

Formation of C₆₀ Adducts with Two Different Alkyl Groups via Combination of Electron Transfer and S_N2 Reactions

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Abstract: The formation of organofullerenes of the type R₂C₆₀ and R(R')C₆₀ from C₆₀²⁻ and alkyl halides (RX or R'X) in benzonitrile was mechanistically investigated for 15 different alkyl halides which vary in electrophilicity and electron acceptor ability. The first step in the reaction leads to RC₆₀⁻ via an electron-transfer mechanism, followed by formation of R₂C₆₀ or R(R')C₆₀ via an S_N2 mechanism. Evidence of the mechanism comes from comparison of rate constants for the stepwise addition of two R groups to C₆₀²⁻ with rate constants for the genuine electron transfer and S_N2 reactions. The formation of *t*-BuC₆₀⁻ and PhCH₂C₆₀⁻ after the first R group addition was confirmed by electrospray ionization mass spectroscopy. The *t*-BuC₆₀⁻ derivative will not react further with excess *t*-BuI, but this is not the case for the less sterically hindered PhCH₂Br, which adds to *t*-BuC₆₀⁻ in benzonitrile to give *t*-Bu(PhCH₂)C₆₀. A protonation of *t*-BuC₆₀⁻ with trifluoroacetic acid can also occur to give 1,4-*t*-Bu(H)C₆₀, which rearranges rapidly to yield 1,2-*t*-Bu(H)C₆₀. Rate constants for the second alkylation of *t*-BuC₆₀⁻ with a variety of different alkyl halides are compared with values of genuine S_N2 reactions and indicate that the second step in the fullerene alkylation reaction proceeds via an S_N2 mechanism. The rate constants of electron transfer from C₆₀²⁻ to RX span a range of 10⁵, but are insensitive to the steric effect of the alkyl group, i.e., they depend only on the electron-acceptor ability of RX. In contrast, the S_N2 rate constants of *t*-BuC₆₀⁻ with RX are highly susceptible to the steric effect of the alkyl group and no reaction at all takes place between *t*-BuC₆₀⁻ and *t*-BuI. Thus, the first addition of one sterically hindered alkyl group to C₆₀²⁻ occurs via electron transfer and cannot be followed by further addition of a second sterically hindered group (via an S_N2 reaction). This is not the case for less sterically hindered alkyl groups such as benzyl bromide which can add via an S_N2 reaction to yield C₆₀ adducts with two different alkyl groups.

Introduction

Fullerenes such as C₆₀ are easy to reduce,¹ but difficult to oxidize electrochemically,² and thus are generally regarded as

electrophiles, or electron acceptors, rather than nucleophiles or electron donors. The derivatization of fullerenes has therefore been focused on reactions with a variety of nucleophiles³ such as electron-rich olefins,⁴ carbenes,⁵ carbanions,⁶ alkoxides,⁷ and organometallic reagents.⁸ On the other hand, when electrons are chemically or electrochemically added to C₆₀, the resulting anions are expected to behave as strong nucleophiles or electron donors. In fact, C₆₀ anions, such as C₆₀^{•-}, C₆₀²⁻, and C₆₀³⁻, can be considered as potential nucleophiles in that they react with electrophiles such as alkyl halides^{9,10} and also act as electron donors in redox catalytic reactions.¹¹

It is now well-known that the reactions of electrochemically and chemically generated C₆₀²⁻ with alkyl halides in benzonitrile yield dialkyl and tetraalkyl adducts of C₆₀ such as R₂C₆₀ and R₄C₆₀.^{9a,10} This alkylation could proceed via one of two probable mechanisms. One is an electron-transfer mechanism where C₆₀²⁻ acts as an electron donor and the other is an S_N2

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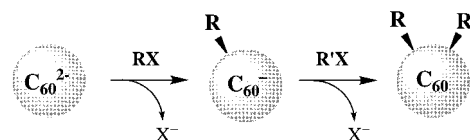
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mechanism where C₆₀²⁻ acts as a nucleophile. The electron transfer vs nucleophilic process alternative has been one of the most central propositions in reaction mechanism,¹²⁻¹⁶ but it has never been examined in the case of C₆₀. The heterogeneous electron-transfer reactions of fullerenes with electrodes¹ as well as their photoinduced electron-transfer reactions have been

Scheme 1



studied extensively,^{17,18} but few studies have been carried out with respect to the homogeneous electron-transfer reactions of C₆₀.

