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Accounts

Monofunctionalized C_{60} Ions: Their Generation, Stability, and Reactions

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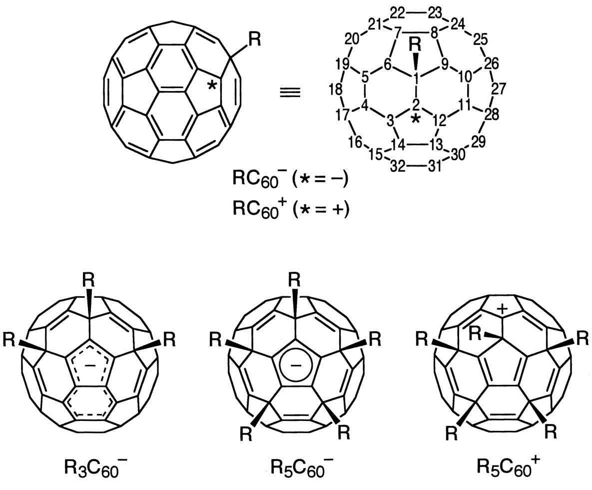
Though numerous investigations have appeared on the reduced and oxidized forms of parent C_{60}, investigations on C_{60} ions that contain exohedral functional group(s) have been rather few. This account deals with the chemistry of such ions, in particular, the chemistry of monofunctionalized species RC_{60}^- and RC_{60}^+. Studies of the anions RC_{60}^- were initiated early in the history of the fullerene chemistry, and they are generally considered appreciably stable carbanions. This account focuses on our recent synthesis of a hydrocarbon salt and ionically dissociable hydrocarbons which contain the C_{60} framework. These are unusual classes of hydrocarbons that could be obtained by making use of the high thermodynamic stability of a hydrocarbon anion t-BuC_{60}^-. Some of the properties which are characteristic of these hydrocarbons are also discussed. In contrast, studies of the chemistry of the cation RC_{60}^+ have only recently been launched. In this account, advances in the studies of these cations, including observations of their existence, the evaluation of their stabilities, and the role of these cations as a reactive intermediate, are described.

The discovery of [60]fullerene (C_{60}) introduced a new carbon-cage structural unit and a spherical π-cojugated system to the field of organic chemistry. Despite the fact that C_{60} is remarkably stable toward heat, it is capable of reacting with a wide variety of reagents. It is, therefore, reasonable to assume that new families of fullerene-based reactive species, e.g. carbocations, carbanions, and radicals, could be constructed by the functionalization of this cage, since C_{60} is an assembly of sp^2 carbons, the $2p$ orbitals of which are capable of resonance interaction with a nearby reactive center.

A functionalized C_{60} ion is a derivative of C_{60} that contain an odd number of attached groups and has an overall negative or positive charge on its spherical surface. Such an ion is distinguished from the radical ions $C_{60}^{\bullet+}$ and $C_{60}^{\bullet-}$ by the absence of an unshared electron and by its nonradical behavior. To date, ions which contain one, three, and five attached groups, i.e. RC_{60}^-, [1-3] $R_3C_{60}^-$, [4] $R_5C_{60}^-$, [5,6] RC_{60}^+, [7,8] and $R_5C_{60}^+$ [9] (Scheme 1), have been obtained pure as structurally defined species. A dimeric analogue, $^-C_{60}$–C≡C–C_{60}^-, has been also reported.[10]



Scheme 1.

Our current understanding of the chemistry of C_{60} indicates that it is a fairly electronegative molecule. Such character has been demonstrated by the ease of release of electron(s) on an electrode or by treatment with reducing agents.[11,12] A closely related behavior of C_{60} is its facile reactions with nucleophiles, which frequently form a functionalized C_{60} anion as a reaction intermediate.[1–3,13–16] These observations display pronounced anion-stabilizing effect of the spherical π-conjugated system and suggest the importance of the C_{60} framework as a building block in the synthesis of highly stabilized carbanions. In fact, C_{60} anions are reasonably stable species, which can be prepared in the form of a long-lived species and fully characterized. In the first half of this account we present the chemistry of the monofunctionalized fulleride ion, RC_{60}^-, and the synthesis of hydrocarbons in particular, which exhibit unusual properties based on the strong tendency of the RC_{60}–C bond to

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undergo heterolytic cleavage to give RC_{60}^- and a carbenium ion.

In contrast to facile reduction and nucleophilic addition, C_{60} shows a considerable resistance to oxidation and electrophilic addition. Although a number of reports have appeared which support the existence of $C_{60}^{\bullet +}$, it is an elusive species, and the preparation of its salt was achieved only very recently. A very few reports have appeared on the addition of electrophiles to C_{60}, where the number of the attacking molecules and their sites are difficult to control, in most cases. Functionalized C_{60} cations are possible intermediates in most of these reactions, but the existence of such cations has long been unclear. The latter half of this account focuses on the recent achievements relative to the observation, isolation, and properties of monofunctionalized fullerenium ions, RC_{60}^+.

1 Synthesis and Properties of Some Unusual Hydrocarbons Derived from RC_{60}^-

1.1 Background. (1) Monofunctionalized C_{60} Anions (RC_{60}^-). The simplest family of functionalized fulleride ions, RC_{60}^-, can be prepared by the addition of a nucleophile to C_{60}.[1–3,13–16] They are also generated by reactions involving the coupling between $C_{60}^{\bullet -}$ and a radical $R^\bullet$.[17,18] In the former reaction, C_{60} is treated with RLi,[1,2,13–15] RMgX,[14] CN^-,[3] MeO^-,[16] etc. to form RC_{60}^-, which is converted to the conjugate acid $RC_{60}H$ by treatment with an acid. Multiple addition to form $R_nC_{60}H_n$ frequently occurs even by treatment with an equimolar amount of a nucleophile, but a reasonable yield of the monoadduct can be attained by careful monitoring of the product during the addition of the reagent. An adduct $RC_{60}H$ is a convenient precursor of RC_{60}^-, since the proton which is attached on the C_{60} cage is readily abstracted in solution by a base such as *t*-BuOK. The RC_{60}^- anions have a characteristic dark green color and can be determined by their vis/NIR absorptions near 650 and 1000 nm. The $t\text{-BuC}_{60}^-Li^+\bullet 4CH_3CN$ salt has been isolated by Fagan et al.[1] as an analytically pure solid. An NMR study demonstrated that the rotation of the *t*-butyl group of this anion is significantly hindered. These workers, as well as Komatsu et al.[2] reported the ^{13}C NMR spectra of $t\text{-BuC}_{60}^-$ and $CH_3(CH_2)_5C{\equiv}CC_{60}^-$, respectively, which shows 30 and 26 separated sp^2 carbon signals in the aromatic region, indicating the C_s symmetry. The most upfield peak in each case (δ 126.50 and 120.99) was assigned to C-2.

Semiempirical MO calculations indicate that the negative charge of RC_{60}^- is largely distributed in the vicinity of group R (i.e., C-2, C-4, and C-11) with the population at C-2 being the largest (Fig. 1).[2,15,19] Based on this result and on the tendency for RC_{60}^- to react at C-2 with sterically undemanding electrophiles, its molecular structure is usually depicted as an anion having a negative charge which is localized at C-2 (Scheme 1). According to recent ab initio calculations at the HF/3-21G//AM1 level, however, the negative charge is dispersed more extensively over the entire cage (Fig. 2, lower half).[20] Thus, the preferential addition of a proton and other electrophiles at C-2 is not the result of charge control; rather, the thermodynamic stability of the product appears to be the major factor that governs the regioselectivity.

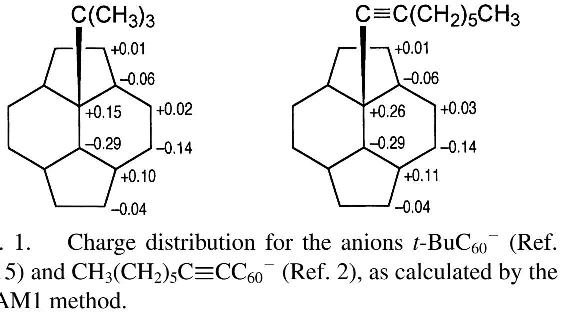


Fig. 1. Charge distribution for the anions $t\text{-BuC}_{60}^-$ (Ref. 15) and $CH_3(CH_2)_5C{\equiv}CC_{60}^-$ (Ref. 2), as calculated by the AM1 method.

(2) High Acidity of Hydrofullerenes. The thermodynamic stability of a carbanion can be determined by measurement of the pK_a value of the conjugate acid. The parent dihydro[60]fullerene, $C_{60}H_2$, which is known to have a 1,2-addition structure in its most stable form, has a pK_a of 4.7.[21] The derivatives 1,2-$RC_{60}H$ (R = *t*-Bu and CN) have been reported to exhibit pK_as of 5.7[1] and 2.5,[3] respectively. The pK_a of a related radical $HC_{60}^\bullet$, the conjugate acid of $C_{60}^{\bullet -}$, has been estimated to be 3.4[22] or 9.[21] The low pK_a values for hydrocarbons 1,2-$C_{60}H_2$ and 1,2-*t*-$BuC_{60}H$ are close to the pK_a of **1**–H (Scheme 2),[23] which had formerly been known as the most acidic hydrocarbon (pK_a 5.9,[23a] 3.2[24]). It is rather surprising that, regardless of the more or less localized nature of RC_{60}^-, this anion has an even lower basicity than $C_{60}^{\bullet -}$, where the negative charge is perfectly delocalized. The highly acidic character of hydrofullerenes has been explained by the high degree of electron delocalization on ionization. Figure 2 (upper half) indicates that when 1,2-$RC_{60}H$ is deprotonated, the developing negative charge is dispersed over the entire cage.[20]

The pK_a value reflects the difference between the free energy of the carbanion and that of the protonated form. The change in orbital hybridization of the deprotonating carbon from sp^3 to sp^2 might lead to an increase in the pK_a of hydrofullerenes to some extent, since it has been proposed that such a change relieves the strain in the sp^2 carbons of C_{60} due to deviation from planarity.[25–27]

Oxidation potential (E_{ox}) is another measure of the stability of carbanions, which is affected only negligibly by a change in orbital rehybridization. Cyclic voltammetry showed that $t\text{-BuC}_{60}^-$ and $CH_3(CH_2)_5C{\equiv}CC_{60}^-$ are oxidized at -0.37 V[28] and -0.32 V[2] vs Fc/Fc^+, respectively. These E_{ox} values are comparable to the potential for $\mathbf{1}^-/\mathbf{1}^\bullet$ redox couple (-0.18 V vs $Ag/AgNO_3$,[24] which corresponds to -0.26 V vs Fc/Fc^+ [29]). Both the pK_a and the E_{ox} values show that the stabilities of RC_{60}^- and $\mathbf{1}^-$ are similar, implying that the orbital rehybridization has only a small influence on the pK_a.

