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Gas-phase reactions of the buckminsterfullerene cations $C_{60}^{\cdot+}$, C_{60}^{2+}, and $C_{60}^{\cdot3+}$ with aldehydes, ketones, carboxylic acids, and esters

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Abstract

The reactions of the fullerene ions $C_{60}^{\cdot+}$, C_{60}^{2+}, and $C_{60}^{\cdot3+}$ with the carbonyl and carboxyl-containing molecules R–CHO (R = H, CH_3, CH_2H_5), CH_3–CO–R (R = CH_3, C_2H, C_2H_5, n-C_3H_7), C_2H_5–CO–C_2H_5, c-C_5H_8O, R–COOH (R = H, CH_3), and R–$COOCH_3$ (R = H, CH_3), have been studied using a Selected-Ion Flow Tube (SIFT) at 294 ± 2 K and 0.35 ± 0.01 Torr of helium. A wide range in reactivity was observed. The monocation $C_{60}^{\cdot+}$ was unreactive with all of the neutrals surveyed. The dication C_{60}^{2+} was observed to add to most of the neutrals: the efficiency of adduct formation was seen to be strongly dependent upon the functional group, and was also observed to increase with increasing size of the alkyl substituents. The adducts of ketones, aldehydes and carboxylic acids were observed to undergo proton transfer to the reactant neutral, as a secondary process; in contrast, proton transfer did not occur from the adducts of esters. Structural factors can account for these differences in reactivity. Proton transfer from carbonyl-containing adducts is presumed to involve deprotonation from an α carbon atom, as indicated by the failure of the dicationic adducts of benzaldehyde to undergo deprotonation. Proton transfer from the carboxylic acid adducts involves loss of the carboxyl proton rather than α C–H proton loss, since the ester adducts did not display proton transfer. The reaction chemistry of $C_{60}^{\cdot3+}$ with these neutrals was dominated by charge transfer, although addition to some neutrals with an ionization energy, IE > 9.9 eV was noted also. General features of the secondary chemistry of the triply-charged adducts were similar to the features of the dication adduct chemistry: similar structural factors appear to influence the dication and trication adduct chemistry, although a greater tendency towards charge separation reactions was apparent in the chemistry of the tricationic adducts. Notably, a methyl cation transfer channel was observed in the reactions of the tricationic ester adducts with the parent neutrals.

Keywords: Fullerene cations; Selected-ion flow tube; Gas-phase ion–molecule reactions

1. Introduction

A staggering diversity of studies of fullerene chemistry [1] has followed in the wake of the discovery [2] and synthesis [3] of this exotic new carbon allotrope. The organic chemistry of fullerenes is a natural field of interest, given the novelty of the notion of attempting to functionalise a spherical molecule: there are obvious parallels with the development of aromatic chemistry following Kekulé's

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determination of the benzene structure. Some of the features of the new fullerene organic chemistry are: a remarkable affinity of fullerenes for radicals [4]; a tendency for hydrogenation [5], halogenation [6], and epoxidation [7] of fullerenes to be reversible, and not to go to completion; a propensity for various modes of cycloaddition to, and insertion into, the π bonds of the fullerene cage [1(b),1(d),8]; and a tendency for repeated addition to produce derivatives featuring a multiple of 6 or of 8 substituents upon the fullerene cage [9].

Mass-spectrometric studies upon fullerenes in the gas phase have also produced surprises, not least of which was the original detection of C_{60}, via its positive ion, by time-of-flight mass spectrometry [2]. Conventional studies of fullerene ionization have indicated the remarkable robustness of the strained fullerene cage, allowing the accessibility of mono-, di-, tri-, tetra-, and pentacations, and mono- and dianions of C_{60} or C_{70} [10,11], and the unprecedented formation of endohedral complexes involving, among other possibilities, "trapped" rare-gas atoms [12], metal ions [13], and CO molecules [14]. The mode of fullerene ion formation from carbon vapour has also been investigated by the groups of Bowers [15] and Jarrold [16] who have advocated high-temperature conversion of large monocyclic rings to fullerenes as the crucial feature in formation of the carbon cage surface.

Our own studies of fullerene chemistry have been concerned with the gas-phase ion/molecule reactivity of fullerenes [17]. In this light we have studied several aspects of electron transfer to and from the fullerene surface: the Penning ionization of C_{60} by metastable rare-gas atoms [17(n)], the single and double ionization of C_{60} and C_{70} by $He^{\cdot+}$ and $Ne^{\cdot+}$ [17(b)], and tendencies for charge transfer from C_{60}^{2+} [17(a)] and $C_{60}^{\cdot 3+}$ [17(l),(m)], including some double-charge-transfer reactions of $C_{60}^{\cdot 3+}$ [17(v)].

More often, our investigations have been concerned with the chemical reactivity of fullerene cations with simple organic molecules; in these systems, functionalization is often seen to be extensive albeit strongly dependent upon the fullerene's charge state and upon the existence of competing charge transfer in many reactions. We have reported on the reactivity of C_{60}^{n+} ($n = 1, 2, 3$) with regard to the occurrence of adduct formation [17(e),(k)] as well as on the occurrence of proton transfer from hydrogenated [17(o)] and derivatized [17(i)] fullerene dications. We have also described in detail several remarkable aspects of the reactions of $C_{60}^{\cdot+}$, C_{60}^{2+} and $C_{60}^{\cdot 3+}$ with amines [17(k)], alcohols and ethers [17(p)], and nitriles [17(q)]. We have observed reactions of C_{60}^{2+} with conjugated dienes [17(h),(r)] and with epoxides [17(y)] which appear to include examples of the initiation, propagation and termination of polymerization. Our preliminary studies on the influence of fullerene ion size and structure upon reactivity have indicated that the adjacent-pentagon ions C_{56}^{n+} and C_{58}^{n+} are substantially more reactive than the isolated-pentagon ion C_{60}^{n+} [17(s)]. Also, C_{70}^{n+} is generally less reactive than C_{60}^{n+} [17(e),(q)]. A motivation for this research has been scientific curiosity regarding fundamental aspects of the ion/molecule reaction chemistry of fullerenes [17(u)]. A second rationale has been an interest in the possible role of fullerenes, including cations and dications, in the chemical evolution of interstellar clouds and circumstellar shells [17(f),18–20].

Here we present the results of a study of fullerene ion reactivity with a series of carbonyl- and carboxyl-containing molecules. Such a study provides opportunities to compare and contrast the reactivity of C_{60}^{n+} with formally unsaturated oxygen-containing molecules and with the saturated alcohols and ethers of an earlier study [17(p)]. The present work also allows comparison of the efficiency of association of C_{60}^{n+} with oxygen-containing and with nitrogen-containing [17(d),(k),(q)] nucleophiles; and, involving (as it does) more complicated organic molecules than those in our previous studies, affords further insight into the mechanistic and structural considerations which influence fullerene adduct ion reactivity.

2. Experimental

All reactions were performed at 0.35 ± 0.01 Torr and 294 ± 2 K, using helium buffer gas in a Selected-Ion Flow Tube which has been described previously [21]. Fullerene ions were produced by 50 V (100 V for $C_{60}^{\cdot 3+}$) electron impact upon a vaporised C_{60}/C_{70} sample, obtained from Strem Chemicals Co. (C_{60}/C_{70}, containing 2–12% C_{70}) and from Texas Fullerenes Corp. (mixed fullerene extract, >80% C_{60}). The fullerene ions were mass selected with a quadrupole mass filter, injected into the flow tube, and allowed to thermalize by collisions with the helium buffer-gas atoms for more than 5 ms (about 10^5 collisions) before entering the reaction region at the point of addition of the neutral reagent molecules. Reactions proceeded for about 10 ms before the reacting mixture was sampled with a second mass filter downstream. Reactant and product ions were monitored as a function of addition of the reagent gas. Rate coefficients for the reactions of the fullerene ions were determined in the usual manner [21] from the exponential decay of the fullerene ion signal as a function of added reagent gas. The rate coefficients reported here have an accuracy estimated to be ±30%.

Formaldehyde was prepared using the method of Spence and Wild [22]; all other neutral reagents were obtained commercially and were not less than 98% pure. All neutral reagents were additionally vacuum-distilled prior to use and were used as dilute mixtures (1–50%, depending upon the neutral's vapour pressure at 294 K) in helium (>99.995% pure) to facilitate their introduction into the flow tube.

3. Results and discussion

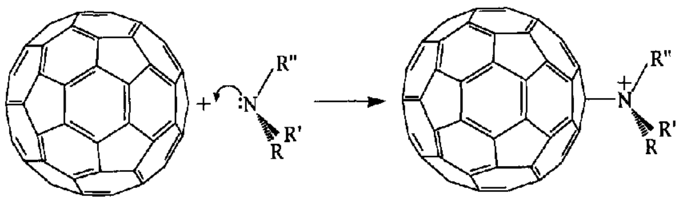
The reactions of the fullerene ions $C_{60}^{\cdot +}$, C_{60}^{2+}, and $C_{60}^{\cdot 3+}$ with the carbonyl and carboxyl-containing molecules R–CHO (R=H, CH_3, C_2H_5), CH_3–CO–R (R=CH_3, C_2H, C_2H_5, n-C_3H_7), C_2H_5–CO–C_2H_5, c-C_5H_8O, R–COOH (R=H, CH_3), and R–$COOCH_3$ (R=H, CH_3), have been studied in helium at 294 ± 2 K and 0.35 ± 0.01 Torr.

