* and *trans* isomers of 1,2-dichloroethathane than with 1,1-dichloroethylene. (Cl)$_2$ transfer with tri- and tetrachloroethylene also seems energetically more favourable (less so with trichloroethylene), but these two molecules react preferentially by addition (with trichloroethylene) and electron transfer (with tetrachloroethylene) because of their low ionization energies. Up to three molecules of tetrachloroethylene were observed to add sequentially to C_{60}^{2+}.

The competition between electron transfer, addition and (Cl)$_2$ transfer may also be viewed in terms of a curve-crossing model introduced by Herman to account for the observed reactivities of other, smaller doubly charged ions [21] and adapted recently to the chemistry of C_{60}^{n+} cations [1]. A nonbonding reaction involving electron transfer that leads to charge separation is described in this model in terms of a repulsive potential-energy surface that crosses the attractive dication potential-energy surface of the reactants. For the small exoergicities for electron transfer (less than about 2 eV or IE > 9.5 eV in Fig. 3), the crossing occurs at large separations and the Landau-Zener probability of crossing to the electron-transfer product surface is small. The electron-transfer probability is then small and the reactants may continue on the dication surface to smaller internuclear separations and then may effectively be collisionally stabilized as an adduct ion or react by (Cl)$_2$ transfer.



Scheme 1

3.3. Reaction mechanisms

We propose that the sequential additions to C_{60}^{2+} observed with vinyl chloride, 1,1-dichloroethylene and trichloroethylene are similar to that we have previously reported with ethylene and proceeds by ball-and-chain polymerization [2]. For example, a possible structure for the third 1,1-dichloroethylene adduct $C_{60}(C_2H_2Cl_2)_3^{2+}$is presented in Scheme 1.

The mechanism for the transfer of $(Cl)_2$ and concomitant loss of C_2H_2 in reactions (3a), (4), and (5a) is less clear. Possibilities include the sequential (or concerted) transfer of two chlorine atoms from the initially formed π adduct to the C_{60} surface. Possibly such a transfer is geometrically optimal with the Cl–Cl separation in the *trans* isomer of dichlorethylene, thereby giving rise to a higher rate of $(Cl)_2$ abstraction.

A plausible mechanism for the loss of one and two molecules of Cl_2 in reactions (5a) and (5c) is shown in Fig. 4. Addition of 1,2-dichloroalkenes to C_{60}^{2+} is pictured as proceeding through an initial π adduct that then either loses acetylene, as described previously, or rearranges to the more stable σ adduct. In the latter ion, one of the positive charges is formally located on the terminal carbon atom of the chain, thereby insulating the two positive charges from one another and achieving some stabilization by delocalizing positive charge onto the chlorine atom that is directly attached to the cationic carbon.

Subsequent addition of another 1,2-dichloroethylene molecule produces a diadduct (as in Scheme 1), which we have chosen to depict as being bridged, by analogy with the simpler $C_2H_4Cl^+$ ion. On the $C_2H_4Cl^+$ potential energy surface the β-chloroethyl cation, $ClH_2CCH_2^+$, is not at a minimum and rearranges without barrier to the symmetrical Cl-bridged ion, the chloronium ion [22]. Similarly, $C_{60}(HClC{=}CHCl)_2^{2+}$ is expected to contain a terminal chloronium ion. Loss of Cl_2 from this chloronium ion gives a β-substituted vinyl cation that can rearrange, via a hydride shift, to give a tertiary carbenium ion that is stabilised by two π donors, a vinyl group and a Cl atom. Loss of a further Cl_2 molecule, presumably through another chloronium ion, generates a vinyl cation that is heavily stabilized by an α-vinyl substituent. This could possibly be the observed product, but on the basis of a theoretical study of isomers on the $C_4H_5^+$ potential energy surface [23], it seems probable that a further 1,3-hydride shift occurs and that this is followed by cyclization to the more stable protonated cyclobutadiene derivative.