(3) Hydrocarbon Salts and Ionically Dissociable Hydrocarbons. Hydrocarbons generally consist of molecules that are entirely covalent in nature. The high acidity of hydrofullerenes led us to synthesize two classes of exceptional hydrocarbons, i.e., hydrocarbon salts and ionically dissociable hydrocarbons. Attempts to isolate an ionic hydrocarbon, or a hydrocarbon salt, are usually unproductive, since carbocations and carbanions are generally so highly reactive that they cannot coexist since they immediately react with each other. A few carbocation–carbanion salts have been synthesized using ions stabilized by heteroatom substituents.[30–36] Furthermore, we demonstrated that the hydrocarbon can also be isolated as

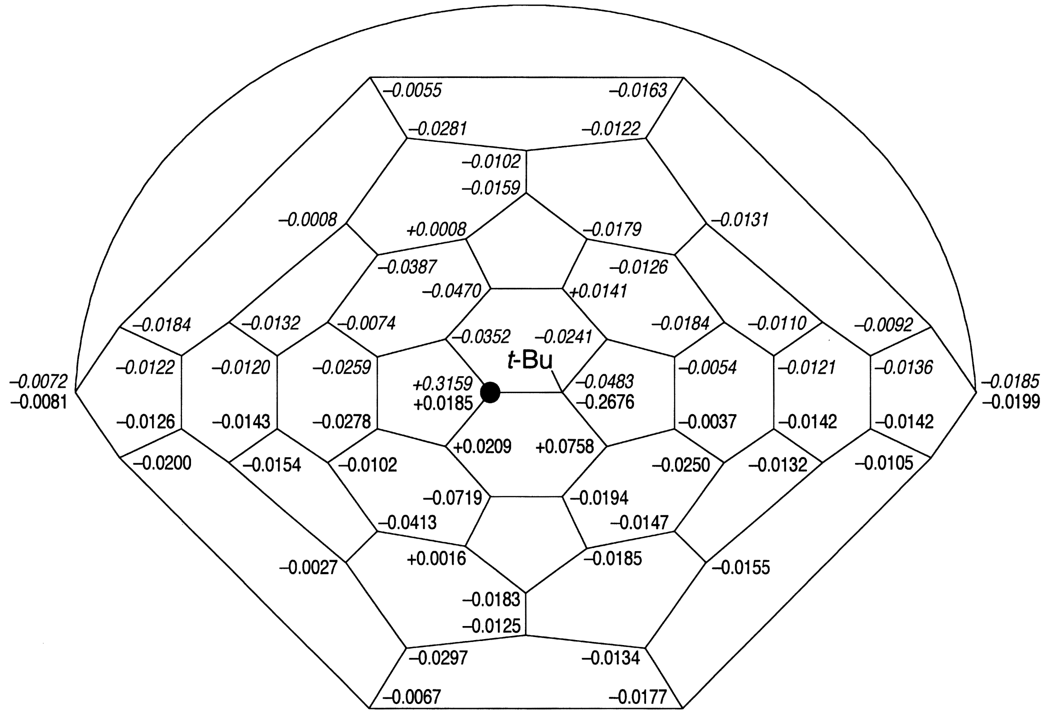
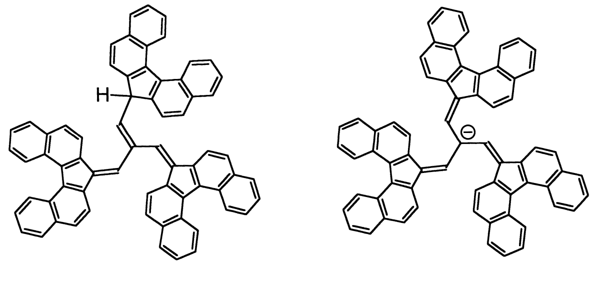


Fig. 2. Planar graph showing charge differences for the deprotonation of *t*-BuC_{60}H (upper half) and the charge distribution for *t*-BuC_{60}^- (lower half) obtained by ab initio calculations at the HF/3-21G//AM1 level. The deprotonated carbon is indicated by •. A part of the data has been published in Ref. 20c. The authors are grateful to Profs. Gregory Van Lier and Paul Geerlings for providing a complete set of data for this diagram.



1–H

1$^-$

Scheme 2.

an ionic solid when sufficiently stabilized ionic components are employed.[37–46] All the previously synthesized hydrocarbon salts were comprised of anion $\mathbf{1}^-$ and a highly stabilized Hückel aromatic cation (a substituted tropylium ion or a cyclopropenylium ion).

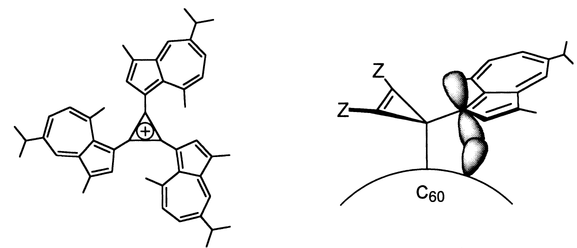
Hydrocarbon cations with lower thermodynamic stabilities formed a carbon–carbon covalent bond with $\mathbf{1}^-$. In the case of moderately stable cations (R^+), the obtained covalent hydrocarbon **1**–R dissociated in polar media to regenerate R^+ and $\mathbf{1}^-$.[37-45,47,48] This observation provided a clear example of heterolytic cleavage of a carbon–carbon bond in a hydrocarbon;[49] such a bond normally cleaves homolytically due to its nonpolarized nature.

One of the practical advantages in using $\mathbf{1}^-$ for the study of such unusual hydrocarbons was that its precursor **1**–H can be prepared in gram quantities in pure form relatively easily, and its structure has been unambiguously determined. The RC_{60}^- ions also appear to be good candidates for the preparation of the anionic component of such hydrocarbons, since they have the same advantages. We chose *t*-butylated [60]fulleride ion (*t*-BuC_{60}^-) as our anionic component, since its physical and chemical properties have been extensively studied,[1,17b,28,50] and it has been isolated as the lithium salt.[1]

1.2 Hydrocarbon Salt Containing the C_{60} Framework.

(1) Stable Coexistence of [60]Fulleride Ions and a Substituted Cyclopropenylium Ion. To determine whether the fulleride ions can survive in the presence of a carbocation, the reactivity of some fulleride ions toward stabilized cation $\mathbf{2}^+$ [51] (pK_{R^+} 13.6[52]) was examined. The vis/NIR and ^{1}H NMR spectra of mixed solutions of $\mathbf{2}^+ClO_4^-$ and *t*-Bu$C_{60}^-K^+$, $C_{60}(CN)^-K^+$, or $C_{60}^{\bullet -}Na^+$ showed the coexistence of the ions without decomposition via carbon–carbon covalent bond formation.[52]

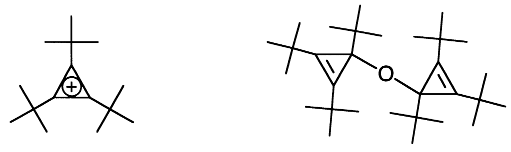
The observed stability of the fulleride ions against $\mathbf{2}^+$ appears to be due principally to the sufficiently high thermodynamic stabilities of both the cationic and the anionic species. However, according to Arnett's empirical relationship,[53] which correlates the heat of carbocation–carbanion coordination with the thermodynamic stabilities of the ions [pK_{R^+} and pK_a(RH)], the coordination of these anions with $\mathbf{2}^+$ would be predicted to be energetically favorable by 3–12 kcal mol^{-1}. The inconsistency between the prediction and the observed persistence of the ions suggests that coordination is prevented by steric repulsion as well. Notably, the inertness of $C_{60}^{\bullet -}$, which has no sterically protecting group on the C_{60} cage, suggests that the



2^+ (pK_{R^+} 13.6)

$2–C_{60}^{\bullet}$
(Z = guaiazulenyl)

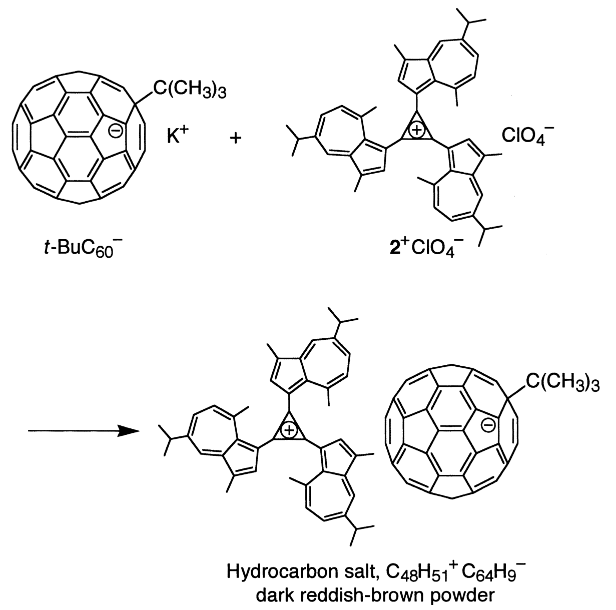
Scheme 3.



3^+ (pK_{R^+} 6.5)

4

Scheme 4.



Scheme 5.

