ELSEVIER International Journal of Mass Spectrometry and Ion Processes 165/166 (1997) 249–255

International Journal of Mass Spectrometry and Ion Processes

Gas-phase reactions of singly and multiply-charged fullerene cations, C_{60}^{x+} ($x = 1$–3), with iron pentacarbonyl: kinetic control by Coulombic barriers[1]

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Received 2 April 1997; accepted 29 May 1997

Abstract

Selected-ion flow tube measurements of rate coefficients and product distributions are reported for the reactions of $C_{60}^{\cdot+}$, C_{60}^{2+} and $C_{60}^{\cdot 3+}$ with iron pentacarbonyl in helium buffer gas at 0.35 ± 0.01 torr and 294 ± 3 K. A fast bimolecular reaction is observed with $C_{60}^{\cdot+}$ leading to a stable derivatized C_{60} cation, $C_{60}Fe(CO)_4^{\cdot+}$, but the chemistry switches for the higher charge states to charge separation by dissociative-electron transfer leading to the elimination of one and two molecules of CO with C_{60}^{2+} and $C_{60}^{\cdot 3+}$, respectively. The specificity of these CO eliminations is rationalized in terms of favourable entropy changes and kinetic control by energy barriers arising from Coulombic repulsion between product ions. © 1997 Elsevier Science B.V.

Keywords: Fullerene ions; Iron pentacarbonyl; Charge separation; Coulombic barriers

1. Introduction

The remarkable stability and ready availability of multiply-charged fullerene cations affords an opportunity to explore the chemistry of these cations as a function of charge state. We have shown previously in our laboratory that new chemical pathways often become accessible in the gas phase at room temperature (in helium buffer

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[1] Dedicated to Keith Jennings on the occasion of his 65th birthday, in part for his outstanding contributions in the field of mass spectrometry and gas-phase ion chemistry.

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PII S0168-1176(97)00160-2

at 0.35 torr) to reactions of C_{60} cations as the charge state is increased from 1 to 2 to 3 [1]. Briefly, we have found monocations of C_{60} to react with only a few molecules and to do so by addition, rather than by the formation of bimolecular products. In contrast, C_{60}^{2+} is very reactive towards many molecules and exhibits 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. Here we report the influence of the charge state of C_{60} on the rate and mode of reaction with iron pentacarbonyl, including the first example of a reaction of $C_{60}^{\cdot +}$ to yield bimolecular products under our experimental conditions.

There has been previous interest in the reaction of neutral and singly-ionized C_{60} with iron pentacarbonyl. The $Fe(CO)_4(\eta^2\text{-}C_{60})$ derivative of C_{60} has been produced in benzene solution in the presence of a suspension of $Fe_2(CO)_9$ at room temperature [2] and the ionized form of this derivative has been generated in a Fourier transform mass spectrometer in an argon bath gas at 2×10^{-6} torr from the reaction of $C_{60}^{\cdot +}$ with $Fe(CO)_5$ [3]. We report here that the latter derivatization reaction also occurs in helium at 0.35 torr, and with a measurable rate, but that a completely different bimolecular chemistry, leading to charge separation with CO elimination, predominates with the higher charge states of C_{60}.

2. Experimental

Reactions of the fullerene cations with iron pentacarbonyl were achieved within the reaction region of a Selected-Ion Flow Tube (SIFT) mass spectrometer in helium carrier gas at 0.35 ± 0.01 torr and 294 ± 3 K [4,5]. The fullerene cations were produced in an ion source by electron impact ionization of the vapour of a sample of fullerene powder (~ 90% C_{60} and 9% C_{70}, Termusa Inc.): $C_{60}^{\cdot +}$ at ~ 50 V, C_{60}^{2+} at ~ 80 V and $C_{60}^{\cdot 3+}$ at ~ 100 V. 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 (~ 4×10^5 collisions) prior to entering the reaction region further downstream. $Fe(CO)_5$ (Aldrich) vapour was introduced into the reaction region as a 2.4% mixture in helium. Rate coefficients were measured in the usual manner [4,5] and have an uncertainty estimated to be less than ±30%.