In this paper, we report the mechanism for formation of C₆₀ adducts with two different alkyl groups via a combination of electron transfer and S_N2 reactions. The general reaction pathway involves an initial reaction of C₆₀²⁻ with one alkyl halide (RX) to generate the monoalkyl adduct anion, RC₆₀⁻, and this is followed by the reaction of RC₆₀⁻ with another alkyl halide (R'X) to give the bis-alkyl derivatives, R(R')C₆₀, as shown in Scheme 1. This sequential process for the derivatization of C₆₀ is made possible by differences in alkyl halide reactivity in the first and the second steps of the reaction. The detailed kinetics of each step is examined and compared with the kinetics of authentic electron transfer and S_N2 reactions involving alkyl halides and provides valuable insights into a novel reaction mechanism which is specific to the C₆₀ anions which have electrons highly delocalized over the fullerene skeleton. The present study also provides a new synthetic route for the precise and selective functionalization of fullerenes with two different addends.

Experimental Section

Materials. C₆₀ (>99.95% pure) was purchased from Science Laboratories Co., Ltd., Japan, and used as received. Benzonitrile (PhCN) was purchased from Wako Pure Chemical Ind. Ltd., Japan, and distilled over P₂O₅ prior to use.¹⁹ All alkyl halides, naphthalene, trifluoroacetic acid, and sodium were obtained commercially from Aldrich and Wako Pure Chemical Ind. Ltd., Japan in special grade. *tert*-Butyl iodide (*t*-BuI) from Wako Pure Chemical Ind. Ltd. was distilled in the dark under a reduced pressure of 100 mmHg at 333 K. Tetrahydrofuran (THF) was dried by refluxing under nitrogen with

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sodium prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized from ethanol and dried in a vacuum at 313 K. The sodium salt of the naphthalene radical anion (2.4×10^{-1} M in THF) was prepared by reduction of naphthalene (5.5 mmol) with sodium (5.0 mmol) under deaerated conditions in distilled THF at 298 K. Cobalt(II) tetraphenylporphyrin, CoTPP, was prepared as described in the literature.²⁰ Cobalt(I) tetraphenylporphyrin anion, CoTPP⁻, was obtained by an electron-transfer reduction of CoTPP with 2,3-dimethylhydroquinone that had been formed by the reaction of 2,3-dimethylhydroquinone with tetramethylammonium hydroxide.²¹