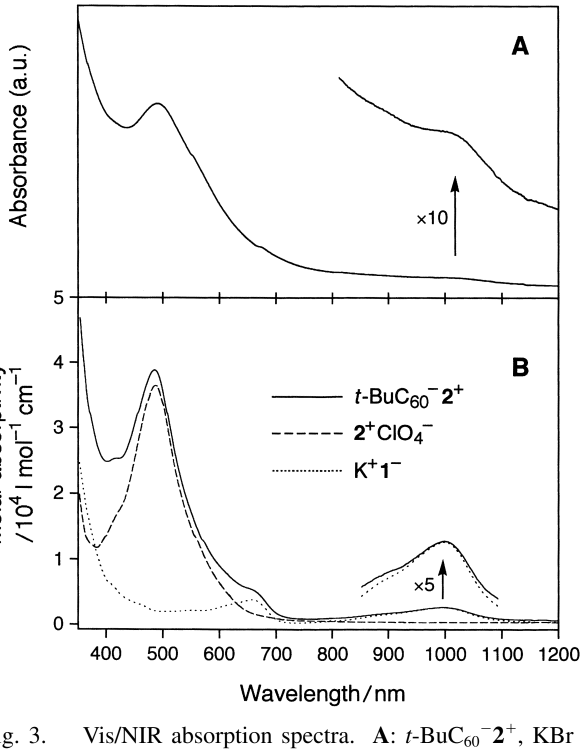


Fig. 3. Vis/NIR absorption spectra. **A**: t-$BuC_{60}^-\mathbf{2}^+$, KBr disk. **B**: t-$BuC_{60}^-\mathbf{2}^+$, $\mathbf{2}^+ClO_4^-$, and $K^+\mathbf{1}^-$ in DMSO–THF (4:1 v/v) solutions.

origin of the repulsion involves the interaction between the guaiazulenyl groups of cation $\mathbf{2}^+$ and the π-electron cloud on the surface of the C_{60} sphere. The molecular model of a hypothetical coordination product $\mathbf{2}–C_{60}^{\bullet}$ suggests that there is a serious overlap between the occupied 2*p* orbital of a guaiazulenyl group and that of the C_{60} framework (Scheme 3).

The importance of steric effects was demonstrated by the reaction of t-BuC_{60}^- with the highly crowded cation $\mathbf{3}^+$ [54] (Scheme 4).[55] This cation (pK_{R^+} 6.5[54b]) would be expected to be far more reactive than $\mathbf{2}^+$, but the reaction sites are protected by bulky *t*-butyl groups. NMR analysis of the mixture, obtained from the reaction of t-$BuC_{60}^-K^+$ with $\mathbf{3}^+ClO_4^-$ in THF-d_8, indicated that approximately two thirds of the original ions remained unchanged, and that the remainder had been converted to hydrolysis products: t-$BuC_{60}H$ and **4**. The coexistence of $\mathbf{3}^+$ and t-BuC_{60}^-, and the absence of the coordination product, indicate that steric hindrance effectively suppresses carbocation–carbanion coordination. This result is not surprising, considering that the coordination would be severely hindered because of repulsion between the *t*-butyl groups of $\mathbf{3}^+$ and the π-electron cloud of the C_{60} sphere. The intrinsically high reactivity of the cation, however, can be a driving force for the simultaneous collapse of both ions, even due to the presence of a trace amount of water.

(2) Isolation of a Hydrocarbon Salt. Salts of $C_{60}^{\bullet -}$ has been previously isolated with a variety of counteranions.[11] t-BuC_{60}^- has been isolated as the lithium salt.[1] The observed coexistence of RC_{60}^- and $\mathbf{2}^+$ led us to attempt the isolation of a new salt by use of a combination of these ions. The synthesis of the salt t-$BuC_{60}^-\mathbf{2}^+$ is of particular interest, because it contains no heteroatom and will provide a new example of a hydrocarbon salt.

To prepare this salt, a THF solution of $\mathbf{2}^+ClO_4^-$ was added to an equimolar amount of t-$BuC_{60}^-K^+$ in THF, which was prepared by the deprotonation of 1,2-t-$BuC_{60}H$ with *t*-BuOK (Scheme 5).[52,55] The addition of CH_3CN to the mixture resulted in the precipitation of the hydrocarbon salt, whereas $KClO_4$ remained in solution. The precipitate was isolated as a dark, reddish-brown powder by filtration.

The salt structure of the powder was demonstrated by IR and vis/NIR (Fig. 3, A) spectra using KBr disks, which showed absorptions corresponding to both $\mathbf{2}^+$ and t-BuC_{60}^-. The vis/NIR absorption of a solution in DMSO–THF (4:1 v/v) had maxima at 482 and 995 nm, and was consistent with the sum of independently measured absorptions of t-BuC_{60}^- and $\mathbf{2}^+$

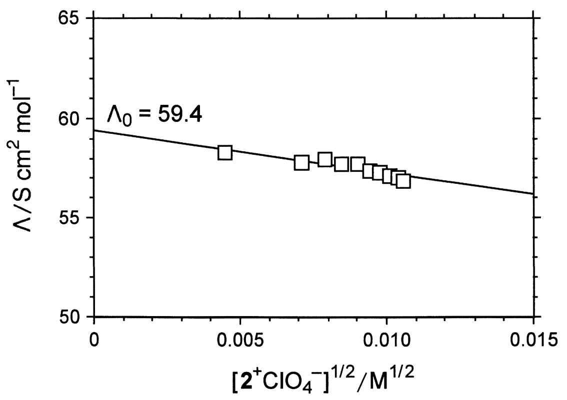


Fig. 4. An Onsager plot for mixtures of t-$BuC_{60}^-K^+$ and $\mathbf{2}^+ClO_4^-$ in DMSO at 25 °C ($[t\text{-}BuC_{60}^-K^+]/[\mathbf{2}^+ClO_4^-] = 1.27$).

(Fig. 3, B). This result indicates that dissolution occurs without carbon–carbon coordination or tight ion-pair formation.

(3) Electrical Conductivity. A characteristic physical property of t-$BuC_{60}^-\mathbf{2}^+$ that distinguishes it from ordinary hydrocarbons is its ionic electrical conductivity in a DMSO solution.[52,55] A practical difficulty in measuring the conductivity of this salt was the slow rate of dissolution, during which some deterioration of the sample occurred. Accordingly, the sample solutions were prepared by mixing DMSO solutions of t-$BuC_{60}^-K^+$ and $\mathbf{2}^+ClO_4^-$ at a constant molar ratio (1.27 : 1), and the measurement was carried out in the presence of inorganic counterions. A linear dependence of molar conductivity against the square root of concentration was obtained (Fig. 4), indicating that the mixed salt is a strong electrolyte. An extrapolation of the plot to infinite dilution gave the limiting molar conductivity (Λ_0) of 59.4 S cm^2 mol^{-1} for $[t\text{-}BuC_{60}^-K^+]_{1.27}[\mathbf{2}^+ClO_4^-]$, which is in fairly good agreement with the value (62.8 S cm^2 mol^{-1}) calculated from the individually measured Λ_0s of t-$BuC_{60}^-K^+$ (25.7 S cm^2 mol^{-1}) and $\mathbf{2}^+ClO_4^-$ (30.2 S cm^2 mol^{-1}). This observation is a clear indication of the independent migration of ions, and is evidence for the absence of covalent bond formation and of the association of the ions.

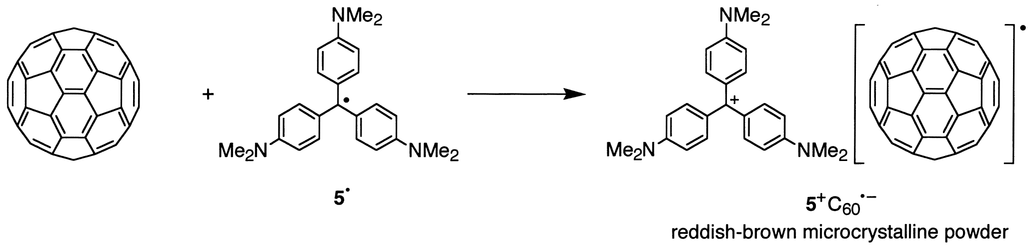
(4) $C_{60}^{\bullet-}$–Carbocation Salts. Although possible hydrocarbon salts that contain $C_{60}^{\bullet-}$ as an anionic moiety have not been reported, similar salts that consist of nitrogen-containing, stable carbenium ions as the cationic moiety have been synthesized by two different approaches, i.e., the single-electron reduction of C_{60} by crystal violet radical $\mathbf{5}^\bullet$ and electrochemical reduction of C_{60} in the presence of $\mathbf{5}^+$ or a related cation.

The former approach[56] is based on the fact that the oxidation potential of $\mathbf{5}^\bullet$ (−1.19 V vs Fc/Fc$^+$ [56]) is more negative than the first reduction potential of C_{60} (−1.09 V vs Fc/Fc$^+$ [19]). Although many reactive carbon-centered radicals, such as alkyl, benzyl, and haloalkyl radicals, and some heteroatom-centered radicals, are known to add to C_{60} to give $RC_{60}^\bullet$,[57–60] our findings show that $\mathbf{5}^\bullet$ does not add to C_{60}, but rather reduces it to give $C_{60}^{\bullet-}$. Further reduction to form C_{60}^{2-} does not occur, since the second reduction potential of C_{60} (−1.48 V vs Fc/Fc$^+$ [19]) is more negative than the oxidation potential of $\mathbf{5}^\bullet$. Radical $\mathbf{5}^\bullet$ is a non-dimerizing, persistent radical which can be readily prepared by treatment of crystal violet iodide with zinc.[61] Mixing C_{60} with an equimolar amount of this radical in hexane–CS_2 resulted in immediate precipitation of $\mathbf{5}^+C_{60}^{\bullet-}$ as reddish brown microcrystalline powder (Scheme 6). Vis/NIR and EPR spectra and elemental analysis indicated the presence of $\mathbf{5}^+$ and $C_{60}^{\bullet-}$ in 1 : 1 ratio and showed that the solid contained 90 ± 10% of the theoretical amount of unpaired spins. Similar to the case of t-$BuC_{60}^-\mathbf{2}^+$, the formation of carbon-carbon covalent bond was prevented by the high stability of $\mathbf{5}^+$ (pK_{R^+} 9.36) as well as repulsion between the aromatic rings of $\mathbf{5}^+$ and the C_{60} cage.