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

The monocation $C_{60}^{\cdot +}$ was unreactive with all of the neutrals surveyed here, with experimental upper limits of $k < 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for ethanoic acid, cyclopentanone, and 2- and 3-pentanone, and $k < 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for the other reagents. The higher upper limit for the less volatile reagents named reflects the lower concentrations of these species which could be attained within the reaction region.

The observed unreactivity is in keeping with previous studies of $C_{60}^{\cdot +}$ chemistry: fullerene monocations appear to react solely by charge transfer (with neutrals having IE < 7.6 ev [23]) or by association. The observation of association is limited, to date, to the reactions of $C_{60}^{\cdot +}$ with atomic hydrogen [17(c)], with ammonia and amines [17(e),(k)], and with conjugated cyclodienes [17(t)], and we have proposed [17(e),(j)] that the reactions with ammonia and amines occur by nucleophilic attack on the charge site of the fullerene.

We anticipate [17(e),(j)] that the occurrence of nucleophilic addition to $C_{60}^{\cdot +}$ requires the localization of a charge which is probably



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highly delocalized in the isolated fullerene cation, and thus addition is likely only if the reactant is a sufficiently strong nucleophile. In the present study, the carbonyl- and carboxyl-group-containing compounds are less effective nucleophiles than the amines, and so do not detectably undergo addition to $C_{60}^{\cdot+}$. A further factor (applying equally to all nucleophiles) which is expected to impede adduct formation is the necessity of distorting the spherical carbon surface in the vicinity of the fullerene-adduct bond, since a transition is required from largely sp^2 hybridization to sp^3 hybridization at this point on the fullerene surface [17(s)]. Such a distortion is likely to constitute an activation energy barrier to exothermic adduct formation. This barrier, which we presume arises between the initial, electrostatically-bound collision complex and the chemically-bonded adduct ion, is likely to be more easily overcome with increasing initial electrostatic interaction between the fullerene ion and the neutral reactant [17(u)].

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

Rate coefficients and product distributions for the primary reactions of C_{60}^{2+} with the neutrals surveyed are summarized in Table 1.

The dominant primary product channel is addition, as typified by the data shown in

Table 1
Reactions of C_{60}^{2+} with various neutrals

Reactant	Products[a]		k_{obs}[b]	k_c[c]	IE[d]
H_2CO	none		<0.001[e]	3.37	10.874
CH_3CHO	none		<0.001[e]	3.40	10.229
CH_3CH_2CHO	$C_{60}\cdot C_3H_6O^{2+}$		0.06	3.15	9.953
CH_3COCCH	$C_{60}\cdot C_4H_4O^{2+}$		0.13	2.89	10.17
CH_3COCH_3	$C_{60}\cdot C_3H_6O^{2+}$		0.27[e]	3.42	9.705
$CH_3COCH_2CH_3$	$C_{60}\cdot C_4H_8O^{2+}$		1.2[e]	3.06	9.51
$CH_3COCH_2CH_2CH_3$	$C_{60}\cdot C_5H_{10}O^{2+}$	[0.9]	1.8	2.99	9.38
	$C_{60}^{\cdot+} + CH_3COC_3H_7^{\cdot+}$	[0.1]			
$CH_3CH_2COCH_2CH_3$	$C_{60}\cdot C_5H_{10}O^{2+}$	[0.75]	1.9	2.99	9.31
	$C_{60}^{\cdot+} + C_2H_5COC_2H_5^{\cdot+}$	[0.25]			
$c\text{-}C_5H_8O$	$C_{60}\cdot C_5H_8O^{2+}$	[0.3]	2.8	3.31	9.25
	$C_{60}^{\cdot+} + c\text{-}C_5H_8O^{\cdot+}$	[0.7]			
HCOOH	$C_{60}\cdot CH_2O_2^{2+}$		0.015[e]	2.23	11.33
CH_3COOH	$C_{60}\cdot C_2H_4O_2^{2+}$		0.40[e]	2.42	10.66
$HCOOCH_3$	$C_{60}\cdot C_2H_4O_2^{2+}$		0.011	2.43	10.815
CH_3COOCH_3	$C_{60}\cdot C_3H_6O_2^{2+}$		0.016	2.33	10.27

[a] Where more than one product was detected, the branching ratio is given in square brackets.
[b] Observed effective bimolecular rate coefficient, at 294 ± 2 K and 0.35 ± 0.01 Torr of helium, in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. The accuracy is estimated to be ±30%.
[c] ADO collision rate coefficient, calculated according to the method of Su and Bowers [24], in units of 10^{-9} cm^3 molecule^{-1} s^{-1}.
[d] Ionization energy, in electronvolts, from the tabulation of Lias et al. [27].
[e] Results previously reported in Ref. [17(j)].

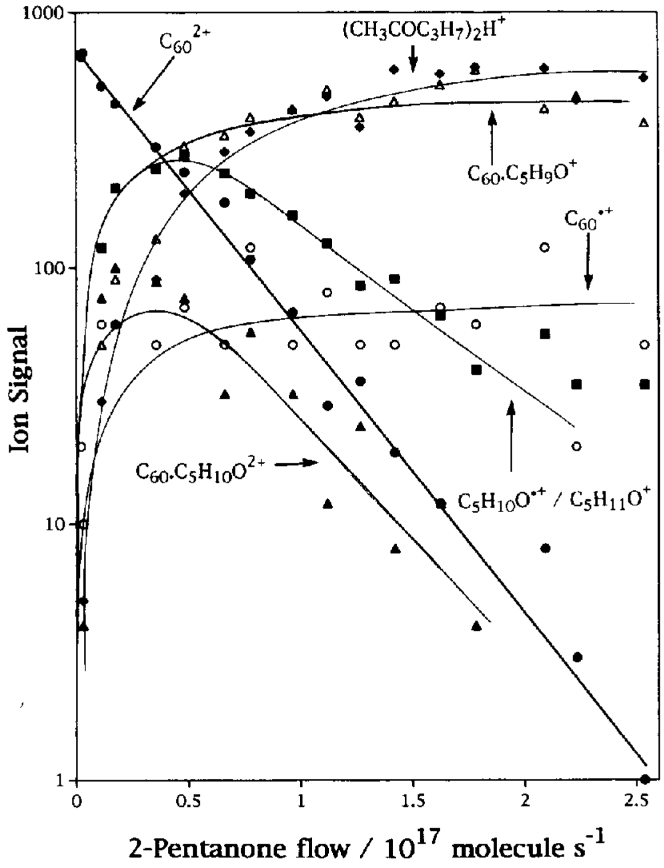
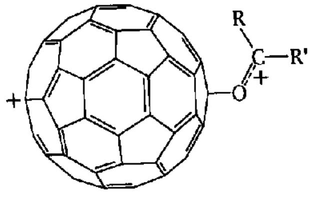


Fig. 1. Experimental data for the reaction of C_{60}^{2+} with 2-pentanone, $CH_3COCH_2CH_2CH_3$, at 294 ± 2 K and 0.348 ± 0.001 Torr of helium. Addition (90%) is the dominant primary product channel, occurring in competition with charge transfer (10%). The dominant secondary reaction of the adduct $C_{60}{\cdot}C_5H_{10}O^{2+}$ is proton transfer: the deprotonated adduct $C_{60}{\cdot}C_5H_9O^+$ does not display further reaction. Protonated 2-pentanone also undergoes a subsequent reaction to form the proton-bound dimer of 2-pentanone. The data shown was obtained using the downstream quadrupole mass spectrometer (QMS) in the high-mass mode (0–1000 u): in this mode, *m/z* 86 ($C_5H_{10}O^+$) and *m/z* 87 ($C_5H_{11}O^+$), both formed as reaction products, could not be resolved and are shown here as a composite signal (filled squares). With the QMS in the low-mass mode (0–200 u), these signals could be satisfactorily resolved but the mass range of this mode was insufficient to allow detection of the fullerene reactant or product ions involved.