Synthesis of 1-*tert*-Butyl-4-benzyl-1,4-dihydro[60]fullerene. To a deaerated PhCN solution (500 mL) of chemically generated C₆₀²⁻ (0.14 mmol) was added *t*-BuI (1.66 mL) at room temperature. The solution was stirred for 1 h to give *t*-BuC₆₀⁻, after which PhCH₂Br (33.3 mL) was added to the reaction solution to give a major product ($\approx 36\%$, 43.7 mg) along with unreacted C₆₀ after evaporation of PhCN under evacuation. The reaction mixture was washed with MeCN, after which the brown solid was collected by centrifugation. The HPLC separation of the solid was performed with a preparative "Buckyclutcher I" column²² of 25 cm \times 21.1 mm (Regis, Morton Grove, IL). A hexane/toluene mixture was used as an eluent with a flow rate of 2 mL/min. The product was monitored at 450 nm with a UV-vis detector, UV970 (JASCO Corporation, Japan). The major product was collected and identified as 1-*tert*-butyl-4-benzyl-1,4-dihydro[60]fullerene (1,4-*t*-Bu-(PhCH₂)C₆₀) by elemental analysis, FAB mass, and ¹H and ¹³C NMR spectroscopy. ¹H and ¹³C NMR spectra were recorded on JEOL GSX-400 (400 MHz) and Bruker AM600 (600 MHz) NMR spectrometers, respectively. FAB mass spectra were obtained with a JEOL JMS-DX303 mass spectrometer. Anal. Calcd for C₇₁H₁₆, *t*-Bu(PhCH₂)C₆₀: C, 98.14; H, 1.86. Found: C, 97.78; H, 2.22. UV-vis [CS₂, λ_{\max} , nm (ϵ , M⁻¹ cm⁻¹)] 331 (3.2×10^4), 447 (6.8×10^3), 539 (1.4×10^3), 620 (sh, 8.0×10^2), 687 (3.6×10^2). FAB-MS (negative): mass calcd for C₇₁H₁₆, 868; found 868. ¹H NMR (CD₂Cl₂) δ (ppm) 1.94 (s, 9H), 4.25 (d, 1H, $J_{\text{ab}} = 13.2$ Hz), 4.46 (d, 1H, $J_{\text{ab}} = 13.2$ Hz), 7.47–7.21 (m, 5H); ¹³C NMR (CD₂Cl₂/CS₂) δ (ppm) 192.37 (CS₂), 157.52, 157.12, 151.74, 150.87, 149.47, 148.64, 148.49, 148.42, 147.62, 147.10, 147.04, 146.81, 146.73, 145.69, 145.62, 145.45, 145.41, 144.77, 144.74, 144.64, 144.52, 144.42, 144.25, 144.19, 144.15, 144.04, 143.95, 143.93, 143.92, 143.56, 143.45, 143.32, 143.19, 143.08, 143.04, 142.98, 142.95, 142.92, 142.90, 142.82, 142.59, 142.51, 142.48, 142.27, 142.20, 142.07, 141.67, 141.15, 140.25, 138.95, 138.46, 137.93, 137.52, 135.40 (54 peaks assignable to 58 sp² C of C₆₀), 130.73 (C₆H₅-), 128.20 (C₆H₅-), 127.28 (C₆H₅-), 68.33 (C₆₀, sp³), 60.06 (C₆₀, sp³), 47.50 (-CH₂-), 40.13 (-C(CH₃)₃), 28.30 (-CH₃).

Synthesis of 1-*tert*-Butyl-1,2-dihydro[60]fullerene. The successive reaction of C₆₀²⁻ (0.14 mmol) with *t*-BuI (14 mmol) and CF₃COOH (2.5 mmol) was carried out in 500 mL of deaerated PhCN at room temperature and the crude product was isolated by HPLC. A major product (60%, 64.9 mg) along with unreacted C₆₀ (40%, 40 mg) was obtained. The major product was collected as described above and identified as 1-*tert*-butyl-1,2-dihydro[60]fullerene (1,2-*t*-Bu(H)C₆₀) by FAB-mass and ¹H NMR spectroscopy. UV-vis [CS₂, λ_{\max} , nm] 437. Mass calcd for C₆₄H₁₀, 779; found 778 [M - 1]. ¹H NMR (CDCl₃/CS₂) δ (ppm) 1.99 (s, 9H), 6.53 (s, 1H). ¹³C NMR (CDCl₃/CS₂) δ (ppm) 192.36 (CS₂), 157.48, 154.47, 153.87, 147.53, 146.90, 146.25, 146.23, 146.09, 146.00, 145.70, 145.23, 145.21, 144.57, 144.37, 143.11, 142.94, 142.52, 142.50, 142.07, 142.05, 141.94, 141.57, 141.47, 141.32, 140.25, 138.96, 136.37, 136.31 (28 peaks assignable to 58 sp² C of C₆₀), 73.38 (C₆₀, sp³), 56.90 (C₆₀, sp³), 41.06 (-C(CH₃)₃), 29.90 (-CH₃).