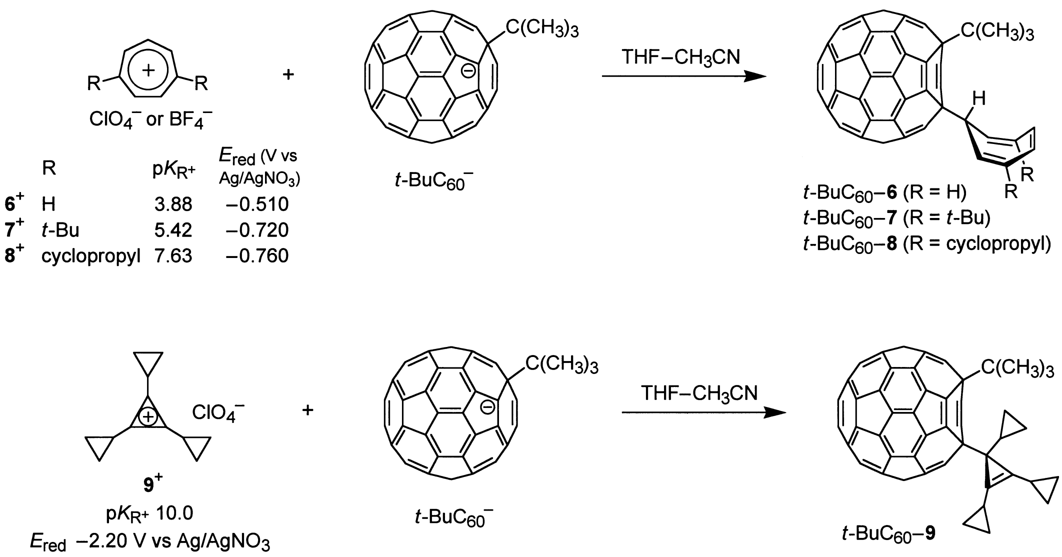
In the latter approach, Moriyama et al.[62] electroreduced C_{60} in a PhCl/EtOH solution in the presence of chloride salts of $\mathbf{5}^+$, methyl green $[(4\text{-}Me_2NC_6H_4)_2(4\text{-}EtMe_2N^+C_6H_4)C^+]$, or ethyl violet $[(4\text{-}Et_2NC_6H_4)_3C^+]$ to give the $C_{60}^{\bullet-}$–carbocation salts as crystalline products. The ethyl violet salt prepared by this method showed semiconducting behavior. The salt of methyl green was semiconducting at temperatures down to ca. 150 K, then metallic to ca. 100 K, and showed a sharp transition to an insulator around this temperature.

1.3 Carbon–Carbon Covalent Bond Formation between t-BuC_{60}^- and Some Hückel Aromatic Carbocations.

The reaction of t-BuC_{60}^- with carbocations with somewhat lower stabilities resulted in carbon–carbon covalent bond formation (Schemes 7 and 8).[19,55,63,64] When one of the perchlorate or tetrafluoroborate salts of tropylium ions $\mathbf{6}^+$ (pK_{R^+} 3.88[65]), $\mathbf{7}^+$ [65] (pK_{R^+} 5.42[65]), and $\mathbf{8}^+$ [65] (pK_{R^+} 7.63[65]) and cyclopropenylium ions $\mathbf{9}^+$ [66] (pK_{R^+} 10.0[66b]) and $\mathbf{10}^+$ [39,41] (pK_{R^+} 7.29[39]) were added to t-$BuC_{60}^-K^+$ in THF–CH_3CN at room temperature, the dark green color disappeared immediately, indicating the consumption of t-BuC_{60}^- by cation–anion coordination to form a covalent bond. The NMR spectra of the obtained products, measured in $CDCl_3$–CS_2, indicated that the reactions yielded only one regioisomer (the reaction of $\mathbf{10}^+$ is an exception, see below). The ^{13}C NMR spectrum showed 58 aromatic carbon signals, discounting the possibility that a 1,2-adduct with C_s symmetry had been formed. Semiempirical MO calculations for

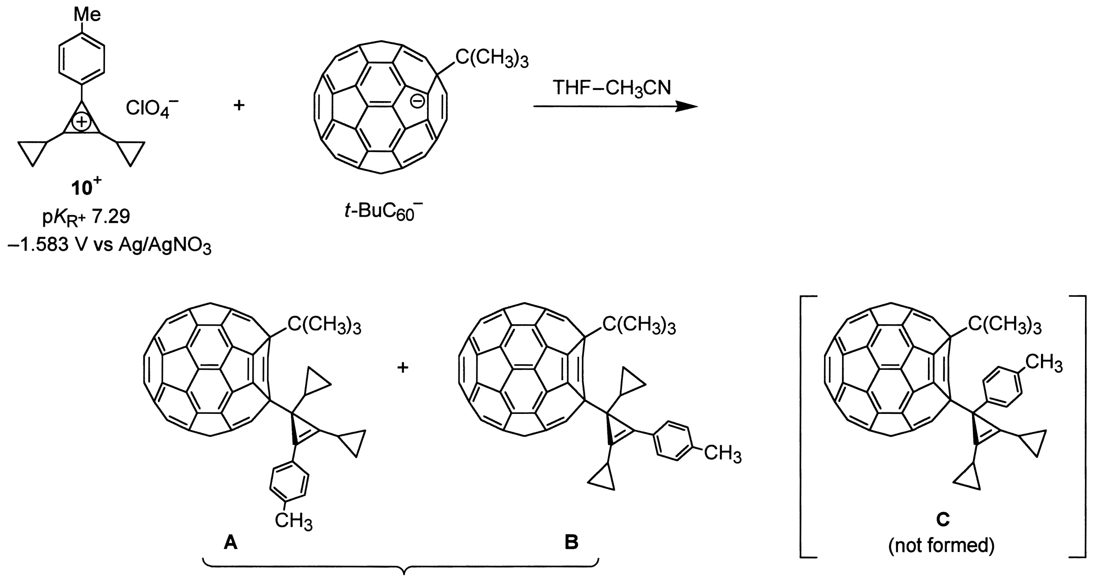


Scheme 6.



	R	pK_{R^+}	E_{red} (V vs Ag/AgNO$_3$)
6^+	H	3.88	−0.510
7^+	t-Bu	5.42	−0.720
8^+	cyclopropyl	7.63	−0.760

Scheme 7.



t-BuC$_{60}$–**10** (A:B = 55:45 or 45:55)

Scheme 8.

the regioisomers of $C_{60}H_2$ have shown that the 1,2-adduct has the lowest heat of formation.[67–69] When 1,2-addition causes a strong steric repulsion between addends, the 1,4-adduct (and its mirror image 1,11-adduct) is the next possible regioisomer. This structure has no symmetry and is in agreement with the observed number of ^{13}C signals. Strong support for the formation of 1,4-adducts comes from the observation of intense nuclear Overhauser enhancements between the protons of the *t*-butyl groups and those of another attached group. The broad absorption at 440–446 nm, which was observed in the absorption spectra (in cyclohexane), is also typical of 1,4-adducts.[13b,70,71]

While in principle RC_{60}^- has 30 different reaction sites, the attack by an electrophile generally occurs at C-2 or C-4. The protonation of t-BuC$_{60}^-$ gives the 1,2-adduct as a thermodynamically controlled product.[1,72] The addition of the tropylium ion to $CH_3(CH_2)_5C{\equiv}CC_{60}^-$ gives a mixture of 1,2- and 1,4-adducts.[2] The above-mentioned exclusive formation of 1,4-adducts in the reaction of t-BuC$_{60}^-$ with Hückel aromatic cations demonstrates the possibility that the position of the attachment of R'^+ to RC_{60}^- can be controlled by the sizes of R and R′, thus enabling the regioselective introduction of two unlike alkyl groups into C_{60}.

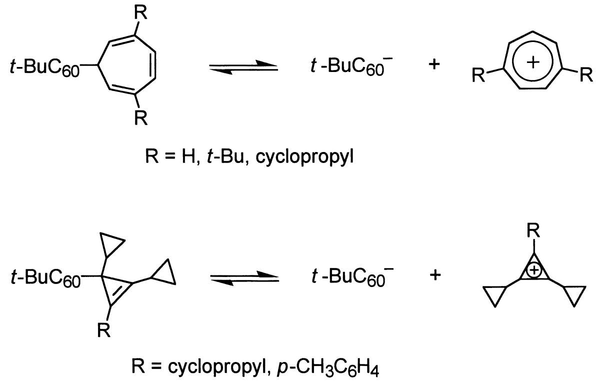
The reaction of t-BuC$_{60}^-$ and $\mathbf{10}^+$ gave two isomers in a ratio of 55:45; both of these are 1,4-adducts and are assigned to a pair of diastereomers A and B (Scheme 8). The absence of isomer C can be ascribed to steric hindrance by the phenyl ring. The charge distribution of $\mathbf{10}^+$ does not explain the observed regioselectivity, since PM3 calculations for this cation indicated that the cyclopropenylium ring carbon bearing the phenyl group has a somewhat greater positive charge (+0.121) than those bearing cyclopropyl groups (+0.096 and +0.085).

The adducts obtained by the reactions shown in Schemes 7 and 8 were found by NMR to be essentially pure. Although stable in the solid state and in nonpolar solvents, they decomposed rapidly when dissolved in polar solvents because of ionic dissociation to regenerate t-BuC$_{60}^-$ followed by hydrolysis or air-oxidation. They also rapidly decomposed during chromatography analysis/purification on SiO$_2$, giving t-BuC$_{60}$H. In the FAB mass spectra, in addition to the molecular ion (M) and C$_{60}$, a signal corresponding to t-BuC$_{60}^-$ *(m/z* 777) was present. All these facts indicate the susceptibility of the t-BuC$_{60}$–C bond to facile heterolytic cleavage, which will be discussed in section 1.4.

It should be noted that formal covalent bond formation between a carbocation and a carbanion might involve an initial single-electron transfer to produce a pair of radicals.[43,73] However, the electron transfer from t-BuC$_{60}^-$ to 6^+–10^+ is not likely to occur, since the reduction potentials of these cations (values[39,65] are given in Schemes 7 and 8) are much more negative than the oxidation potential of t-BuC$_{60}^-$ (−0.37 V vs Fc/Fc$^+$,[28] which corresponds to −0.29 V vs Ag/AgNO$_3$[29]).