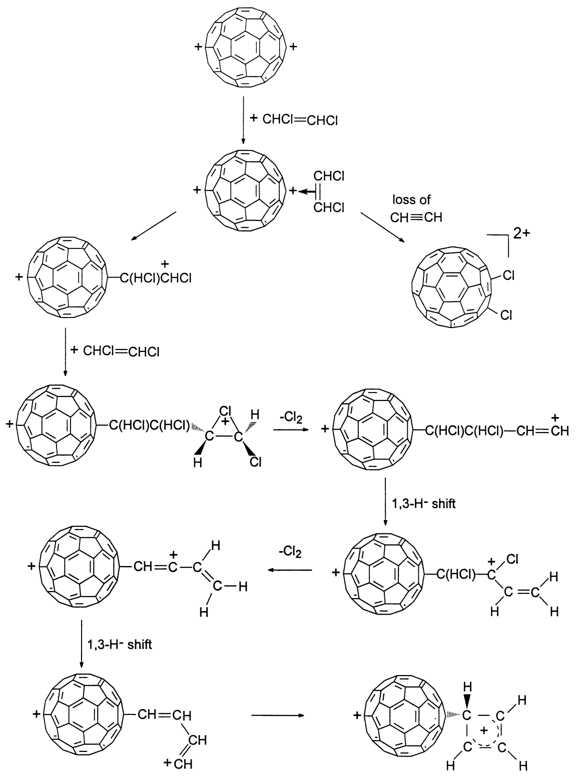


Fig. 4. A plausible mechanism for the loss of acetylene and two molecules of Cl_2 in the chemistry initiated by C_{60}^{2+} with *trans*-1,2-dichloroethylene.

The reason for our failure to observe higher-order

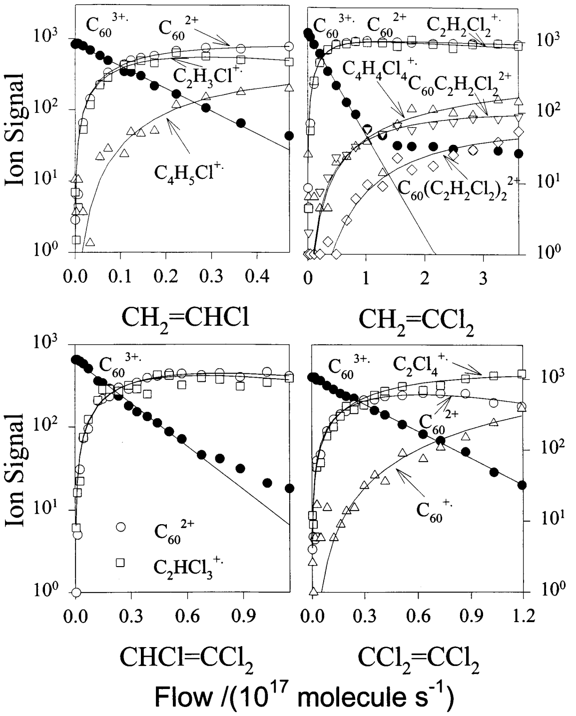


Fig. 5. Experimental data for the chemistry initiated by the reaction of $C_{60}^{\cdot 3+}$ with $CH_2{=}CHCl$ (left top), $CH_2{=}CCl_2$ (right top), $CHCl{=}CCl_2$ (left bottom), and $CCl_2{=}CCl_2$ (right bottom). $C_{60}^{\cdot 3+}$ was produced in a low pressure ion source by electron impact at 100 eV with C_{60} vapor derived from a fullerene powder. The measurements were performed at 295 ± 2 K and at a helium buffer gas pressure of 0.35 ± 0.02 Torr.

chemistry of types (5a)–(5c) with *cis*-1,1-dichloroethylene isomer may lie in the nature of electrostatic interaction of C_{60}(*cis*-CHCl═CHCl)$^{2+}$ with *cis*-CHCl═CHCl. This molecule, in contrast to *trans*-CHCl═CHCl, has a substantial dipole moment that may act to align the incoming *cis*-CHCl═CHCl molecule in such a way so as to prevent formation of a chloronium ion. The two relatively large *cis* chlorine atoms may "block" the formation of an initial π adduct.