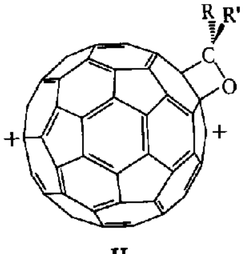
Fig. 1 for the example of $C_{60}^{2+} + CH_3COC_3H_7$. We shall discuss the observed chemistry in detail for each class of reagents, but it is useful to contrast the occurrence of efficient association in several of these reactions with the absence of any detectable association in the reactions of $C_{60}^{\cdot+}$ with the same reactants. We expect that the enhancement in association efficiency for C_{60}^{2+} compared to $C_{60}^{\cdot+}$ arises primarily as a consequence of the greater electrostatic interaction between the dication and the neutral [17(k),(q)], since the lifetime of the collision complex is dependent upon the depth of the potential well and the number of degrees of freedom available for energy dispersal within the collision complex. The greater well depth anticipated for the electrostatic interaction between C_{60}^{2+} and a reactant neutral implies that the collision complex formed in this case will have a substantially longer lifetime than the collision complex formed in the analogous reaction of $C_{60}^{\cdot+}$. Furthermore, since the activation energy (associated, at least in part, with the required change in hybridization of the fullerene carbon atom involved in bond formation) is not expected to increase proportionately with the depth of the potential well for the collision complex, the probability of adduct formation from the collision complex is substantially higher for the dication than for the monocation. Finally, association is likely to be more exothermic for C_{60}^{2+} than for $C_{60}^{\cdot+}$ because the adduct resulting from reaction of the fullerene dication is stabilised by Coulombic relaxation, arising from an increase in the effective intercharge separation as we have discussed elsewhere. This Coulombic relaxation can amount to $\approx 6\,\mathrm{kcal\,mol^{-1}}$ for an increase in the intercharge separation from 7.0 Å (the C_{60} cage diameter) to ≈ 8.5 Å (following formation of a fullerene/substituent bond). All of these aspects, which favour association of C_{60}^{2+}, are discussed in further detail elsewhere [17(u)].

Although we have ascribed the observed association reactions to the occurrence of nucleophilic addition producing structures such as **I**, the possibility of addition *across* the C=O bond (leading to cyclization as shown in structures **II** and **III**) should be considered also. Cycloaddition reactions of this type are, however, unlikely for several reasons. Firstly, the electrostatic interaction between the fullerene ion and the polar and polarizable CO-containing neutral will favour an orientation in which the electronegative oxygen atom is prominently presented towards a charge site upon the fullerene surface, promoting nucleophilic addition and disfavoring addition across the C=O bond. Secondly, were cycloaddition to occur, it would produce either a four-membered ring (as in **II**) with a high degree of strain or a larger ring (5- or 6-membered, as in **III**, although several other isomers are also possible) which would still be highly strained because the majority of the constituent atoms of such a ring are located on the fullerene surface: closure of such a ring is obstructed by the uniformly convex nature of the surface of C_{60}. Thirdly, the observed addition chemistry is consistent with the occurrence of nucleophilic addition and not with cycloaddition [25]. To date, the only apparent examples of cycloaddition reactions of fullerene cations are in the reactions of $C_{60}^{\cdot+}$ with the conjugated dienes cyclopentadiene and 1,3-cyclohexadiene [17(t)].

General trends evident in the observed secondary and tertiary chemistry of functionalised



I



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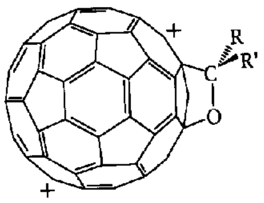


III

Table 2

Subsequent reactivity of the derivatized fullerene ions $C_{60}{\cdot}XH^{2+}$, $C_{60}{\cdot}(XH)_2^{2+}$, and $C_{60}{\cdot}X^+$ with the parent neutral XH

Reaction[a]	Products[b]		k_{obs}[c]
$C_{60}{\cdot}RCH_2CHO^{2+} + RCH_2CHO$	$C_{60}{\cdot}RCHCHO^+ + (RCH_2CHO)H^+$		>1.0
$C_{60}{\cdot}RCHCHO^+ + RCH_2CHO$	none		<0.01
$C_{60}{\cdot}RCH_2COR'^{2+} + RCH_2COR'$	$C_{60}{\cdot}RCHCOR'^+ + (RCH_2COR')H^+$	[>0.5]	>1.0
	$C_{60}{\cdot}(RCH_2COR')_2^{2+}$	[<0.5]	
$C_{60}{\cdot}(RCH_2COR')_2^{2+} + RCH_2COR'$	$C_{60}{\cdot}RCH_2COR'{\cdot}RCHCOR'^+ + (RCH_2COR')H^+$		>1.0
$C_{60}{\cdot}RCHCOR'^+ + RCH_2COR'$	none		<0.01
$C_{60}{\cdot}RCH_2COR'{\cdot}RCHCOR'^+ + RCH_2COR'$	none		<0.01
$C_{60}{\cdot}RCOOH^{2+} + RCOOH$	$C_{60}{\cdot}RCOO^+ + RCOOH_2^+$	[>0.5]	>1.0
	$C_{60}{\cdot}(RCOOH)_2^{2+}$	[<0.5]	
$C_{60}{\cdot}(RCOOH)_2^{2+} + RCOOH$	$C_{60}{\cdot}RCOOH{\cdot}RCOO^+ + RCOOH_2^+$		>1.0
$C_{60}{\cdot}RCOO^+ + RCOOH$	none		<0.01
$C_{60}{\cdot}RCOOH{\cdot}RCOO^+ + RCOOH$	none		<0.01
$C_{60}{\cdot}RCOOR'^{2+} + RCOOR'$	$C_{60}{\cdot}(RCOOR')_2^{2+}$		~0.01
$C_{60}{\cdot}(RCOOR')_2^{2+} + RCOOR'$	none		<0.005

[a] Reaction featuring the specified ion, formed by the chemistry initiated by the reaction of C_{60}^{2+}, with the reactant neutral shown.

[b] Where more than one product channel was detected, the branching ratio is given in square brackets.

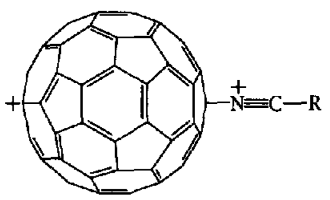
[c] Observed rate coefficient at 294 ± 2 K and 0.35 ± 0.01 Torr of helium in units of $10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$. The rate coefficient is generally expressed as an upper or lower limit indicating the range of values observed for different reactant neutrals featuring the functional group indicated. The accuracy is estimated to be ±30%.

fullerene ions (adducts and deprotonated adducts) are given in Table 2, and are discussed in further detail below.

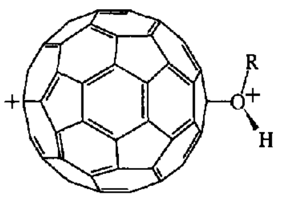
3.2.1. *Aldehydes and ketones*

The dependence of association efficiency upon reagent size (molecular complexity) is evident in the reactions of C_{60}^{2+} with carbonyl-containing compounds. We have previously proposed [17(j),(k)] that the tendency for association efficiency to increase with increasing reagent size is a consequence of the dependence of collision complex lifetime upon the number of modes available for energy dispersal: furthermore, this tendency suggests that the excitation modes of fullerene cations (presumably stretching vibrational modes, since the rigidity of the fullerene lattice precludes bending vibrational or internal rotational modes) are much less efficient than the rotational and bending vibrational modes of the neutral reagent for purposes of energy dispersal in the collision complex [17(j),(u)].

We have also discussed previously the apparent effect of molecular geometry on association efficiency. For example, the increase in efficiency with increasing molecular complexity is greater for the series of reactions $C_{60}^{2+} + RCN$ than for the series $C_{60}^{2+} + ROH$ ($R = H, CH_3, C_2H_5, C_3H_7$) [17(p)]. This may reflect the differences in the geometries of the adduct structures IV and V expected for nucleophilic addition in these instances: free rotation of alkyl groups in the nitrile RCN is



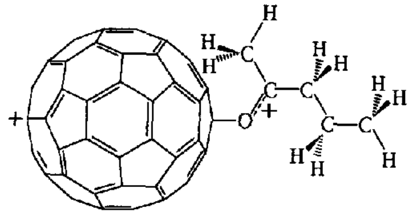
IV



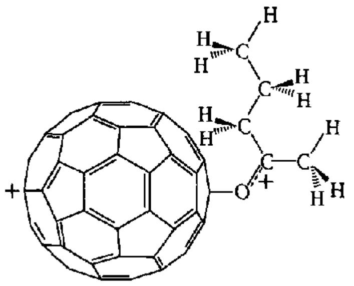
V

unlikely to be substantially affected by formation of the adduct **IV**, while free rotation in the alcohol ROH is progressively more likely to become hindered with increasing chain length R in the adduct **V** due to repulsive nonbonding interactions arising from the proximity of the alkyl chain to the fullerene surface. This effect will tend to reduce the effective number of available rotational modes in the collision complex $[C_{60}{\cdot}ROH^{2+}]^*$, reducing the lifetime of the complex and the efficiency of adduct formation: furthermore, this reduction in efficiency will be more severe for more bulky alkyl groups R. A consideration of the structure of the adduct **I** resulting from the nucleophilic addition reaction $C_{60}^{2+} + R{-}CO{-}R'$ leads to the expectation that ketones, which are more sterically demanding than nitriles but less so than alcohols, should display a dependence (of association efficiency upon molecular complexity) intermediate between that of alcohols and nitriles. As it happens, the reaction of C_{60}^{2+} with the smallest ketone CH_3COCH_3 is already reasonably efficient ($k_{obs} \approx 0.1\,k_c$) at the pressure regime of our apparatus, so that there is comparatively little scope for increasing efficiency of adduct formation with increasing molecular complexity. By analogy with the observed higher efficiency of C_{60}^{2+} adduct formation with alcohols than with ethers of comparable molecular weight [17(p)], it might be expected that the lower steric demand for an aldehyde adduct **I** (R = H) would lead to a greater propensity of aldehydes (than their ketone isomers) for association. This is not supported by the results reported here: association of propanal is substantially less efficient than association of acetone. In part, this may reflect the larger dipole moment (and consequent greater electrostatic attraction with C_{60}^{2+}) for CH_3COCH_3 ($\mu = 2.88$ D) than for CH_3CH_2CHO ($\mu = 2.52$ D [26]). Another factor which is likely to disfavor association of C_{60}^{2+} with aldehydes is the reduction in the inductive stabilization of the carbonyl group's positive charge: aldehydes possess only one inductively electron-donating alkyl group, while ketones have two such substituents. This aspect corresponds to the generally greater stability of tertiary carbocations relative to secondary carbocations.