Table 1
Rate coefficients (in units of cm^3 $molecule^{-1}$ s^{-1}) and product channels measured for reactions of C_{60}^{x+} cations with iron pentacarbonyl in helium buffer gas at 0.35 ± 0.01 torr and 294 ± 3 K using the SIFT technique

Reaction	Rate coefficient
$C_{60}^{\cdot +} + Fe(CO)_5 \rightarrow C_{60}Fe(CO)_4^{\cdot +} + CO$	4.0×10^{-10}
$C_{60}Fe(CO)_4^{\cdot +} + Fe(CO)_5 \rightarrow$ products	$< 1 \times 10^{-13}$
$C_{60}^{2+} + Fe(CO)_5 \rightarrow C_{60}^{\cdot +} + Fe(CO)_4^{\cdot +} + CO$	5.8×10^{-10}
$C_{60}^{\cdot 3+} + Fe(CO)_5 \rightarrow C_{60}^{2+} + Fe(CO)_3^{\cdot +} + 2CO$	2.2×10^{-9}

3. Results and discussion

Table 1 provides a summary of the measured rate coefficients for the primary and higher-order reactions of $C_{60}^{\cdot +}$, C_{60}^{2+} and $C_{60}^{\cdot 3+}$ with iron pentacarbonyl that were observed in this study. Relevant thermochemical information for the Fe–CO bond dissociation of the iron-carbonyl ions $(CO)_nFe^{\cdot +}\text{–}CO$ with $n = 2\text{–}4$ is provided in Table 2.

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

The monocation $C_{60}^{\cdot +}$ was observed to react rapidly, $k_1 = 4.0 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, with iron pentacarbonyl in a bimolecular fashion according to reaction (1)

$$C_{60}^{\cdot +} + Fe(CO)_5 \rightarrow C_{60}Fe(CO)_4^{\cdot +} + CO \qquad (1)$$

as shown in Fig. 1. This is in sharp contrast to our previous observations with many other molecules which indicate that $C_{60}^{\cdot +}$ is either completely unreactive or reacts by simple addition under our SIFT conditions [1]. Electron transfer is just endothermic since the recombination energy of $C_{60}^{\cdot +}$, $RE(C_{60}^{\cdot +}) = 7.64 \pm 0.02$ eV [6], is only slightly

Table 2
Summary of reported bond dissociation energies (in kcal mol^{-1}) for the iron-carbonyl ions $(CO)_nFe^{+}$–CO with $n = 2$–4

$(CO)_nFe^{+}$–CO	HAB[a]	SCA[b]	NAFN[c]	RB[d]
$(CO)_2Fe^{+}$–CO	18.7 ± 2.3	15.9 ± 1.4	25.7 ± 1.4	19.8
$(CO)_3Fe^{+}$–CO	25.4 ± 2.3	24.7 ± 1.4	25.2 ± 1.1	24.2
$(CO)_4Fe^{+}$–CO	18.2 ± 2.3	26.8 ± 1.9	17.8 ± 0.9	20.9

[a] [19].
[b] [20].
[c] [21].
[d] [22].

smaller than the ionization energy of iron pentacarbonyl, $IE(Fe(CO)_5) = 7.96 \pm 0.01$ eV [7], and so is not expected to occur. The $C_{60}Fe(CO)_4^{\cdot+}$ ion produced in reaction (1) did not react further with iron pentacarbonyl, $k_2 < 1 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}.

$$C_{60}Fe(CO)_4^{\cdot+} + Fe(CO)_5 \rightarrow \text{products} \qquad (2)$$

The bimolecular reaction (1) has been observed previously by Jiao et al. in a Fourier transform mass spectrometer (FTMS) at a background argon pressure of 2×10^{-6} torr [3]. A second channel leading to the elimination of two CO molecules was also observed by these authors but attributed to kinetically or internally excited $C_{60}^{\cdot+}$ since it disappeared after a 1-s cooling period [3]. The results reported here support this interpretation. However, we cannot support the observation of a further reaction of $C_{60}Fe(CO)_4^{\cdot+}$ with iron pentacarbonyl according to reaction (3) which was also reported by these authors. Perhaps the $C_{60}Fe(CO)_4^{\cdot+}$

$$C_{60}Fe(CO)_4^{\cdot+} + Fe(CO)_5 \rightarrow C_{60}Fe_2(CO)_8^{\cdot+} + CO \qquad (3)$$

cations produced in reaction (1) were insufficiently quenched at the low pressure of the FTMS experiments prior to secondary reaction.