1.4 Reversible Heterolysis of Carbon–Carbon Bonds to Form RC$_{60}^-$. (1) Structural Dependence of the Dissociation Energy. A notable feature of the covalent hydrocarbons t-BuC$_{60}$–R (R = **6–10**) based on the high stability of the fulleride ion, is heterolytic dissociation. Although carbocations **6**$^+$–**10**$^+$ were not sufficiently stable to form hydrocarbon salts with t-BuC$_{60}^-$, the produced covalent hydrocarbons were found to dissociate into t-BuC$_{60}^-$ and a tropylium or a cyclopropenylium ion via the reversible heterolysis of C$_{60}$–C bond in polar solvents (Scheme 9).[19,55,63,64] These are unusual reactions, since the thermal breaking of a carbon–carbon σ bond in a hydrocarbon, which is a typical nonpolarized bond, occurs homolytically in most cases.

Experimentally, the heterolytic dissociation was observed by dissolving one of the hydrocarbons in an aprotic dipolar solvent DMSO. The solution turned a greenish color, indicating the generation of t-BuC$_{60}^-$ (λ_{max} 656 and 995 nm). The reversible dissociation was further demonstrated by the ^{1}H NMR spectrum of t-BuC$_{60}$–**9** in DMSO-d_6–THF-d_8 (1:1 v/v), which indicated the formation of t-BuC$_{60}^-$ and **9**$^+$, along with unchanged t-BuC$_{60}$–**9**. In contrast to the ionization in polar solvents, no dissociation was detected in relatively nonpolar solvents such as cyclohexane, chloroform, and CS$_2$.



Scheme 9.

Table 1. Degree of Dissociation (α) and the Free Energy of Heterolysis (ΔG°_{het}) of t-BuC$_{60}$–R (R = **6–10**) in DMSO–CS$_2$ (4:1 v/v) at 25 °C[a)]

Compound	Initial conc. /10^{-5} M	Degree of dissociation[b)]/%	ΔG°_{het} / kcal mol^{-1}
t-BuC$_{60}$–**6**	4.97	5.7	9.3
	8.30	4.0	
	12.3	3.2	
	15.3	2.9	
t-BuC$_{60}$–**7**	1.96	22.4	8.2
	2.76	18.5	
	3.57	14.7	
	4.30	14.3	
	9.31	9.3	
t-BuC$_{60}$–**8**	1.64	28.9	7.7
	5.96	17.8	
	8.76	14.9	
	18.8	10.2	
t-BuC$_{60}$–**9**	5.7–10.3	> 99	< 3
t-BuC$_{60}$–**10**	10.3	40.5	6.2

a) Refs. 19 and 55. b) Determined from the concentration of t-BuC$_{60}^-$ (λ_{max} 995 nm, molar absorptivity 2400).

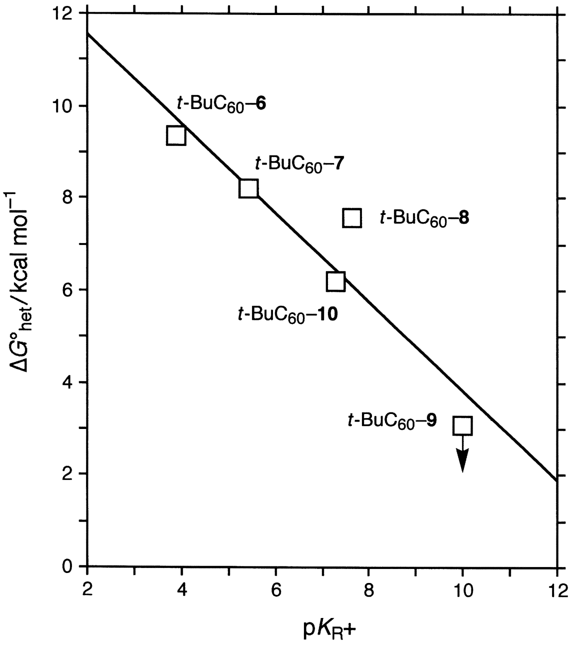


Fig. 5. Plot of the free energy of heterolysis (ΔG°_{het}) in DMSO–CS$_2$ (4:1 v/v) for hydrocarbons t-BuC$_{60}$–R (R = **6–10**) vs pK_{R^+} of R$^+$ in 50% aq CH$_3$CN at 25 °C. The point of t-BuC$_{60}$–**9** indicates the upper limit for ΔG°_{het}.

The degree of dissociation (α) could be determined from the visible absorption of t-BuC$_{60}^-$. In these experiments, THF or CS$_2$ was added, in order to produce homogenious solutions, since undissociated t-BuC$_{60}$–R is sparingly soluble in pure DMSO. In most of the binary solvents studied, the values of α were within a precisely measurable range, allowing the determination of reliable equilibrium constants $K_{het} = c\alpha^2/(1 - \alpha)$

(*c*: total concentration) and the free energies of dissociation $\Delta G^\circ_{\text{het}} = -RT \ln K_{\text{het}}$ (Table 1). It is noteworthy that the heterolysis of t-BuC$_{60}$–**9** was essentially complete (> 99%) in DMSO–CS$_2$ (4:1 v/v), where only the upper limit of $\Delta G^\circ_{\text{het}}$ (3 kcal mol^{-1}) is obtained. A fairly good linear free-energy relationship was found between $\Delta G^\circ_{\text{het}}$ and the pK_{R^+} of the cationic component (Fig. 5), despite the fact that the steric environment is considerably different depending on the structure of the cationic moiety. It is likely that the weakening of the C$_{60}$–C bond by the steric repulsion is partially canceled by the hindered solvation of the carbocation.

(2) Effect of Solvent on Equilibrium. It had been reported previously that the free energy of heterolysis, $\Delta G^\circ_{\text{het}}$, of a C–C covalent bond in non-coordinating solvents is linearly correlated with the reciprocal of the solvent dielectric constant in accordance with the Born equation.[42,49b] In our study, the DMSO–THF binary solvent turned out to be suitable for a further examination of the effect of solvent on the heterolysis of t-BuC$_{60}$–R.[55,64] A plot of the free energy of heterolysis, $\Delta G^\circ_{\text{het}}$, against the mole fraction of DMSO for t-BuC$_{60}$–**9** and t-BuC$_{60}$–**10** showed that $\Delta G^\circ_{\text{het}}$ is not related to the composition of the solvent in a straightforward manner. A large decrease in $\Delta G^\circ_{\text{het}}$ initially occurred when small amounts of DMSO were added to pure THF, while this decrease became much more gradual for mole fractions of DMSO greater than 0.05. The non-dielectric behavior of the heterolysis is demonstrated by the curved $\Delta G^\circ_{\text{het}} - 1/\varepsilon$ plot (Fig. 6). This suggests that the heterolysis is not controlled only by the bulk polarity of the solvent, but also by the preferential solvation of ions by DMSO. Considering the large donor number of DMSO (29.8),[74] one can conclude that a nucleophilic solvation of the sulfoxide oxygen to the carbocation by Lewis-base type coordination may be important (Scheme 10). The development of such an interaction would effectively enhance ionization by the small amounts of added DMSO, but, after the coordination is completed, a linear Born plot would be established, as can be seen in the region $1/\varepsilon < 0.11$ of Fig. 6. A fact which is related to the significance of nucleophilic solvation is the formation of a C–O bond when the less stable cyanotropylium ion is dissolved in DMSO (Scheme 11).[75]

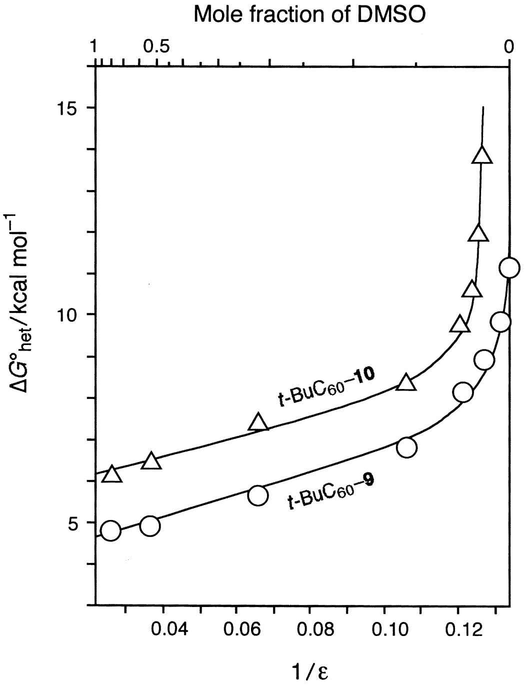
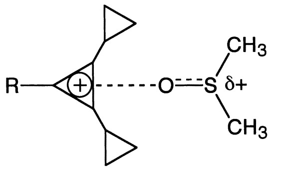
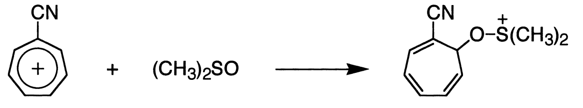


Fig. 6. Free energy of heterolysis ($\Delta G^\circ_{\text{het}}$) for t-BuC$_{60}$–**9** and t-BuC$_{60}$–**10** vs the mole fraction of DMSO and the reciprocal of solvent dielectric constant in DMSO–THF mixed solvents at 25 °C.



9$^+$ (R = cyclopropyl)
10$^+$ (R = *p*-CH$_3$C$_6$H$_4$)

Scheme 10.



Scheme 11.

(3) Kinetics. From the mechanistic point of view, the extent of the ionic character which is developed at the transition state is of interest. The kinetics of the heterolysis of t-BuC$_{60}$–**9** was examined by quickly diluting a chloroform solution, in which the compound exists entirely in the covalent form, with DMSO–THF (1:4 v/v) mixed solvents.[76] The development of the ions toward equilibrium could then be monitored by the growth in carbanion absorption ($t_{1/2}$ was ~3 s at 25 °C, when the initial concentration was ~10^{-4} M), leading to first-order rate constants for the dissociation. A large negative entropy (-22 cal mol^{-1} K^{-1}) was observed, which suggests that a significant degree of solvation had been attained at the transition state. Thus, it is likely that the energies required for bond stretching and solvent organization are both important in the activation process of bond breaking.