Another consideration arising from steric interactions is that an asymmetrical ketone is more likely to form an adduct in which the smaller or less bulky alkyl group is close to the fullerene surface, since the collision complex for this configuration has a greater number of effective degrees of freedom (fewer hindered C–C bond rotational modes, and hence a longer lifetime) than if the larger or more bulky alkyl group is in close proximity to the fullerene surface. Thus, for the case of 2-pentanone and assuming that there are large barriers to rotation about the C–O bond of the ketone functionality in the adduct, the dominant isomeric form of the primary adduct with C_{60}^{2+} is expected to be structure **VI**, rather than **VII**. Similarly, adduct formation in the reaction of C_{60}^{2+} with an aldehyde is most likely to produce an adduct with the alkyl group radiating away from the fullerene



VI



VII

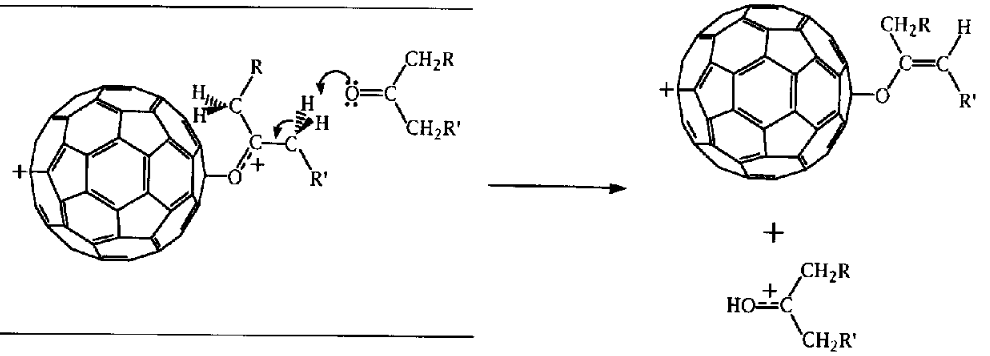
surface and the carbonyl hydrogen in comparatively close proximity to this surface.

In competition with association, charge transfer is evident in the reactions of C_{60}^{2+} with c-C_5H_8O (IE = 9.25 ± 0.01 eV), $CH_3COC_3H_7$ (IE = 9.38 ± 0.01 eV), and $C_2H_5COC_2H_5$ (IE = 9.31 ± 0.0 eV [27]). Charge transfer does not occur in the reactions of the smaller carbonyl compounds which have higher IEs. This is in keeping with previous studies which have indicated that the threshold IE(X) for efficient charge transfer from C_{60}^{2+} to a neutral X is 9.59 ± 0.11 eV [17(a),28]. In the present study, charge transfer is the dominant channel only in the reaction with cyclopentanone: charge transfer to 2- and 3-pentanone is also kinetically possible but occurs to a smaller extent, in keeping with the slightly higher IEs of the two non-cyclic pentanones. Notably, we have recently observed charge transfer from C_{60}^{2+} to diethyl ether [17(p)] ($C_2H_5OC_2H_5$, IE = 9.51 ± 0.03 eV), but not, in the present study, to butanone ($CH_3COC_2H_5$, IE = 9.51 ± 0.04 eV [27]). This may reflect a slight difference (≤ 0.07 eV, upon consideration of the total uncertainty) in the IEs of these two compounds; alternatively, it may arise from the much higher efficiency of association as a competing process in the reaction of butanone than in the case of diethyl ether, since butanone can be considered a less sterically demanding reactant than diethyl ether.

Aside from the apparent correlation between association efficiency and the molecular complexity of the reagent molecule in the reactions between C_{60}^{2+} with ketones, we should also note from Table 1 a parallel correlation with the ionization energy of the ketone which indicates an increasing reaction rate coefficient with decreasing ionization energy. We have found previously a similar correlation for reactions of $C_{60}^{+\bullet}$ with amines and have discussed a model which could account for such a correlation in terms of electronic effects [17k].

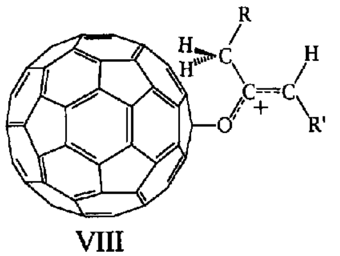
Proton transfer from the adduct dication to the reactant neutral is the dominant secondary reaction observed for the aldehydes and ketones studied, and is consistent with the adduct structures which we have previously proposed as the products of nucleophilic addition to C_{60}^{2+} [17(i),(j)]. We note that proton transfer from a dicationic fullerene species is expected to be inhibited by a reverse activation energy barrier arising from the Coulombic repulsion between the two monocationic product ions [17(i),(o)], in the same manner as for charge transfer [17(a)].

Deprotonation of a ketone adduct must necessarily occur at an alkyl chain, and presumably at one of the two α carbons in the fashion shown in reaction (2):

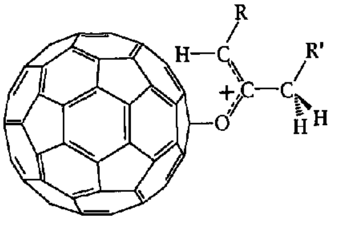


(2)

The enol-type functionality thus produced may permit stabilization of the fullerene's remaining charge in the manner shown in structure **VIII**. Deprotonation is most likely



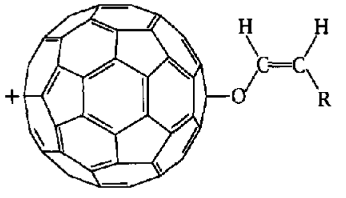
VIII



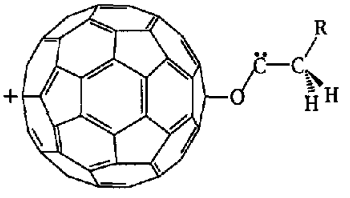
IX

to occur at the α carbon which is further from the fullerene surface, since, to minimize steric repulsion, one or two hydrogen atoms attached to the other α carbon will preferentially be oriented towards the fullerene surface: the hydrogens on the α C closer to the fullerene surface are thus comparatively inaccessible, disfavoring deprotonation to form a structure of type **IX** (although this structure appears to be not so strongly disfavored if R = H; that is, if the dicationic adduct in question is produced from a methyl alkyl ketone). In conjunction with our hypothesis that the dominant adduct isomer is similar to structure **VI**, with the more bulky alkyl substituent oriented away from the fullerene surface, we therefore expect that deprotonation is most likely to occur at the α carbon of the more bulky alkyl substituent (provided, as is the case for all ketones in the present study, that this carbon atom is hydrogenated).