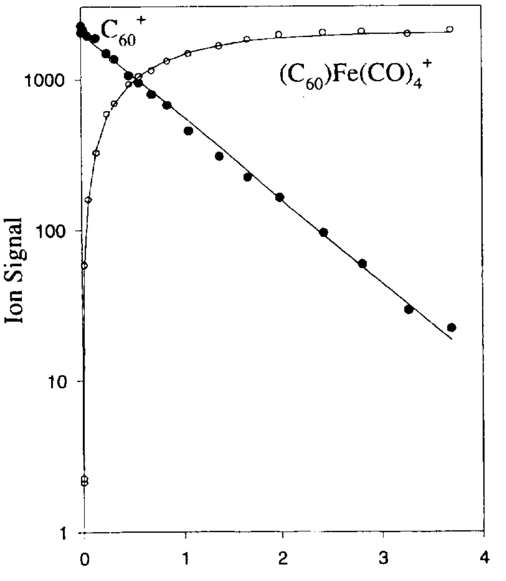
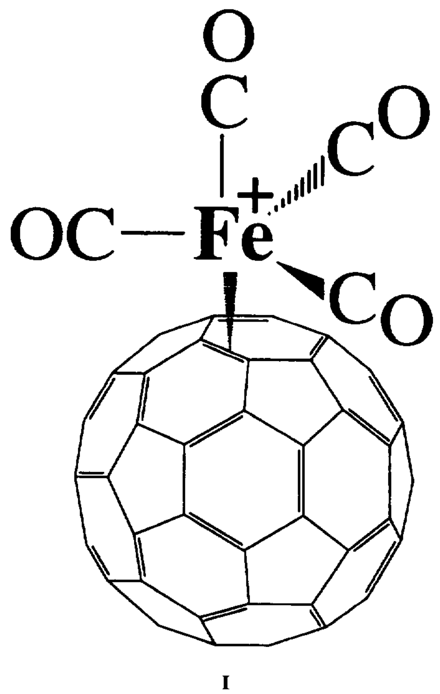


Fig. 1. Experimental data for the chemistry initiated by the reaction of C_{60}^{+} with iron pentacarbonyl. The solid lines represent fits to the experimental data with solutions of the differential equation appropriate for the observed reactions.

We take the occurrence of reaction (1) at room temperature to imply that $D(C_{60}^{+}–Fe(CO)_4) \geq$



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$D(Fe(CO)_4\text{–}CO) = 39$ [8] or 58 ± 12 kcal mol^{-1} [9]. Since $IE(Fe(CO)_4) = 7.39 \pm 0.41$ eV [10] is slightly lower than $IE(C_{60}) = 7.64 \pm 0.02$ eV [6], the charge in $C_{60}Fe(CO)_4^{\cdot +}$ possibly resides on Fe as indicated in the bipyramidal structure I proposed for $C_{60}Fe(CO)_4^{\cdot +}$. But, given the large uncertainty in $IE(Fe(CO)_4)$, it is not possible to be conclusive.

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

The dication C_{60}^{2+} was observed to react rapidly, $k_4 = 5.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, with iron pentacarbonyl solely by the dissociative electron-transfer reaction (4)

$$C_{60}^{2+} + Fe(CO)_5 \rightarrow C_{60}^{\cdot +} + Fe(CO)_4^{\cdot +} + CO \qquad (4)$$

as shown in Fig. 2. Non-dissociative electron transfer, which was not observed, is exothermic by 3.40 eV since $RE(C_{60}^{2+}) = 11.36 \pm 0.05$ eV [11]. This exceeds, by about 1.6 eV, the exothermicity required for the reaction to surmount the energy barrier arising from Coulombic repulsion between the two singly-charged product ions [11,12]. The dissociative electron-transfer reaction (4) is exothermic by at least 2.2 eV, given reported values for $D(Fe(CO)_4^{+}\text{–}CO)$ in the range from 1.16 to 0.79 eV (see Table 2) which is also sufficient to surmount the barrier. But this is not the case for dissociative electron transfer accompanied by the elimination of two CO molecules which is exothermic by at most 1.5 eV, given a value for $D(Fe(CO)_3^{+}\text{–}CO)$ of 1.1 eV (see Table 2). Thus dissociative electron transfer with the elimination of one CO molecule is preferred over dissociative electron transfer with the elimination of two or more CO molecules. Dissociative electron transfer is likely to be entropically preferred over non-dissociative electron transfer.