Spectroscopic Measurements of RC₆₀⁻. Naphthalene radical anion (2.4×10^{-1} M) in THF was generated as described in the literature²³ and added to a quartz cuvette (10 mm i.d.) containing a deaerated PhCN solution (3.0 mL) of C₆₀ (2.8×10^{-4} M) to produce C₆₀²⁻. When *t*-BuI

($8.4 \times 10^{-2} - 4.2 \times 10^{-1}$ mmol) was added to the C₆₀²⁻ solution, the absorption band ($\lambda_{\max} = 955$ nm) due to C₆₀²⁻ disappeared and this was accompanied by an increase in RC₆₀⁻ (R = *t*-Bu) absorption bands at 660 and 995 nm. The same absorption bands were observed in the reaction of C₆₀²⁻ with PhCH₂Br (8.4×10^{-2} to 4.2×10^{-1} mmol). The Vis-NIR spectra were recorded on Hewlett-Packard 8452A and 8453 diode array spectrophotometers which were thermostated at 298 K.

Electrospray mass ionization spectrometry (ESI-MS) was used to identify RC₆₀⁻ (R = *t*-Bu and PhCH₂) in PhCN. A sector type mass spectrometer (JEOL-D300) connected with a homemade ESI (electrospray ionization) interface was used to obtain ESI mass spectra. The interface is similar to that of the ESI ion source designed by Fenn.²⁴ The sample solution was sprayed at the tip of a needle applied at a current 3.5 kV higher than that of the counter electrode. This electrode consisted of a 12-cm-long capillary pipe of stainless steel. A heated N₂ gas (70 °C) flowed between the needle and the capillary electrode to aid the desolvation of charged droplets sprayed. Ions entered the vacuum system through the first and the second skimmer to a mass spectrometer. The flow rate of a sample solution was 1–2 mL min⁻¹. The voltage of the first skimmer was 50 V higher than that of the second, and that of the capillary electrode is 50 V higher than that of the first. For measurements of ESI mass spectra, all of the samples were dissolved in freshly distilled PhCN to prepare a sample concentration of ca. 0.1 mM. ESI-MS: mass calcd for *t*-BuC₆₀⁻ (C₆₄H₉), 777.8; found 778. PhCH₂C₆₀⁻ (C₆₇H₇), 811.8; found 812.

Kinetic Measurements. Rates of electron transfer from C₆₀²⁻ or Me₄Q^{•-} to RX in deaerated PhCN at 298 K were monitored by following a decrease in absorbance due to C₆₀²⁻ ($\lambda = 750$ nm) or Me₄Q^{•-} ($\lambda_{\max} = 442$ nm) under pseudo-first-order conditions where the RX concentrations were maintained at more than 10-fold excess of the C₆₀²⁻ or Me₄Q^{•-} concentration (5.0×10^{-4} M). Rates of the S_N2 reactions of *t*-BuC₆₀⁻ or CoTPP⁻ with RX were determined by following a decrease in absorbance due to *t*-BuC₆₀⁻ ($\lambda = 650$ nm) in PhCN or increase in absorbance due to RCoTPP ($\lambda_{\max} = 406$ nm) in MeCN under pseudo-first-order conditions where the concentrations of RX were maintained at more than 10-fold excess of the *t*-BuC₆₀⁻ and CoTPP⁻ concentrations (2.8×10^{-4} and 2.5×10^{-5} M, respectively). The Vis-NIR spectral changes during these reactions were followed by Hewlett-Packard 8452A or 8453 diode array spectrophotometers which were thermostated at 298 K. Fast reactions of CoTPP⁻ and C₆₀²⁻ with alkyl halides in MeCN (half-lives shorter than 5 s) were determined with a Union RA-103 stopped-flow spectrophotometer. Pseudo-first-order rate constants were determined by a least-squares curve fit with a personal computer. The pseudo-first-order plots were linear for three or more half-lives with a correlation coefficient greater than 0.999.

Cyclic Voltammetry. Cyclic voltammetry measurements were performed at 298 K on a BAS 100W electrochemical analyzer in deaerated PhCN containing 0.1 M NBu₄ClO₄ as supporting electrolyte. A conventional three-electrode cell with a gold working electrode (surface area of 0.3 mm²) and a platinum wire as the counter electrode were utilized. The Pt working electrode (BAS) was polished with a BAS polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to the Ag/AgNO₃ (0.01 M) reference electrode. All potentials (vs Ag/Ag⁺) were converted to values vs SCE by adding 0.29 V.²⁵ All electrochemical measurements were carried out under an atmospheric pressure of argon.