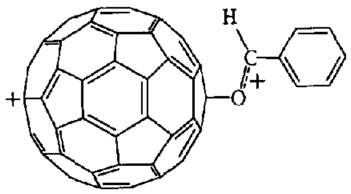
Deprotonation of a dicationic aldehyde adduct is also expected to occur at the α carbon of the alkyl chain, producing structure, **X**: loss of the carbonyl hydrogen leads to a carbene structure **XI** and is unlikely to be favored. We have previously offered a similar rationale for the apparent inability of dicationic fullerene adducts of ethers to undergo proton transfer reactions [17(p)]. If, as we suggest, deprotonation must occur at the α carbon atom, then an adduct formed from an aldehyde in which this C atom was not hydrogenated (such as 2,2 dimethyl propanal or benzaldehyde) should be incapable of proton transfer. We have consequently studied the reaction of C_{60}^{2+} with benzaldehyde; at room temperature, the vapour pressure of C_6H_5CHO was too low ($P_{vap} < 1$ Torr) to permit a kinetic measurement of this reaction, but analysis of the product ions seen at a high flow of benzaldehyde-saturated helium indicated that the sole primary and secondary



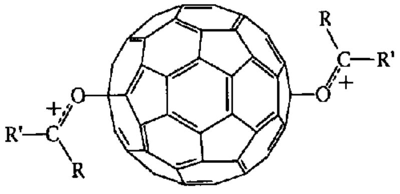
X



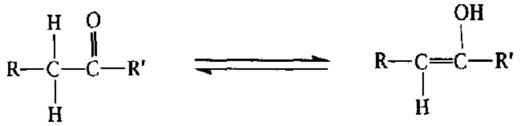
XI



XII



XIII


$$RCH_2C(O)R' \rightleftharpoons RCH{=}C(OH)R' \qquad (3)$$

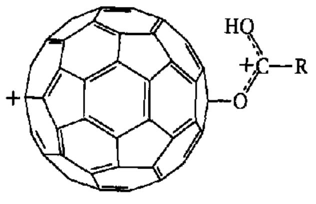
reactions occurring under our experimental conditions were addition, to form the single-handled species **XII** and its double-handled analogue. The absence of observable proton transfer from **XII**, or from the secondary adduct, is consistent with the expectation that deprotonation of ketones and aldehydes occurs solely at the α carbon.

There are obvious similarities between the occurrence of proton transfer from the dicationic carbonyl adducts and the occurrence of keto/enol tautomerism, reaction (3). The deprotonation products in the present study are, formally, ionized fullerenyl enol ethers and arise via the nucleophilicity of the C=O oxygen atom and the reactivity of the α C–H bond. The acid-catalysed keto → enol tautomerism reaction proceeds via protonation of the C=O oxygen and subsequent deprotonation of the α carbon. Given the parallels between these two processes, it is tempting to propose that the derivatization of ketones with fullerene dications might represent a new synthetic procedure: however, it is exceedingly difficult to produce positively charged fullerenes in solution [29], and therefore it seems very probable that functionalization in this manner will be achievable only in the gas phase under conditions which are unlikely to yield macroscopic quantities of the products indicated.

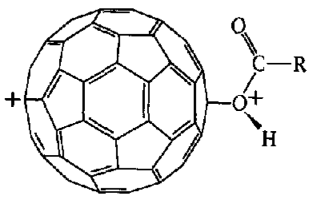
In several instances (acetone, butanone, butynone) adduct formation was observed to compete with proton transfer as a secondary product channel. As we have previously hypothesised, we expect that the secondary adduct resulting will have a 'double-handled' structure such as **XIII**. Secondary adducts of this type appeared to react solely by proton transfer to the parent ketone.

3.2.2. Carboxylic acids

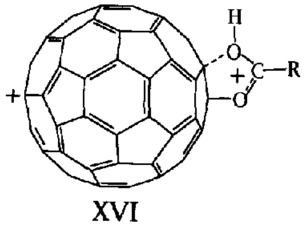
Association of HCOOH and of CH_3COOH was the only primary product channel seen, and was substantially more efficient for these two small carboxylic acids than association of C_{60}^{2+} with other oxygen-containing organic molecules of comparable molecular complexity. Presumably, the association rates for the larger carboxylic acids $C_nH_{2n+1}COOH$ ($n \geq 2$) will show an additional increase with increasing alkyl chain length: however, due to the low vapor pressures of these larger reagents, we were unable to verify this expectation.



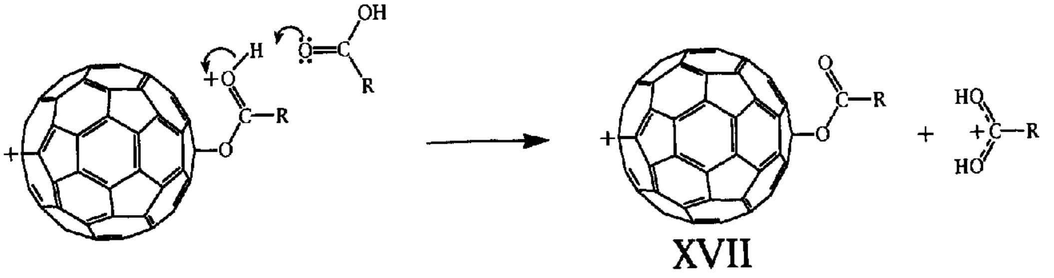
XIV



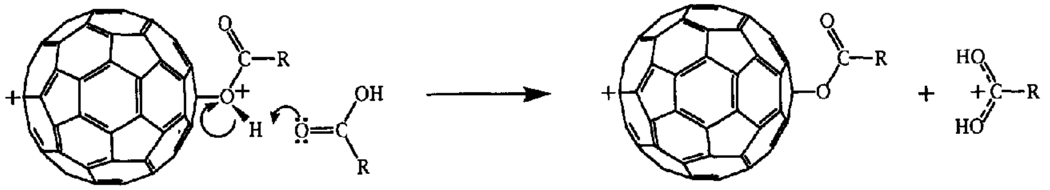
XV



XVI



(4)

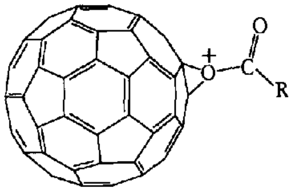


(5)

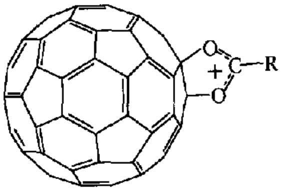
The carboxylic acids possess two oxygen atoms, each of which is a potential lone-pair donor: therefore, there are several possibilities **XIV–XVI** for the primary adduct structure. It seems reasonable to propose that the comparatively high efficiency of association with C_{60}^{2+} is a consequence of the greater electron-donating tendency of a functional group possessing two lone-pair-bearing atoms. Of the adduct structures proposed, it seems probable that **XIV** and/or **XVI** are dominant, since each of these structures has the charge effectively delocalized over several atoms of the carboxylic acid moiety: in contrast, the other possible isomer **XV** has very little opportunity apparent for stabilization by charge delocalization.

Proton transfer was the dominant secondary product channel observed and is presumed to involve loss of the acidic proton in preference to proton loss from the α carbon of the alkyl group: in the case of the formic acid adduct at least, loss of the non-acidic proton is strongly disfavored since this would produce a carbene product ion, by analogy to the arguments presented above concerning deprotonation of aldehyde adducts. Deprotonation of either **XIV** or **XV** gives the structure **XVII**, which may undergo charge migration and rearrangement to produce an alkoxonium structure such as **XVIII** or an acetal-like ion **XIX** (although this rearrangement would require the rehybridization of an additional sp^2-like carbon into a sp^3 carbon). The acetal structure **XIX** is also the product ion expected from proton transfer from **XVI**, and is likely to be favored over **XVIII** (regardless of the structure of the parent dicationic adduct) on the basis of reduced ring strain and greater charge delocalization.

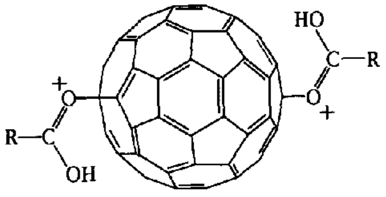
Formation of a secondary adduct was



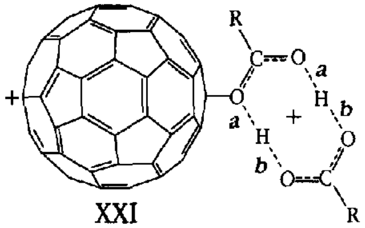
XVIII



XIX



XX

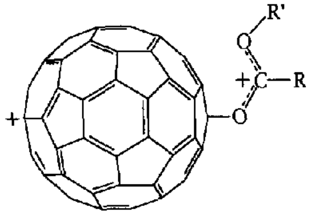


XXI

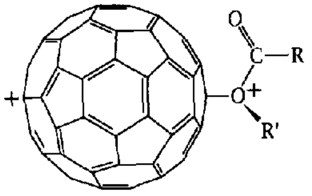
observed to compete with proton transfer in the secondary chemistry of C_{60}^{2+} + CH_3COOH:

$$\begin{aligned} &C_{60}\cdot C_2H_4O_2^{2+} + CH_3COOH \\ &\quad \rightarrow C_{60}\cdot C_2H_3O_2^{+} + CH_3C(OH)_2^{+} \quad [0.7] \quad (6a) \\ &\quad \rightarrow C_{60}\cdot (C_2H_4O_2)_2^{2+} \quad [0.3] \quad (6b) \end{aligned}$$