3.4. Reactions with $C_{60}^{\cdot 3+}$

Only electron transfer was observed between the six chlorinated ethylenes and $C_{60}^{\cdot 3+}$ (see Figs. 5 and 6). The ionization energies of these molecules all fall below the ionization energy of 11.2 eV that has been established as the upper limit for the onset of electron transfer with $C_{60}^{\cdot 3+}$ [8]. This onset is about 4 eV lower than the recombination energy of $C_{60}^{\cdot 3+}$ because of the barrier that arises from the coulombic repulsion between the doubly and singly charged product ions [9]. The rate coefficients for electron transfer all exceed 1×10^{-9} cm^3 molecule^{-1} s^{-1}.

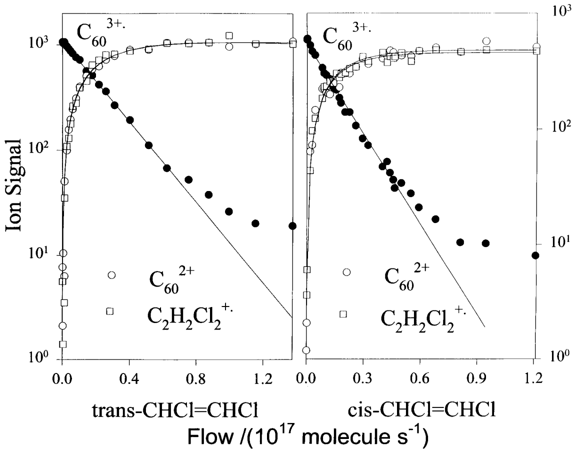


Fig. 6. Experimental data for the chemistry initiated by the reaction of $C_{60}^{\cdot 3+}$ with *cis*-CHCl═CHCl (left) and *trans*-CHCl═CHCl (right). $C_{60}^{\cdot 3+}$ was produced in a low-pressure ion source by electron impact at 100 eV with C_{60} vapor derived from a fullerene powder. The measurements were performed at 295 ± 2 K and at a helium buffer gas pressure of 0.35 ± 0.02 Torr.

4. Conclusions

The observed trends with charge state in the reactivities of C_{60}^{n+} cations toward chlorinated ethylenes in helium at 0.35 Torr and 294 K are consistent with previous results obtained in this laboratory with the SIFT technique. $C_{60}^{\cdot +}$ again is observed to be unreactive, and the chemistry of $C_{60}^{\cdot 3+}$ again is dominated by rapid electron transfer. C_{60}^{2+} reacts with chlorinated ethylenes in three distinctly different ways: electron transfer, addition and $(Cl)_2$ transfer. The variation observed in the occurrence of these three channels with the degree of ionization is consistent with what is now known about the role of charge state in promoting bond formation with the C_{60}

surface and the role of coulombic repulsion between product ions in preventing electron transfer. The $(Cl)_2$ transfer channel leading to the concomitant formation of two C–Cl bonds with C_{60} is the only primary chlorination channel observed; there was no evidence for Cl atom or Cl^- transfer. The $(Cl)_2$ transfer channel is specific to the *cis* and *trans* isomers of 1,2-dichloroethylenes and does not occur with 1,1-dichloroethylene, nor with tri- and tetrachloroethylene.

The higher-order sequential additions to C_{60}^{2+} observed with vinyl chloride, 1,1-dichloroethylene and trichloroethylene are reminiscent of our earlier observation with ethylene and are expected to proceed by ball-and-chain polymerization. The higher-order bimolecular reactions leading to the elimination of acetylene or chlorine are specific to the *trans* isomer of 1,2-dichloroethylene and so should provide a means for the identification of this isomer in a mixture of the three isomers of dichloroethylene using chemical ionization.

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