(4) Redox Potentials of Dialkyl-1,2-dihydrofullerenes. The facile dissociation of the carbon–carbon bond to form t-BuC$_{60}^-$ was also demonstrated by cyclic voltammetry. Compounds t-BuC$_{60}$–R (R = **6**–**10**) exhibited three reversible reduction waves [$E_{\text{red}}(1)$, $E_{\text{red}}(2)$, and $E_{\text{red}}(3)$] and an irreversible oxidation wave. An additional reversible wave at -1.99 V and an irreversible oxidation wave at -0.67 V appeared in the voltammograms in the case of t-BuC$_{60}$–**8**, t-BuC$_{60}$–**9**, and t-BuC$_{60}$–**10**. These redox waves can be attributed to t-BuC$_{60}^-$ which is formed by C$_{60}$–C bond cleavage during the initial reduction processes, since these waves increased in intensity in the presence of added base. Furthermore, the t-BuC$_{60}^-$, generated from 1,2-t-BuC$_{60}$H and t-BuOK, also showed reduction and oxidation waves at the same potentials.

The reduction potentials of t-BuC$_{60}$–R are somewhat more

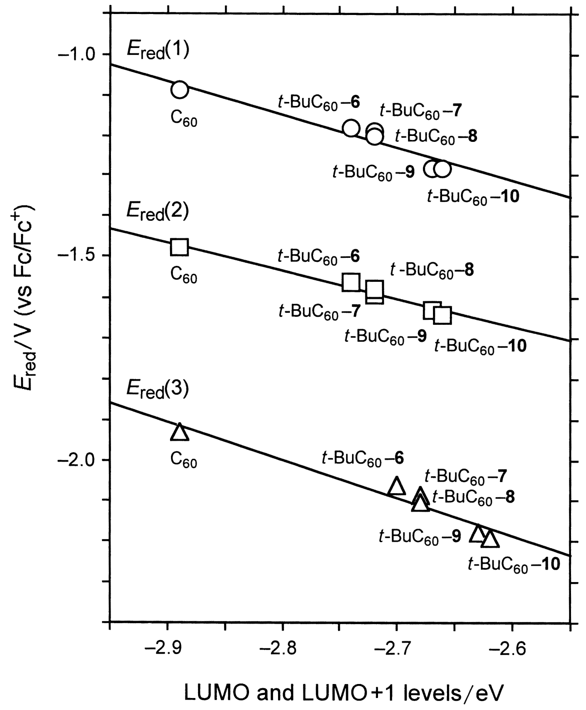
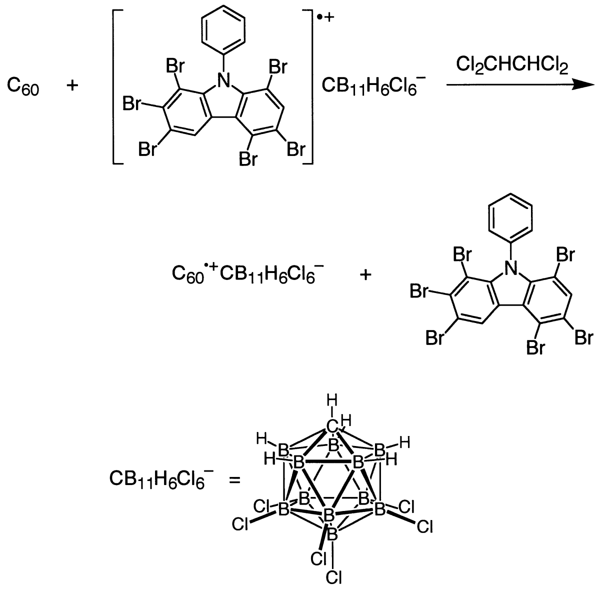


Fig. 7. Plots of $E_{red}(1)$ and $E_{red}(2)$ vs the LUMO energy levels and $E_{red}(3)$ vs the LUMO+1 energy levels. The LUMO and LUMO+1 energy levels were calculated using the PM3 method.

negative than the corresponding reduction waves for C_{60}, consistent with the lowering of unoccupied molecular orbital levels. A linear correlation was confirmed between the initial two reduction waves and the LUMO energy levels and between $E_{red}(3)$ and LUMO + 1 (Fig. 7).[19,55] Such linear relationships between E_{red}s and MO levels have been reported earlier for a series of cycloadducts of C_{60}.[77]



Scheme 12.

2 Functionalized C_{60} Cations

The isolation of a fullerenium ion salt was first achieved for C_{76} by Reed et al.[78] As is commonly observed for higher fullerenes, C_{76} has an oxidation potential which is considerably lower (0.81 V vs Fc/Fc$^+$ [79]) than C_{60}. The radical cation of tris(2,4-dibromophenyl)amine has an oxidizing power which is sufficiently strong to oxidize C_{76}. As a counteranion, these workers employed a carborane anion, $CB_{11}H_6Br_6^-$, which is possibly the least nucleophilic anion known to date. The exceptional inertness of this anion led to the isolation of the salt $(C_{76}^{\bullet+})(CB_{11}H_6Br_6^-)$, as a dark brown solid.

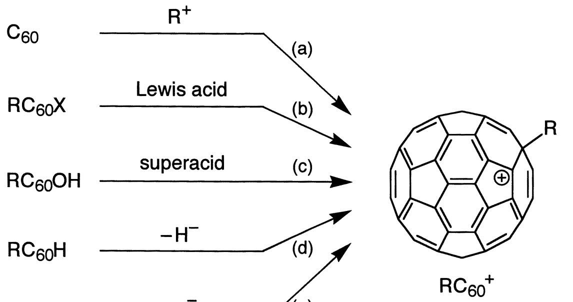
The oxidation of C_{60} is more difficult, owing to the higher oxidation potential (1.26 V vs Fc/Fc$^+$ [80]). Recently, Reed oxidized C_{60} in a manner similar to that used for $C_{76}^{\bullet+}$, but by employing an even stronger oxidizing reagent, the hexabromo-*N*-phenylcarbazole radical cation (Scheme 12).[8,81] A stable solution of $(C_{60}^{\bullet+})(CB_{11}H_6Cl_6^-)$ was obtained, but the isolation of a pure crystalline salt was difficult, perhaps because of the bimolecular disproportionation of $C_{60}^{\bullet+}$ into C_{60}^{2+} and C_{60} at high concentrations.

2.1 Generation of Functionalized C_{60} Cations.

The most simple functionalized fullerenium ion is HC_{60}^+, or protonated C_{60}. Reed et al. were successful in isolating a salt of this cation by treating C_{60} with an superacid having a carborane structure $H(CB_{11}H_6Cl_6)$ (Scheme 13).[8] This acid is not only strong enough to quantitatively protonate C_{60}, but also its non-oxidizing nature and the extremely low nucleophilicity of the conjugate base prevent side reactions and the decomposition of HC_{60}^+, allowing isolation of the salt $(HC_{60}^+)(CB_{11}H_6Cl_6^-)$ as a stable solid.

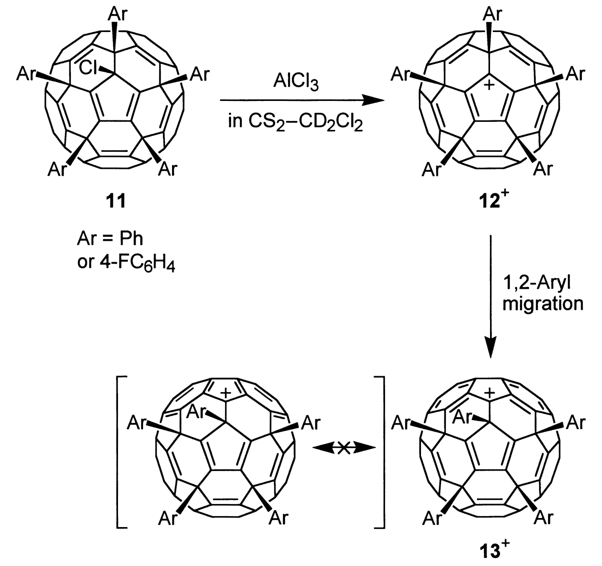
$$C_{60} + H(CB_{11}H_6Cl_6) \xrightarrow{\text{1,2-dichloro-benzene}} (HC_{60}^+)(CB_{11}H_6Cl_6^-)$$

Scheme 13.



Scheme 14.

The cations RC_{60}^+ are carbenium ions (trivalent carbocations), possible approaches to which are presented in Scheme 14. The addition of a cationic electrophile R^+ to C_{60} would lead to RC_{60}^+ [method (a)]. When a halide $RC_{60}X$ or a fullerenol $RC_{60}OH$ is available, the abstraction of X or OH group by a strong acid would be a feasible procedure [methods (b) and (c)]. There are several reports for reactions of types (a) and (b)

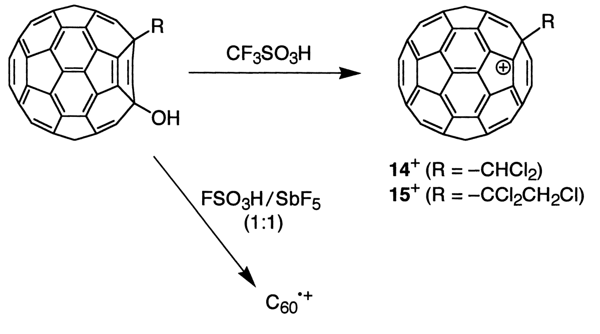


Scheme 15.

in which $R_nC_{60}^+$ cations ($n \geq 1$) are considered as intermediates. Among the examples are nitration of C_{60} and Lewis acid catalyzed arylation of $Ar_5C_{60}Cl$. More examples found in the author's laboratory are described in section 2.3.

Methods (a)–(c) have been also employed for the isolation of or the observation of functionalized fullerenium ions as long-lived species. The above-mentioned isolation of HC_{60}^+ represents an application of method (a). The observation of $Ar_5C_{60}^+$ and RC_{60}^+ by methods (b) and (c), respectively, will be described in section 2.2. Other potential approaches, i.e., the abstraction of a hydride ion from a hydrofullerene [method (d)] and the removal of an electron from a radical [method (e)], have not been reported.