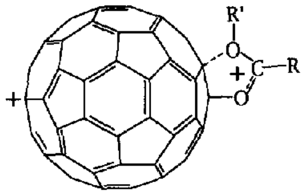
As with the formation of the secondary adduct **XIII** in the reactions of C_{60}^{2+} with ketones, we presume that $C_{60}\cdot(C_2H_4O_2)_2^{2+}$ is a 'double-handled' adduct **XX** although the possibility also exists for formation of a proton-bound secondary adduct such as **XXI** [30]. Although it can be seen that structure **XXI** offers substantial opportunity for charge delocalization, we expect that proton-bound secondary adduct formation is disfavored relative to proton transfer, since the presence of a second positive charge upon the fullerene surface induces an electric field gradient which would weaken the bonds labelled a and strengthen the bonds labelled b on **XXI**. This effect appears to be quite substantial for multiply-charged, proton-bearing ions—for example, multiply-protonated cytochrome C, MH_n^{n+} ($n = 9-15$) produced by electrospray ionization is observed to undergo proton transfer with H_2O [31] even though the proton affinity of water ($PA(H_2O) = 166.5\,kcal\,mol^{-1}$) [32] is substantially below the proton affinity, in isolation, of any of the amino acid residues ($PA \geq 230\,kcal\,mol^{-1}$) which constitute cytochrome C. While the chemical behaviour of large, multiply-protonated biomolecules is expected to be substantially different from the reactivity of the comparatively small dicationic adducts under discussion, the effects of intercharge Coulombic repulsion upon interactions between protons and proton-acceptor sites within a collision complex are likely to be similar in tendency, if not in magnitude, for both types of species. We therefore anticipate that collisions featuring a suitable orientation



XXII



XXIII



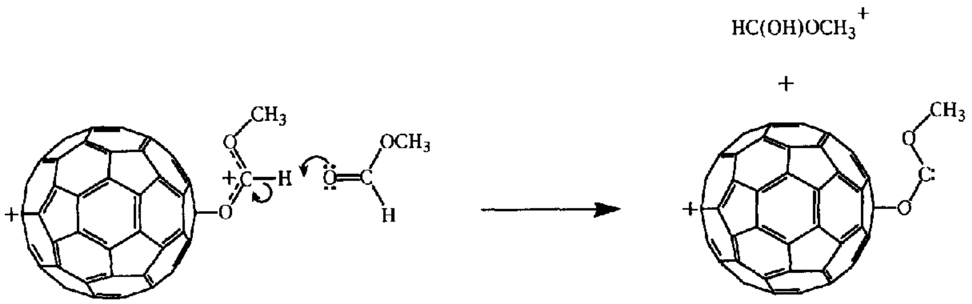
XXIV

of reactants to allow formation of **XXI** will instead access the proton transfer channel. However, while contending that *di*cationic adducts are unlikely to form proton-bound species, we note that there is evidence for the formation of proton-bound secondary adducts in the chemistry initiated by the *mono*cation $C_{60}^{\cdot+}$ with NH_3 and with primary and secondary amines [17(j),(k)], and in the reaction of $C_{60}NH_2^+$ with NH_3 [33].

3.2.3. Esters

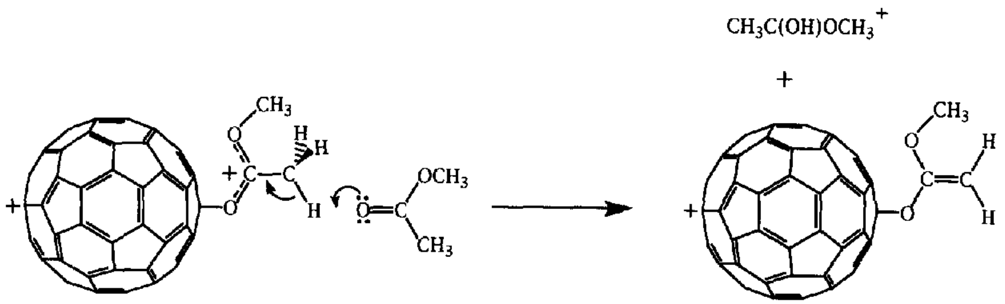
The primary reaction observed for C_{60}^{2+} with methyl formate ($HCOOCH_3$, IE = 10.815 eV) and methyl acetate (CH_3COOCH_3, IE = 10.27 eV) was association. As with the carboxylic acids, the esters contain two potential lone-pair-donor O atoms, and several isomeric adducts such as **XXII**–**XXIV** may be formed in the primary association reaction. The effective bimolecular rate coefficients for formation of the primary adducts were substantially lower for the esters ($k_{obs} = 1.1 \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$ for $HCOOCH_3$ and $1.6 \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$ for CH_3COOCH_3) than for the analogous carboxylic acids. This result is somewhat surprising given the structural similarities between the two classes of compounds, but could result from a higher steric demand for esters than for carboxylic acids, especially if the ester's alkoxy O atom is involved in bonding with the fullerene surface as shown in structures **XXIII** and **XXIV**.

A notable observation is that the primary adducts reacted *solely* by addition, presumably forming a 'double-handled' species as described elsewhere [17(j)] (and in keeping with the secondary adduct formation seen in the reactions of C_{60}^{2+} with the ketones and carboxylic acids discussed above). This observation is contrary to the general trend of derivatized fullerene dications $C_{60}{\cdot}XH^{2+}$ to undergo proton transfer to the neutral HX [17(i)], and does not seem in this instance to reflect a low proton affinity value for the neutral esters. The proton affinities of the esters ($PA(HCOOCH_3) = 188.9\,kcal\,mol^{-1}$; $PA(CH_3COOCH_3) = 197.8\,kcal\,mol^{-1}$) are higher than those of the corresponding carboxylic acids ($PA(HCOOH) = 178.8\,kcal\,mol^{-1}$; $PA(CH_3COOH) = 190.2\,kcal\,mol^{-1}$ [32]), for which proton transfer is the dominant secondary product channel as detailed above. As with the adducts of C_{60}^{2+} with nitriles [17(q)] and with ethers (17(p)], for which proton transfer to the parent neutral does not occur, we contend that structural considerations can account for the failure of the ester adducts to undergo proton transfer. These considerations apply regardless of the structure (**XXII**–**XXIV**) of the primary association product. Deprotonation of the primary and secondary methyl formate adducts is severely hindered: the methoxy group is incapable of proton loss, and deprotonation of the C atom of the carboxyl functionality results in the formation of a carbene product ion **XXV**. The methyl acetate adduct **XXVI** appears to offer greater scope for



XXV

(7)



XXVI

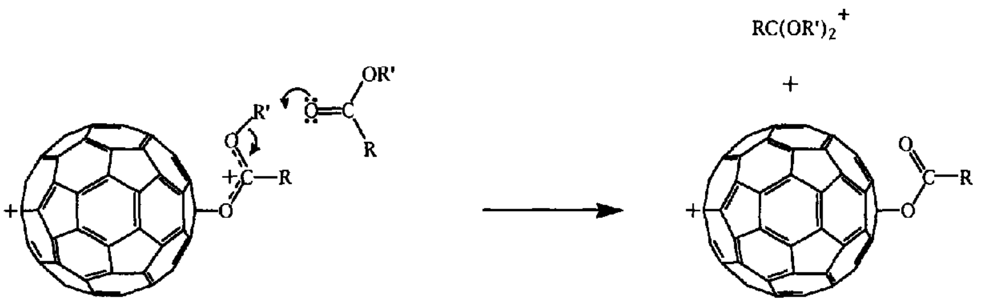
(8)

deprotonation but this pathway for charge separation also appears blocked, since proton transfer was not observed. The failure of reaction (8) substantiates the proposal, presented in the discussion on carboxylic acid chemistry, that deprotonation involves the COOH functionality rather than the alkyl group attached to this functionality. Nevertheless, it is somewhat surprising that deprotonation from the α carbon atoms of ketone adducts (for example, in the case of acetone) is very efficient while deprotonation at this site does not occur measurably for methyl acetate. The adduct structures **XXII** and **XXIV** proposed for the ester adducts do offer a greater degree of charge delocalization than does structure **I** for the ketones, and this may well inhibit deprotonation reactions such as (8).

By comparison with the reactivity of the carboxylic acids, a possible alternative secondary product channel for the esters is alkyl (in the present examples, methyl) cation transfer from the alkoxy group of the primary adduct. This process, also, failed to occur measurably for the dicationic adducts. Alkyl cation transfer is a possible secondary reaction also in the reactions of the adducts of C_{60}^{2+} with ethers, as we have discussed previously [17(p)]. The failure of fullerene dicationic adducts of ethers or esters to undergo *any* charge-separating reactions indicates that the Coulombic relaxation arising from charge separation (whether proton or alkyl cation transfer) is not sufficient to overcome the structural constraints to such processes. As we shall discuss below, this is not the case for the chemistry initiated by the fullerene trication $C_{60}^{\cdot 3+}$.