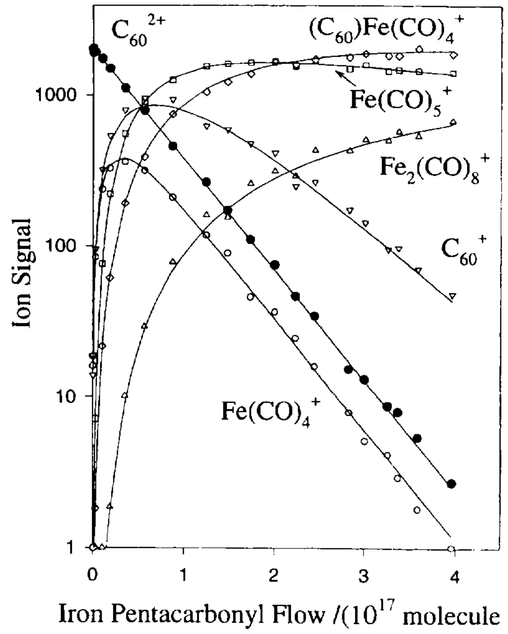

Fig. 2. Experimental data for the chemistry initiated by the reaction of C_{60}^{2+} with iron pentacarbonyl. The solid lines for C_{60}^{2+}, $C_{60}^{\cdot +}$ and $Fe(CO)_4^{+}$ represent fits to the experimental data with solutions of the systems of differential equations appropriate for the observed primary and secondary reactions. All other lines are drawn for clarity.

3.3. Reaction with $C_{60}^{\cdot 3+}$

The $C_{60}^{\cdot 3+}$ cation was observed to react rapidly, $k_5 = 2.2 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, with iron pentacarbonyl solely by the dissociative electron-transfer reaction (5)

$$C_{60}^{\cdot 3+} + Fe(CO)_5 \rightarrow C_{60}^{2+} + Fe(CO)_3^{\cdot +} + 2CO \qquad (5)$$

as shown in Fig. 3. Non-dissociative electron transfer, which was not observed, is exothermic by 7.6 or 8.6 eV depending on the value of $RE(C_{60}^{\cdot 3+})$, 15.6 ± 0.5 eV [13] or 16.6 ± 1 eV [14], used. This exceeds, by 3.1 or 4.1 eV, the estimated threshold in exothermicity of 4.5 ± 0.4 eV [12] required to surmount the energy barrier arising from Coulombic repulsion between the singly and doubly-charged product ions [11,12]. The dissociative electron-transfer reaction (5) is exothermic by at least 5.4 or 6.4 eV, given reported values for $D(Fe(CO)_4^{+}\text{–}CO)$ in the range from 1.16 to 0.79 eV and $D(Fe(CO)_3^{+}\text{–}CO)$ in the range from 1.10 to 1.05 eV (see Table 2), and so is also sufficiently exothermic to surmount the Coulombic energy barrier. However, this may no longer be the case for the elimination of 3 CO molecules, viz. reac-

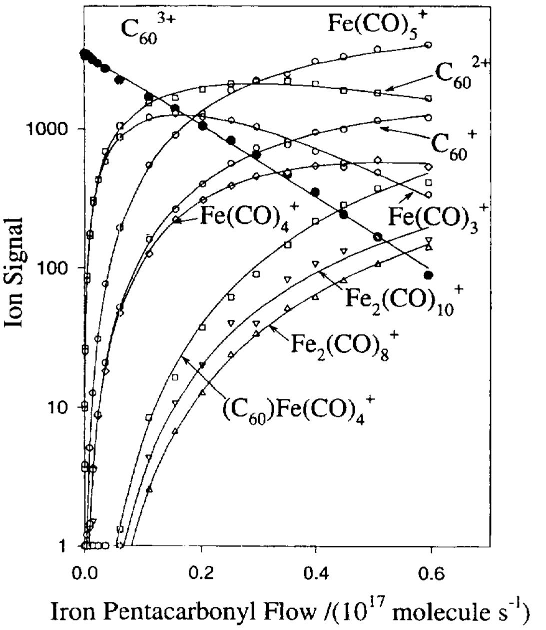

Fig. 3. Experimental data for the chemistry initiated by the reaction of $C_{60}^{\cdot 3+}$ with iron pentacarbonyl. The solid lines for $C_{60}^{\cdot 3+}$, C_{60}^{2+}, $C_{60}^{\cdot +}$, $(C_{60})Fe(CO)_4^{\cdot +}$, $Fe(CO)_3^{\cdot +}$ and $Fe(CO)_4^{\cdot +}$ represent fits to the experimental data with solutions of the systems of differential equations appropriate for the observed primary, secondary and tertiary reactions. All other lines are drawn for clarity.