Theoretical Calculations. Theoretical calculations were performed by using the MOPAC program (Ver. 6) that is incorporated in the MOLMOLIS program by Daikin Industries, Ltd. The PM3 Hamiltonian was used for the semiempirical MO calculations.²⁶ Final geometries and energetics were obtained by optimizing the total molecular energy with respect to all structural variables. The heats of formation (ΔH_f) were calculated with the restricted Hartree-Fock (RHF) formalism with use of a key word "PRECISE".

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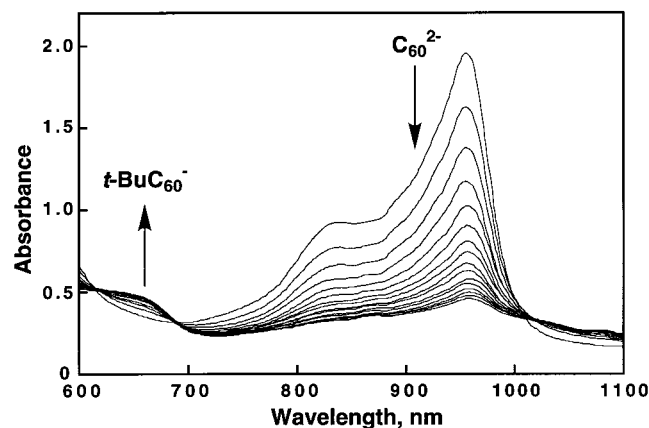
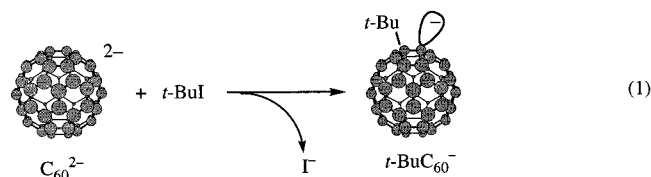


Figure 1. Electronic absorption spectra observed in the first 80 min of the reaction of C₆₀²⁻ (1.0 × 10⁻⁴ M) with *t*-BuI (5.0 × 10⁻² M) in deaerated PhCN at 298 K (200 s interval).

Results and Discussion

Addition of the First Alkyl Group to C₆₀²⁻. A PhCN solution of C₆₀²⁻ was generated by the two-electron reduction of C₆₀ with 2 equiv of naphthalene radical anion after which the progress of the reaction of C₆₀²⁻ with RX was monitored by vis-NIR spectroscopy.

Figure 1 shows the vis-NIR spectral changes observed in the reaction of C₆₀²⁻ with *t*-BuI in PhCN. As the reaction proceeds, the C₆₀²⁻ absorption band at λ_{max} = 955 nm²⁷ decreases, and this is accompanied by the appearance of a new absorption band at 660 nm, which is a diagnostic marker band of monoalkyl C₆₀ adduct anions.²⁸ The same spectral changes were observed in the reactions of C₆₀²⁻ with each alkyl halide (RX) to yield RC₆₀⁻ and the stoichiometry of the reaction is given by eq 1 for the case of RX = *t*-BuI.



The formation of *t*-BuC₆₀⁻ and PhCH₂C₆₀⁻ was confirmed by electrospray ionization mass (ESI-MS) spectra as shown in Figure 2, where peaks appear clearly at the mass number of *t*-BuC₆₀⁻ (778) and PhCH₂C₆₀⁻ (812). The natural isotope abundance patterns agree well with the simulated values, and these are shown as histograms in the insets of Figure 2.