3.3. *Reactions of $C_{60}^{\cdot 3+}$*

As can be seen from an examination of Table 3, the dominant primary product channel in the reactions of $C_{60}^{\cdot 3+}$ with the carbonyl and carboxyl compounds was charge transfer. This observation is in accordance with the value of 11.09 ± 0.09 eV which we have previously reported [17(l),(m)] as the threshold ionization energy IE(M) for charge



(9)

Table 3
Reactions of $C_{60}^{\cdot 3+}$ with various neutrals

Reactant	Products[a]		k_{obs}[b]	k_c[c]	IE[d]
H_2CO	$C_{60}^{2+} + H_2CO^{\cdot +}$		1.8	5.06	10.874
CH_3CHO	$C_{60}^{2+} + CH_3CHO^{\cdot +}$		3.7	5.10	10.229
CH_3CH_2CHO	$C_{60}^{2+} + C_2H_5CHO^{\cdot +}$	[0.75]	4.2	4.72	9.953
	$C_{60}{\cdot}C_3H_6O^{\cdot 3+}$	[0.25]			
CH_3COCCH	$C_{60}^{2+} + CH_3COCCH^{+}$	[0.8]	4.5	4.33	10.17
	$C_{60}{\cdot}C_4H_4O^{\cdot 3+}$	[0.2]			
CH_3COCH_3	$C_{60}^{2+} + CH_3COCH_3^{\cdot +}$		5.8	5.13	9.705
$CH_3COCH_2CH_3$	$C_{60}^{2+} + CH_3COC_2H_5^{\cdot +}$		5.6	4.59	9.51
$CH_3COCH_2CH_2CH_3$	$C_{60}^{2+} + CH_3COC_3H_7^{\cdot +}$		4.8	4.48	9.38
$CH_3CH_2COCH_2CH_3$	$C_{60}^{2+} + C_2H_5COC_2H_5^{\cdot +}$		5.5	4.48	9.31
c-C_5H_8O	$C_{60}^{2+} +$ c-$C_5H_8O^{\cdot +}$		4.3	4.96	9.25
HCOOH	$C_{60}H^{\cdot 2+} + CO_2H^{+}$	[0.5]	2.5[e]	3.34	11.33
	$C_{60}{\cdot}CH_2O_2^{\cdot 3+}$	[0.5]			
CH_3COOH	$C_{60}{\cdot}C_2H_4O_2^{\cdot 3+}$		4.2	3.63	10.66
$HCOOCH_3$	$C_{60}{\cdot}C_2H_4O_2^{\cdot 3+}$		2.9	3.65	10.815
CH_3COOCH_3	$C_{60}^{2+} + CH_3COOCH_3^{\cdot +}$	[0.1]	3.4	3.50	10.27
	$C_{60}{\cdot}C_3H_6O_2^{\cdot 3+}$	[0.9]			

[a–d] See corresponding notes to Table 1.
[e] Result previously reported in Ref. [17m].

transfer from $C_{60}^{\cdot 3+}$ to a neutral M:

$$C_{60}^{\cdot 3+} + M \rightarrow C_{60}^{2+} + M^{\cdot +} \quad (10)$$

Of the compounds studied here, only formic acid (IE = 11.33 ± 0.01 eV), formaldehyde (IE = 10.874 ± 0.002 eV), and methyl formate (IE = 10.815 ± 0.005 eV [27]) have ionization energies near or exceeding the threshold value: charge transfer from $C_{60}^{\cdot 3+}$ to formaldehyde was observed, but not to HCOOH or to $HCOOCH_3$.

It is interesting to note that $HCOOCH_3$ and CH_3COOCH_3, which were comparatively poor addition reagents in the reactions of C_{60}^{2+} as discussed above, were among the few species in the present study which reacted with $C_{60}^{\cdot 3+}$ by association as the major channel despite competition from an accessible charge transfer product channel. Dominant adduct formation in the presence of accessible charge transfer has also been noted previously [17(k)] in the reaction of $C_{60}^{\cdot 3+}$ with NH_3 (IE(NH_3) = 10.16 ± 0.01 eV):

$$C_{60}^{\cdot 3+} + NH_3 \rightarrow C_{60}{\cdot}NH_3^{\cdot 3+} \quad (11)$$

These results appear to indicate that the depth of the potential well corresponding to formation of an electrostatic complex exceeds the depth of the threshold to charge transfer. Therefore it seems likely that the lifetime of the collision complex is important in the competition between charge transfer and association—for example, charge transfer to formaldehyde is less exothermic than charge transfer to ethanoic acid, and yet only the former process is observed: if the $C_{60}{\cdot}X^{\cdot 3+}$ collision complex has a short lifetime, the probability of complex dissociation is high, and charge transfer can presumably occur upon dissociation of the complex. In this scenario adduct formation appears to act as a 'trap' upon the potential energy surface leading to charge transfer, as we have discussed elsewhere [17(e),(u)]. It is rather surprising that the 'trapping' action of the potential well (leading to adduct formation) can apparently be of such a high efficiency, especially for a comparatively compact product ion possessing three positive charges and involving association with a neutral whose adduct-forming tendencies with C_{60}^{2+} have been demonstrated to be quite inefficient (in the cases of CH_3CH_2CHO, CH_3COCCH, $HCOOCH_3$ and CH_3COOCH_3). For a triply-charged collision complex, the well depth will exceed the depth of the potential well for the doubly-charged collision complex, and so the complex lifetime will be larger. The inability of adduct formation to prevail against charge transfer in reactions of $C_{60}^{\cdot 3+}$ with larger neutrals such as $CH_3CH_2COCH_2CH_3$ (for which the collision complex lifetime should be larger) can be attributed to the greater energy release available immediately upon charge transfer to these neutrals—the collision complex lifetime now becomes unimportant, and stabilization by emission of one infrared photon or by collision with one buffer gas (helium) atom may no longer suffice to render the charge transfer channel inaccessible even though dissociation of the complex back to reactants may not be energetically possible. In some cases, it is likely that charge transfer is sufficiently exothermic that the threshold to charge transfer actually lies below the depth of the potential well corresponding to formation of the collision complex, but this need not be the case for charge transfer (a rapid, bimolecular process) to predominate over adduct formation (which, whether bimolecular or termolecular, is not generally as rapid as an exothermic bimolecular process). In this light, it is not so surprising that the only carbonyl compounds to display addition to $C_{60}^{\cdot 3+}$ have ionization energies ($IE(C_2H_5CHO) = 9.953\,eV$, $IE(CH_3COCCH) = 10.17\,eV$ [27]) higher than any of the carbonyl compounds which displayed reasonably efficient association with C_{60}^{2+}.

A competing product channel, hydride abstraction from the carbonyl or carboxyl compound, was observed only in the reaction with formic acid:

$$C_{60}^{\cdot 3+} + HCOOH \rightarrow C_{60}\cdot CH_2O_2^{\cdot 3+} \quad [0.5] \quad (12a)$$

$$\rightarrow C_{60}H^{\cdot 2+} + OCOH^{+} \quad [0.5] \quad (12b)$$

We have previously estimated a value of $536 \pm 22\,kcal\,mol^{-1}$ for the hydride affinity of $C_{60}^{\cdot 3+}$ [17(o)]: this indicates that the exothermicity of channel (**12b**), $-\Delta H = 160 \pm 24\,kcal\,mol^{-1}$. While charge transfer is constrained by a reverse activation energy barrier arising from Coulombic repulsion [17(l)], and adduct stabilization is inhibited by a barrier arising from the change in hybridization (and consequent deformation of the fullerene surface) at the site of addition to the fullerene cation [17(s)], hydride abstraction by $C_{60}^{\cdot 3+}$ is disfavored by both of these effects. Thus, although hydride abstraction by $C_{60}^{\cdot 3+}$ is highly exothermic for all of the carbonyl and carboxyl compounds in the present study, its inefficiency in competition with charge transfer and with adduct formation is not surprising. We note that the hydride abstraction reaction (**12b**) is more exothermic, and substantially more efficient, than the hydride abstraction processes evident in the reactions of C_{60}^{2+} with saturated hydrocarbons which we have reported previously [17(e)].