tion (6) which may be exothermic by as little as 4.3 eV, given reported values for

$$C_{60}^{\cdot 3+} + Fe(CO)_5 \rightarrow C_{60}^{2+} + Fe(CO)_2^{\cdot +} + 3CO \quad (6)$$

$D(Fe(CO)_2^+\text{-}CO)$ in the range from 0.69 to 1.12 eV, and this may explain why two CO molecules are selectively eliminated in this case. A qualitative view of the pertinent potential-energy profiles is given in Fig. 4.

3.4. Proposed model for dissociative electron transfer

We propose that charge separation and dissociation in the reactions of C_{60}^{2+} and $C_{60}^{\cdot 3+}$ with $Fe(CO)_5$ occur synchronously with similar frequencies, rather than sequentially. Sequential dissociative electron transfer appears unlikely since Fe–CO vibrations are expected to occur on a time scale similar to that for charge separation. Also, the observed specificity in CO loss would not be expected since the excess internal energy potentially deposited in $Fe(CO)_5^{\cdot +}$ in the initial electron transfer would be sufficient to boil off all 5 CO molecules and the Coulombic barrier would not come into play. In the synchronous mechanism, loss of 2 or more CO molecules in the reaction of C_{60}^{2+} and 3 or more CO molecules in the reaction of $C_{60}^{\cdot 3+}$ is blocked by the Coulombic barrier. Instead, $Fe(CO)_5^{\cdot +}$ loses a maximum of one molecule in the reaction of C_{60}^{2+} and two CO molecules in the reaction of $C_{60}^{\cdot 3+}$ in order to minimize energy and maximize entropy.

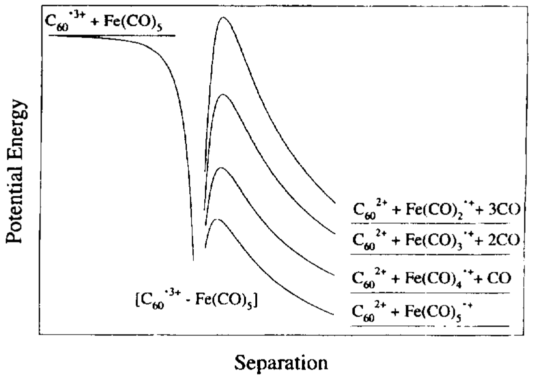

Fig. 4. Hypothetical potential-energy diagram projected into two dimensions for the non-dissociative and dissociative electron transfer between $C_{60}^{\cdot 3+}$ and $Fe(CO)_5$. Accent is given to the initial interaction between the reactants and to the Coulombic barrier for formation of products. Details of the transition complex are not invoked. The Coulombic barrier has been estimated by the addition of a Coulombic (r^{-1}) repulsive potential and an (r^{-4}, r^{-6}) attractive potential.

3.5. Secondary reactions and the influence of kinetic energy release in charge separation

Although no secondary reactions were observed in the chemistry initiated by $C_{60}^{\cdot +}$, the product ions of the charge separation reactions (4) and (5) reacted further with iron pentacarbonyl. Interestingly, a number of these observed secondary reactions are significantly endothermic at room temperature but nevertheless were observed to proceed with measurable rates. Apparently they were driven by the kinetic energy and/or internal energy released in the charge separation. Specifically, the electron-transfer reactions (7) and (8) were observed for $Fe(CO)_4^{\cdot+}$ and $Fe(CO)_3^{\cdot+}$ produced by reactions (4) and (5),

$$Fe(CO)_4^{\cdot+} + Fe(CO)_5 \rightarrow Fe(CO)_5^{\cdot+} + Fe(CO)_4 \quad (7)$$

$$Fe(CO)_3^{\cdot+} + Fe(CO)_5 \rightarrow Fe(CO)_5^{\cdot+} + Fe(CO)_3 \quad (8)$$