The addition of a few microliters of trifluoroacetic acid to a 3 mL solution of *t*-BuC₆₀⁻ in a quartz cuvette results in an instantaneous disappearance of the *t*-BuC₆₀⁻ absorption band at 660 nm and the appearance of a new absorption band at λ_{max} = 437 nm, a value that is diagnostic for 1,2-adducts of C₆₀.^{17,29} This is consistent with the isolated product that was identified as 1-*tert*-butyl-1,2-dihydro[60]fullerene as shown in eq 2 (see

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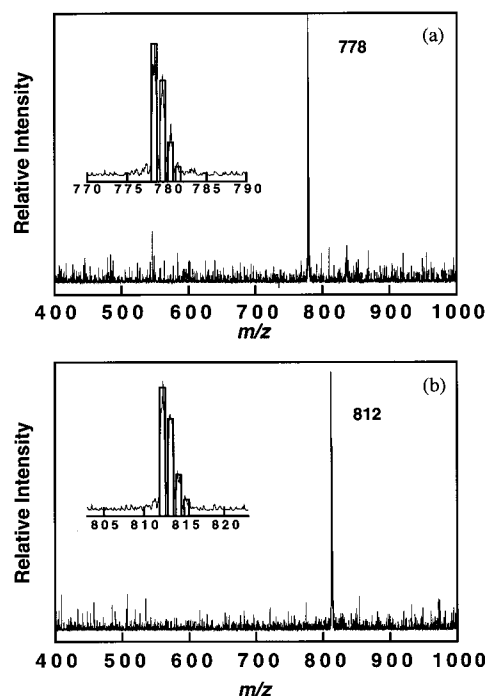
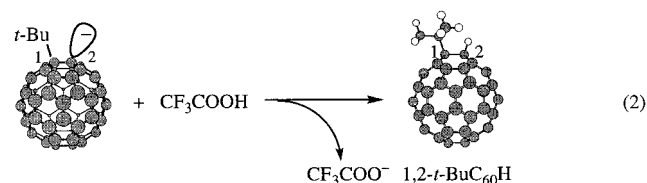


Figure 2. Electrospray ionization mass spectra (ESI-MS) for (a) *t*-BuC₆₀⁻ and (b) *t*-PhCH₂C₆₀⁻. Inset: magnified spectrum in the vicinity of molecular weight of each anion as compared with the natural isotope abundance pattern.

Experimental Section).^{6,30,31}



The treatment of C₆₀ with *tert*-butyllithium followed by an acid quench has been reported to initially give both the 1,2- and 1,4-isomers of *t*-Bu(H)C₆₀, with the 1,4-isomer rearranging to give the more stable 1,2-isomer at prolonged reaction times.^{30,31} This rearrangement is reported to be base-catalyzed,³⁰ and a fast rearrangement of the 1,4-isomer may also occur under our basic reaction conditions.

Addition of a Second Alkyl Group to RC₆₀⁻. The PhCH₂C₆₀⁻, formed in the reaction of C₆₀²⁻, undergoes addition of a second benzyl group with excess PhCH₂Br to yield (PhCH₂)₂C₆₀ (eq 3), which has been shown by X-ray crystallography to exist as the 1,4-isomer, 1,4-(PhCH₂)₂C₆₀ (eq 3).^{10a} On the other hand, *t*-BuC₆₀⁻ does not undergo the addition of a second *tert*-butyl group, even in the presence of a large excess of *t*-BuI (see Figure 3), thus indicating that the addition of a second addend is highly sensitive to the steric effect of the R group. In contrast, addition of PhCH₂Br to a PhCN solution of *t*-BuC₆₀⁻ results in the disappearance of the 660 nm absorption band of *t*-BuC₆₀⁻ (Figure 3). The final product of this reaction was isolated and identified as 1,4-*t*-Bu(PhCH₂)C₆₀ (see Experimental Section) as shown in eq 4. It has a diagnostic absorption band at 447 nm that is similar to the ca.