The secondary chemistry evident in the reactions of the esters is also of note. In other instances (CH_3CH_2CHO, CH_3COOH) where adduct formation occurs between $C_{60}^{\cdot 3+}$ and a carbonyl or carboxyl compound, the dominant secondary product channel is proton transfer (in keeping with the general trend evident in the secondary reactions of adducts of C_{60}^{2+} with amines, alcohols, ketones, aldehydes and carboxylic acids). Adducts of methyl formate with $C_{60}^{\cdot 3+}$ exhibit methyl cation transfer rather than proton transfer:

$$C_{60}\cdot HCOOCH_3^{\cdot 3+} + HCOOCH_3$$

$$\rightarrow C_{60}\cdot (HCOOCH_3)_2^{\cdot 3+} \quad [0.3] \quad (13a)$$

$$\rightarrow C_{60}\cdot OCOH^{\cdot 2+} + HC(OCH_3)_2^{+} \quad [0.7] \quad (13b)$$

$$C_{60}\cdot(HCOOCH_3)_2^{\cdot 3+} + HCOOCH_3$$

$$\to C_{60}\cdot(HCOOCH_3)_3^{\cdot 3+} \qquad [< 0.5] \quad (14a)$$

$$\to C_{60}(OCOH)\cdot HCOOCH_3^{\cdot 2+} + HC(OCH_3)_2^+ \qquad [> 0.5] \quad (14b)$$

$$C_{60}\cdot(HCOOCH_3)_3^{\cdot 3+} + HCOOCH_3 \to \text{no apparent reaction} \quad (15)$$

while proton transfer competes with adduct formation and methyl cation transfer in the secondary reaction of methyl acetate,

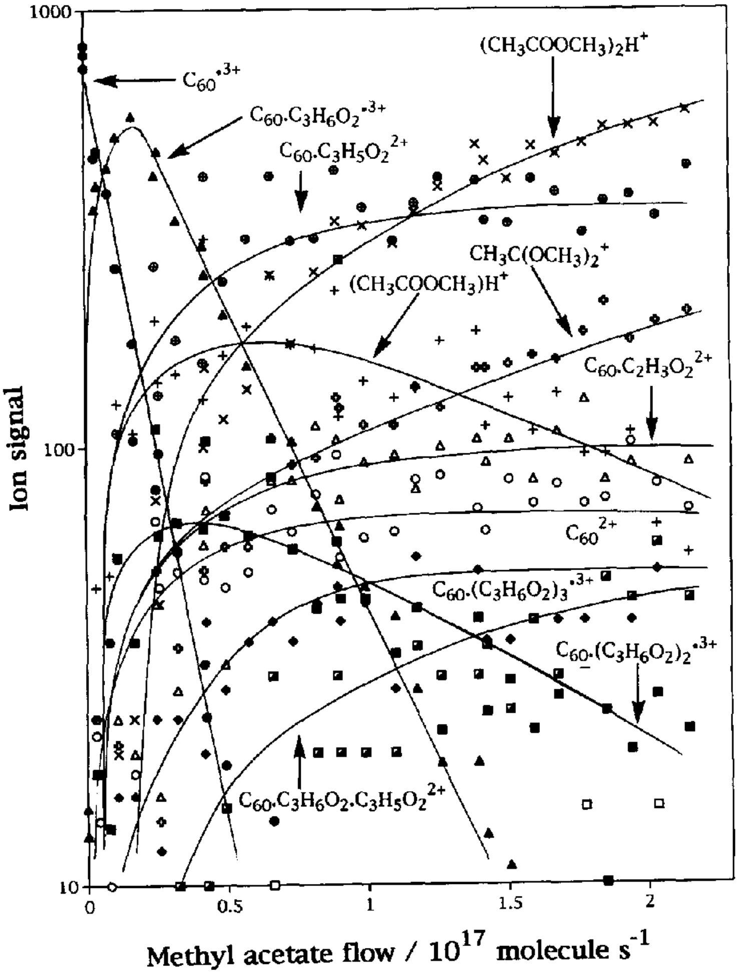
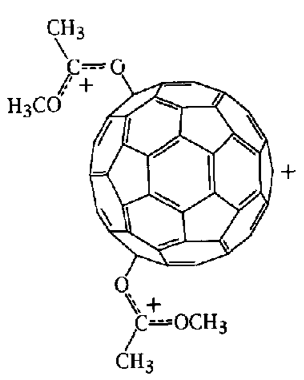
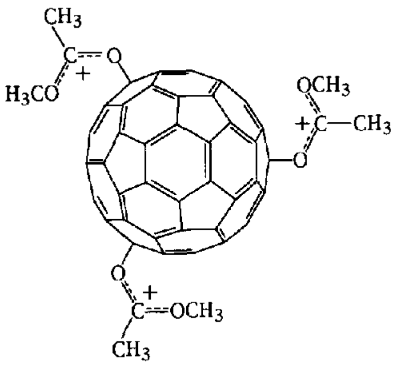


Fig. 2. Experimental data (the line fits are drawn by hand) for the reaction of $C_{60}^{\cdot 3+}$ with methyl acetate, CH_3COOCH_3, at 294 ± 2 K and 0.351 ± 0.001 Torr of helium. The dominant primary product channel is addition, yielding a measured effective bimolecular rate coefficient for this experiment of $k_{obs} = 3.8 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}: secondary product channels observed are proton transfer (producing $C_{60}\cdot C_3H_5O_2^{\cdot 2+} + (CH_3COOCH_3)H^+$), methyl cation transfer (producing $C_{60}\cdot C_2H_3O_2^{\cdot 2+} + CH_3C(OCH_3)_2^+$) and adduct formation ($C_{60}\cdot(C_3H_6O_2)_2^{\cdot 3+}$). The secondary adduct is observed to react in a similar manner to the primary adduct. Dicationic product ions appear unreactive under the conditions of the present experiment: it is possible that the ions $C_{60}\cdot C_2H_3O_2^{\cdot 2+}$ and $C_{60}\cdot C_3H_5O_2^{\cdot 2+}$ undergo further addition with methyl acetate, but the efficiency of this process is not likely to exceed the efficiency of addition of methyl formate to C_{60}^{2+} ($k_{obs} = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}). We note, also, that while protonated methyl acetate was observed to react further to yield the proton-bound dimer $(CH_3COOCH_3)_2H^+$, the methylated ion $CH_3C(OCH_3)_2^+$—which, on structural grounds, cannot form a proton-bound adduct with methyl acetate—did not appear to react further.



XXVII



XXVIII

depicted in Fig. 2:

$$C_{60}{\cdot}CH_3COOCH_3^{\cdot 3+} + CH_3COOCH_3$$

$$\rightarrow C_{60}{\cdot}(CH_3COOCH_3)_2^{\cdot 3+} \quad [0.2] \qquad (16a)$$

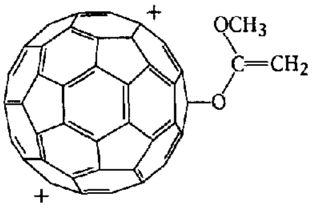
$$\rightarrow C_{60}{\cdot}OCOCH_3^{\cdot 2+}$$

$$+ CH_3C(OCH_3)_2^+ \quad [0.1] \qquad (16b)$$

$$\rightarrow C_{60}{\cdot}OC(CH_2)OCH_3^{\cdot 2+}$$

$$+ CH_3C(OH)OCH_3^+ \quad [0.7] \qquad (16c)$$

Proton transfer from the secondary adduct of methyl acetate **XXVII** was the dominant product channel observed for this ion, but again competition with addition and methyl cation transfer was evident. The tertiary adduct **XXVIII** did not appear to react further. As with the reactions of esters with C_{60}^{2+}, the comparatively low efficiency of proton transfer in reactions (13) to (16) can be accounted for by the structures of the adducts, since the same structural constraints on the reactivity of dicationic ester adducts are also expected to apply to the tricationic adducts. On this basis, it appears reasonable to propose that the deprotonated adduct with methyl acetate **XXIX** results from α carbon deprotonation. The efficiency of these charge separating reactions, in contrast to their absence in the dicationic ester chemistry, can be rationalised on the basis of the greater degree of Coulombic relaxation afforded by proton transfer or methyl cation transfer from the tricationic adducts.



XXIX

4. Conclusion

The ion/molecule reactions of $C_{60}^{\cdot +}$, C_{60}^{2+}, and $C_{60}^{\cdot 3+}$ with several carbonyl- and carboxyl-containing molecules have been studied using the selected-ion flow tube technique. $C_{60}^{\cdot +}$ was found to be totally unreactive with these neutrals. This non-reactivity has been ascribed to the failure to bring about the energy-demanding hybridization of the fullerene C atom potentially involved in bond formation. C_{60}^{2+} was observed to undergo addition as the dominant primary product channel: in most instances, proton transfer to the parent neutral was the dominant secondary product channel in evidence. The efficiency of adduct formation was seen to be strongly dependent upon the functional group, and was also observed to increase with increasing size of the alkyl substituents. $C_{60}^{\cdot 3+}$ reacted in most instances by rapid charge transfer, but was observed to form adducts with several compounds having IE > 9.9 eV, in keeping with the known influence of Coulombic barriers in such charge transfer reactions.

The doubly-charged adducts of ketones, aldehydes and carboxylic acids were observed to undergo proton transfer to the reactant neutral, as a secondary process; in contrast, proton transfer did not occur from the adducts of esters. Structural factors can account for these differences in reactivity. Proton transfer from carbonyl-containing adducts is presumed to involve deprotonation from an α carbon atom, as indicated by the failure of the dicationic adducts of benzaldehyde to undergo deprotonation. Proton transfer from the carboxylic acid adducts involves loss of the carboxyl proton rather than α C–H proton loss, since the ester adducts did not display proton transfer. General features of the secondary chemistry of the triply-charged adducts were similar to the features of the dication adduct chemistry: similar structural factors appear to influence the dication and trication adduct chemistry, although a greater tendency towards charge separation reactions was apparent in the chemistry of the tricationic adducts. Notably, a methyl cation transfer channel was observed in the reactions of the tricationic ester adducts with the parent neutrals.

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