2.2 Observation of Functionalized C_{60} Cations as Long-lived Species. (1) Pentaarylated [60]Fullerenium Ions ($Ar_5C_{60}^+$). A stable functionalized carbocation having a positive charge on the C_{60} cage was first observed by Birkett et al., by the abstraction of chloride ion from $Ar_5C_{60}Cl$ (**11**, Ar = Ph, 4-FC_6H_4) using $AlCl_3$ (Scheme 15).[9a] The ^1H and ^{13}C NMR of the resulting purple-red solution in CS_2–CD_2Cl_2 or $CDCl_3$ showed the generation of a cation with structure **13**$^+$, which can be explained by initial formation of an antiaromatic cyclopentadienyl cation **12**$^+$, followed by 1,2-aryl shift to avoid the unfavorable cyclic 4π electron system. In the ^{13}C NMR spectrum of **13**$^+$ (Ar = Ph), the cationic center was observed at δ 173.74. The endohedral helium-3 derivative of **13**$^+$ (Ar = 4-FC_6H_4) was subjected to ^3He NMR analysis, which indicated that this cation is less aromatic than **11**.[9b] This is due to the restricted delocalization in the adjacent six-membered ring to reduce the resonance contribution of the antiaromatic cyclopentadienyl cation structure.



Scheme 16.

(2) Monoalkylated [60]Fullerenium Ions (RC_{60}^+). The generation of more simple functionalized fullerenium ions RC_{60}^+ has been accomplished for R = $-CHCl_2$ and $-CCl_2CH_2Cl$ by dissolving the corresponding fullerenols 1,4-$RC_{60}OH$ in a strong acid (Scheme 16).[7] Although the ionization of alcohols in a superacid is a powerful method for the generation of carbenium ions, the use of this method for C_{60} derivatives suffers from undesirable oxidation, since the frequently used superacids are often very strong oxidants. Thus, it is known that the parent C_{60} is oxidized to $C_{60}^{\bullet +}$ by strongly oxidizing media such as magic acid (FSO_3H/SbF_5), SbF_5/SO_2ClF, $CF_3SO_3H/K_2S_2O_8$, and oleum.[82,83] Although magic acid is an excellent superacid for the generation of many carbocations, dissolving $RC_{60}OH$ in FSO_3H/SbF_5 (1:1) resulted in the formation of a paramagnetic dark green solution, which can be reasonably explained by the generation of $C_{60}^{\bullet +}$ via the further oxidation of once formed RC_{60}^+. On the other hand, trifluoromethanesulfonic acid (CF_3SO_3H), although being a weaker acid, is non-oxidizing, and is fortunately sufficiently strong to ionize $RC_{60}OH$ to give stable reddish purple cation solutions of RC_{60}^+ (**14**$^+$, R = $-CHCl_2$; **15**$^+$, R = $-CCl_2CH_2Cl$). These cations showed characteristic absorption maxima at around 500, 790, and 1200 nm (Fig. 8). Quenching these solutions with methanol led to the regioselective bonding of a methoxy group to form 1,4-$RC_{60}OMe$.

The ^{13}C NMR spectra of **14**$^+$ and **15**$^+$ (Fig. 9) gave signals corresponding to a cationic center at δ 175.6 and 174.9, respectively. The high-field shift of the cationic centers, as compared with ordinary carbenium ions (e.g., triphenylmethyl cation shows a resonance at δ 211.8[84]), suggests the existence of appreciable charge delocalization. In addition to resonance de-

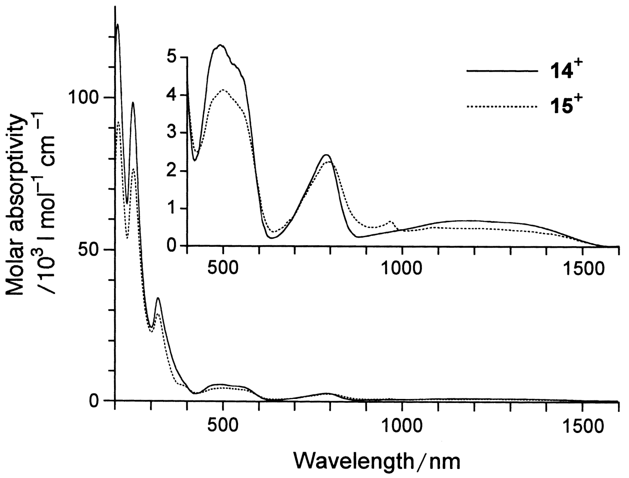


Fig. 8. The absorption spectra of **14**$^+$ and **15**$^+$ in CF_3SO_3H at room temperature. The inset shows an expansion plot of the vis/NIR region.

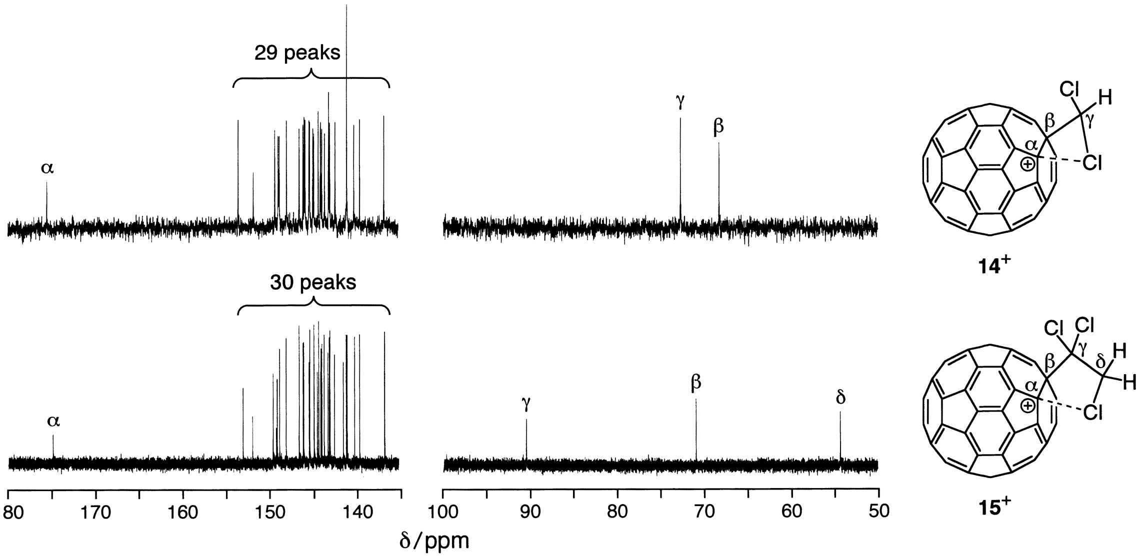
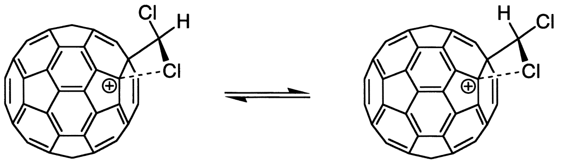


Fig. 9. ^{13}C NMR spectra of **14**$^+$ and **15**$^+$ (rt, 100 MHz, in CF_3SO_3H; cyclohexane-d_{12} external standard).



Scheme 17. Interconversion between enantiomers of **14**$^+$.

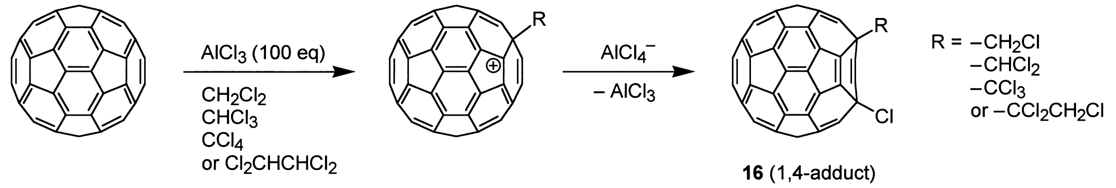
localization over the C_{60} cage, the coordination of a chlorine atom in the group R to the cationic center is suggested (see structures in Fig. 9). In support of the $C_{60}{}^+$---Cl coordination is the fact that the C–H coupling constants ($^1J_{CH}$) of the $-CHCl_2$ and $-CCl_2CH_2Cl$ groups are, respectively, 7 and 3 Hz larger than expected. This can be attributed to the increase in the *s*-character of these carbon atoms, because the carbons belong to four- and five-membered cyclic structures, respectively. PM3 calculations suggest that the coordination lowers the heat of formation of the cations by 7.2 and 18.1 kcal mol^{-1}, respectively.

Cations **14**$^+$ and **15**$^+$ showed 29 and 30 aromatic carbon signals, respectively, indicating the presence of a plane of symmetry in the molecules. The proposed cyclic structure of **14**$^+$ (Fig. 9) is, however, nonsymmetrical owing to the presence of a chiral carbon atom. The observed symmetry suggests that the $C_{60}{}^+$---Cl coordination is rather weak and that a pair of enantiomers is in rapid equilibrium with each other (Scheme 17). The interconversion is very fast and could not be frozen, even at −45 °C, on the ^{13}C NMR time scale.

2.3 Reactions via $RC_{60}{}^+$. (1) Addition of Electrophiles to C_{60}. Although the addition of electrophiles to ordinary olefins is quite common, examples of such reactions with respect to C_{60} are very few in number. The isolation of a $HC_{60}{}^+$ salt by protonation of C_{60} (Scheme 13) is the most simple and distinct example of electrophilic addition. Earlier reports on the reaction of C_{60} with $NO_2{}^+PhCO_2{}^-$ proposed the electrophilic addition of nitronium (nitryl) ions.[85] The halogenation of C_{60} represents another formal electrophilic addition, but the assumed mechanism involves radicals.[86]

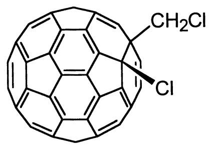
The issue of whether or not C_{60} is sufficiently nucleophilic to undergo attack by a carbocation is interesting, because such a possibility could be used in carbon–carbon bond forming reactions for the derivatization of C_{60}. Nevertheless, not a single report could be found regarding the electrophilic addition of a carbocation to C_{60} until we reported the first example in 1999.[7] The lack of such a report was surprising and even strange, since the attack of electrophilic reagents is so fundamental a reaction for carbon–carbon double bonds that it can be found in textbooks for beginning organic chemistry students. We speculate that many researchers have unsuccessfully attempted such a reaction, and have concluded that C_{60} is inert with respect to this type of reaction or that the addition is totally uncontrollable, if it proceeds at all.