respectively. We did not observe the condensation reactions of $Fe(CO)_4^{\cdot+}$ and $Fe(CO)_3^{\cdot+}$ with $Fe(CO)_5$ to produce $Fe_2(CO)_x^+$ ions (with x = 6–8) reported to occur under ICR conditions when these ions are produced directly by electron impact of iron pentacarbonyl [15]. Reactions (7) and (8) are endothermic by 0.57 and 0.71 eV, respectively, given ionization energies of 7.39 ± 0.41 and 7.25 ± 0.35 eV for $Fe(CO)_4$ and $Fe(CO)_3$, respectively [16]. Curve fitting of the ion profiles for $Fe(CO)_4^{\cdot+}$ and $Fe(CO)_3^{\cdot+}$ in Fig. 2 and Fig. 3 provided rate coefficients of $(1.9 \pm 0.8) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} for both reactions (7) and (8). Given that reactions (2) and (3) are endothermic at room temperature, the large measured rate coefficients imply that the $Fe(CO)_4^{\cdot+}$ and $Fe(CO)_3^{\cdot+}$ ions are kinetically or internally hot. Kinetic excitation is expected on account of the kinetic-energy release associated with the dissociative charge-separation reactions which form these ions which are exothermic by 2.2 and at least 5.4 eV, respectively. It is of interest to note here that the exothermicity of analogous single-electron transfer reactions of $W(CO)_6$ with doubly-charged rare-gas ions has been shown to be disposed of largely as internal energy [17]. We have noted previously the possible influence of kinetic-energy release in charge-separation reactions on the occurrence of secondary ion-molecule reactions under SIFT operating conditions, specifically on the occurrence of secondary reactions of protons produced in charge-separation reactions of $C_{60}^{\cdot 3+}$ with HCl and HBr [18].

No influence of kinetic excitation was observed on the rate coefficients for the secondary reactions of $C_{60}^{\cdot+}$ and C_{60}^{2+} produced in reactions (4) and (5). Curve fitting of the ion profiles for $C_{60}^{\cdot+}$ in Fig. 2 and for C_{60}^{2+} and $C_{60}^{\cdot+}$ in Fig. 3 provided rate coefficients within experimental error equal to those determined for the primary reactions of these ions. Indeed, relatively little kinetic excitation, due to the kinetic-energy release associated with the charge-separation reactions which form them, is expected for these ions because of their relatively high mass.

We also observed the tertiary reaction (9) with $Fe(CO)_5^{\cdot+}$ formed in the chemistry

$$Fe(CO)_5^{\cdot+} + Fe(CO)_5 \rightarrow Fe_2(CO)_8^{\cdot+} + 2CO \quad (9)$$

initiated by C_{60}^{2+} and $C_{60}^{\cdot 3+}$. This reaction is identical to that observed under ICR conditions [15]. Fig. 3 shows that the chemistry initiated by $C_{60}^{\cdot 3+}$ also leads to some production of $Fe_2(CO)_{10}^{\cdot+}$, presumably as a consequence of the tertiary reaction (10).

$$Fe(CO)_5^{\cdot+} + Fe(CO)_5 \rightarrow Fe_2(CO)_{10}^{\cdot+} \quad (10)$$

Curiously, this ion was not produced in the chemistry initiated by C_{60}^{2+} and the reason for this is not clear. One possible explanation lies in the sequential energy deposition which will be different in the chemical sequence initiated by C_{60}^{2+} and $C_{60}^{\cdot 3+}$ and which may leave $Fe(CO)_5^{\cdot+}$ more favourably disposed to produce $Fe_2(CO)_{10}^{\cdot+}$ in the sequence initiated by $C_{60}^{\cdot 3+}$.

4. Conclusions

A fast bimolecular reaction has been observed under SIFT conditions between $C_{60}^{\cdot+}$ and iron pentacarbonyl leading to a stable derivatized C_{60} cation, $C_{60}Fe(CO)_4^{\cdot+}$. The chemistry switches completely for the higher charge states to charge separation by dissociative-electron transfer leading to the elimination of one and two molecules of CO with C_{60}^{2+} and $C_{60}^{\cdot 3+}$, respectively. The specificity of these CO eliminations can be rationalized in terms of favourable entropy changes and kinetic control by energy barriers arising from Coulombic repulsion between product ions. Further evidence has been gained for the possible influence of kinetic-energy release in charge-separation reactions on the occurrence of secondary ion-molecule reactions under SIFT operating conditions.

Acknowledgements

D.K.B. thanks the Natural Sciences and Engineering Research Council of Canada for the financial support of this research.

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