A controlled electrophilic addition of a carbon electrophile was first achieved by the reaction of C_{60} with CH_2Cl_2, $CHCl_3$, CCl_4, or $Cl_2CHCHCl_2$ in the presence of $AlCl_3$ (Scheme 18).[7,87] C_{60} is moderately soluble in these chloroalkanes, and



16 (1,4-adduct)

Scheme 18.



17 (1,2-adduct)

Scheme 19.

they can be used as solvents for the reaction. The treatment of C_{60} with a large excess of $AlCl_3$ in one of these solvents resulted in the addition of one molecule of solvent to C_{60}. All the C_{60} was consumed in several hours (the addition of $Cl_2CHCHCl_2$ required heating at 60 °C), and the reactions were clean. However, partial hydrolysis during chromatography separation (SiO_2) reduced the yield of monoadducts to 50–70%.

The obtained adduct was shown to be isomerically pure and to have structure **16**, in which an alkyl group and a chlorine atom is attached at the 1,4-positions. An exception was the addition of CH_2Cl_2, which yielded the 1,2-adduct **17** (Scheme 19) along with the 1,4-isomer **16** (R = $-CHCl_2$) in approximately a 1 : 1 ratio.[87] The two regioisomers could be isolated by GPC. It should be noted that the cation that was initially formed from 1,1,2,2-tetrachloroethane, $^{+}CHClCHCl_2$ (or its complex with $AlCl_4^-$), underwent a rapid hydride shift to form an isomeric cation, $^{+}CCl_2CH_2Cl$, and then added to C_{60}. This cation is stabilized by effective $p(\pi)$ donation of unshared $3p$ electrons from two chlorine atoms.[88,89]

The expected intermediate in these reactions, RC_{60}^{+}, should be identical to those directly observed by the ionization of fullerenols in strong acids (see section 2.2). The stabilization of RC_{60}^{+} by the coordination of a chlorine atom to the cationic center seems important for the ready addition of R^+ to C_{60}. Such coordination is allowed in all the reactions in Scheme 18, since the solvent molecules have at least two chlorine atoms. This might provide an explanation for why the addition of monohaloalkanes such as *t*-BuCl, *i*-PrCl, and CH_3I under similar conditions was unsuccessful.[87]

The coordination of a chlorine lone pair is (at least partially) responsible for the regioselectivity of the addition reaction. PM3 calculations for $(Cl_2CH)C_{60}Cl$ indicated that the heats of formation of the 1,2- and 1,4-adducts are much lower than those for any other possible regioisomers. Although these isomers are very similar in terms of energy, the 1,4-adduct was obtained exclusively. This result can be adequately explained by the protection of the C-2 by the chloroalkyl group, which allows chloride ion only an S_N2'-type attack to C-4 (Scheme 20).

(2) Ionic Dissociation of RC_{60}–X Bond to Form RC_{60}^{+}. As discussed in previous sections, the use of the Lewis acid catalyzed ionization of the C_{60}–Cl bond and ionization of fullerenols in strong acid led to the direct observation of functionalized C_{60} cations. Another example for the ionization of C_{60}–Cl bond is the initial step in the synthesis of aryl derivatives of C_{60}, e.g. the Friedel–Crafts substitution of aromatic compound by $C_{60}Cl_6$ to give $Ar_5C_{60}Cl$ in the presence of a $FeCl_3$ catalyst.[90–93] Similarly, the treatment of chlorides **16** (R = $-CHCl_2$, $-CCl_2CH_2Cl$) with $AlCl_3$ in anisole resulted in 1,4-$RC_{60}An$ (An = p-$CH_3OC_6H_4$).[94]

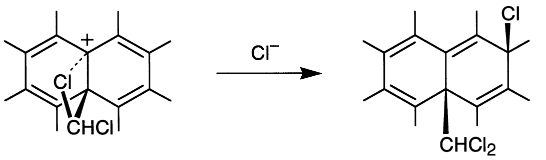
The chloride ion can also be abstracted from $RC_{60}Cl$ by Ag^+.[94] An advantage of this method over the reaction with $AlCl_3$ is that it can be carried out in the presence of compounds which contain a hydroxy group. Thus, the addition of $AgBF_4$ to a solution of **16** in anisole, MeOH/PhCN, and CF_3CH_2OH/$Cl_2CHCHCl_2$ afforded 1,4-$RC_{60}An$, 1,4-$RC_{60}OMe$, and 1,4-$RC_{60}OCH_2CF_3$, respectively. This reaction proceeds under non-acidic conditions and is instantaneous, due to the insolubility of AgCl. These examples suggest the potential utility of this reaction for the syntheses of ethers and esters containing a fullerenyl group under mild conditions.

A fact that demonstrates the facile ionization of $RC_{60}Cl$ is its clean hydrolysis in the presence of silica gel.[7] Purification of **16** (R = $-CHCl_2$, $-CCl_2CH_2Cl$) on a silica-gel column required a rapid elusion with CS_2 at −20 °C. However, the chlorides were completely converted to fullerenols, 1,4-$RC_{60}OH$, when the elution was done with benzene at an ordinary rate at room temperature.

Compound **16** (R = $CHCl_2$) was found to even undergo S_N1 solvolysis.[87] When a solution of this chloride in CF_3CH_2OH/anisole (9 : 1 v/v) was heated at 50 °C, it was quantitatively converted in 22 h to a mixture of 1,4-$RC_{60}OCH_2CF_3$ and 1,4-$RC_{60}An$.

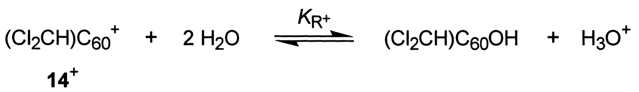
(3) Evaluation of the Thermodynamic Stability of RC_{60}^{+}. The cations $\mathbf{14}^+$ and $\mathbf{15}^+$, generated from fullerenol precursors in CF_3SO_3H, were remarkably stable, showing little or no decomposition over several weeks at room temperature. Furthermore, the formation of $\mathbf{14}^+$ also occurred quantitatively in H_2SO_4 and even in a more weakly acidic medium such as sulfuric acid containing 20% p-toluenesulfonic acid, indicating that superacidic media are not required for the generation of $\mathbf{14}^+$. Lowering the acidity by the addition of more p-toluenesulfonic acid shifted the ionization equilibrium toward the fullerenol. Spectrometric estimation of the position of equilibrium (Scheme 21) indicated that this cation has a stability which is comparable to that of tris(4-nitrophenyl)methyl cation, whose pK_{R^+} is −16.60.[94]

Another approach to the evaluation of stability involves a rate measurement of S_N1 reactions. The rate constant for the solvolysis for 1,4-$(Cl_2CH)C_{60}Cl$ in CF_3CH_2OH/anisole (9 : 1 v/v) is approximately 10^2 times faster than the solvolysis of *t*-



$\mathbf{14}^+$

Scheme 20.



$$\underset{\mathbf{14}^+}{(Cl_2CH)C_{60}^{+}} + 2\,H_2O \xrightleftharpoons{K_{R^+}} (Cl_2CH)C_{60}OH + H_3O^+$$

$$pK_{R^+} \equiv -\log K_{R^+}$$

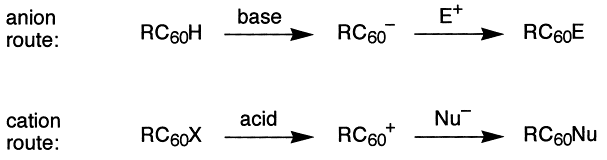
Scheme 21.

BuCl under the same conditions.[87] This suggests that **14**$^+$ is more stable, in the solvolytic sense, than the t-butyl cation by ~3 kcal mol^{-1}.

The pK_{R^+} values and solvolysis rate constants correspond to the free energy of the cation (or the transition state for the ionization) relative to alcohol or chloride precursors, which contain sp^3 hybridized carbon atoms on the C_{60} framework. Therefore, these stability parameters include the contribution of the change in molecular strain by rehybridization of this carbon from sp^3 to sp^2. Reports on the oxidation potential of a functionalized C_{60} cation are not found in the literature, although it would serve as a measure for the cation stability that is not influenced by orbital rehybridization.

3 Concluding Remarks

Monofunctionalized anions RC_{60}^- are, owing to the strongly electron-attracting nature of the C_{60} core, remarkably stable carbanions. If R contains only carbon and hydrogen, a stable hydrocarbon anion can be constructed. Normally, the stabilization of a carbanion is not readily achieved without the electronic effect of a heteroatom-containing substituent. The *t*-butylated fulleride ion (*t*-BuC_{60}^-), an intensively studied example of functionalized fulleride ions, was successfully applied to the preparation of ionically dissociable hydrocarbons and a hydrocarbon salt. These are unusual hydrocarbons, which have been obtained only by using specially stabilized hydrocarbon anion components.



Scheme 22.

In contrast to anions, it had been generally believed that functionalized C_{60} cations are far more difficult to generate, based on the well-known resistance of C_{60} toward oxidation. Although the direct observation and isolation of the cations had been considered a challenging task, significant progress was made during the past three years. This includes the isolation of the parent cation HC_{60}^+, the generation of $Ar_5C_{60}^+$ as stable cation by use of a common Lewis acid $AlCl_3$, and the observation of RC_{60}^+ and an evaluation of their stabilities.

It was also found that C_{60} is sufficiently nucleophilic to be alkylated by carbenium ions via a RC_{60}^+ intermediate. This reaction would be of synthetic use as a new method for the derivatization of C_{60}. Furthermore, the in situ formation of RC_{60}^+ from the corresponding halides, followed by trapping with a nucleophile (Nu$^-$), would constitute the "cation route" for the synthesis of dihydrofullerene derivatives (Scheme 22). This reaction represents the counterpart of the well-established "anion route," examples of which are seen in Schemes 7 and 8.

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