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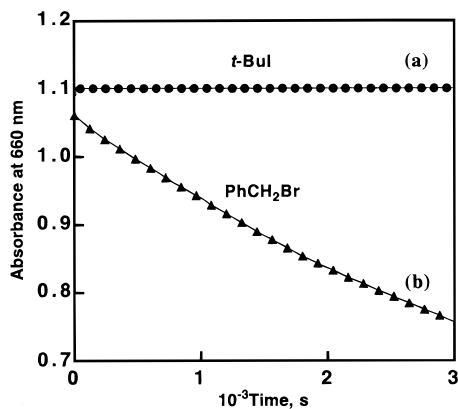
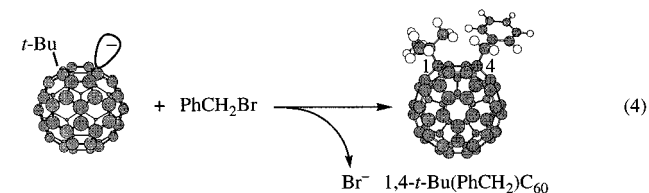
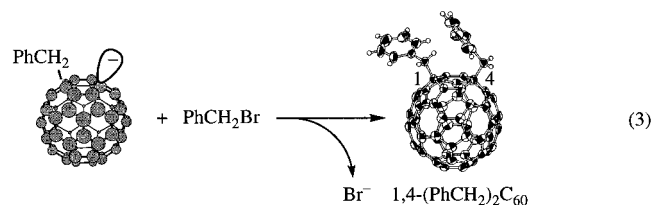


Figure 3. Time-dependent changes of the 660 nm band of $t\text{-BuC}_{60}^-$ after addition of $t\text{-BuI}$ (4.0×10^{-2} M) (●) and PhCH_2Br (4.0×10^{-2} M) (▲) to $t\text{-BuC}_{60}^-$ (4.0×10^{-4} M) in deaerated PhCN at 298 K.

450 nm band observed for 1,4- $(\text{PhCH}_2)_2\text{C}_{60}$ and other 1,4-adducts.^{10a,31}



Theoretical heats of formation (ΔH_f) for the 1,4- and 1,2-isomers of both $t\text{-Bu}(\text{PhCH}_2)\text{C}_{60}$ and $t\text{-Bu}(\text{H})\text{C}_{60}$ were calculated by using the PM3 method and gave the results shown in Figure 4. The calculations indicate that the 1,4-isomer of $t\text{-Bu}(\text{PhCH}_2)\text{C}_{60}$ is thermodynamically more stable than the 1,2-isomer of the same compound and that the 1,2-isomer of $t\text{-Bu}(\text{H})\text{C}_{60}$ is more stable than the 1,4-isomer. The 15 kcal mol⁻¹ smaller ΔH_f for the 1,4-isomer of $t\text{-Bu}(\text{PhCH}_2)\text{C}_{60}$ as compared to the 1,2-isomer may be due to a steric repulsion between the bulky $t\text{-Bu}$ and PhCH_2 groups.

The first, second, and third one-electron reduction potentials of 1,4- $t\text{-Bu}(\text{PhCH}_2)\text{C}_{60}$ are shown in Table 1, which also includes data for 1,4- $(\text{PhCH}_2)_2\text{C}_{60}$ and two 1,2-adducts of C_{60} . There is no noticeable effect of the isomer type on $E_{1/2}$, and the addition of two addends to C_{60} by which one C–C double bond of C_{60} is transformed to a single bond results in ca. a 0.1 V negative shift in both the first and the second one-electron reduction potentials as compared with the parent C_{60} , irrespective of the type of added group.

Electron Transfer vs $\text{S}_{\text{N}}2$ Pathway. The conversion of C_{60}^{2-} to R_2C_{60} or $\text{R}(\text{R}')\text{C}_{60}$ passes through a RC_{60}^- intermediate. The first and second steps in formation of the bis-adduct may both proceed via an electron transfer or an $\text{S}_{\text{N}}2$ reaction as shown in Scheme 2. An electron transfer from C_{60}^{2-} to RX would give a radical pair ($\text{C}_{60}^{\bullet-}\text{R}^+\text{X}^-$) where the R–X bond is cleaved upon dissociative electron transfer.³² A facile radical coupling in the radical pair may give the same RC_{60}^- product as expected from the alternative $\text{S}_{\text{N}}2$ pathway shown in the first R group

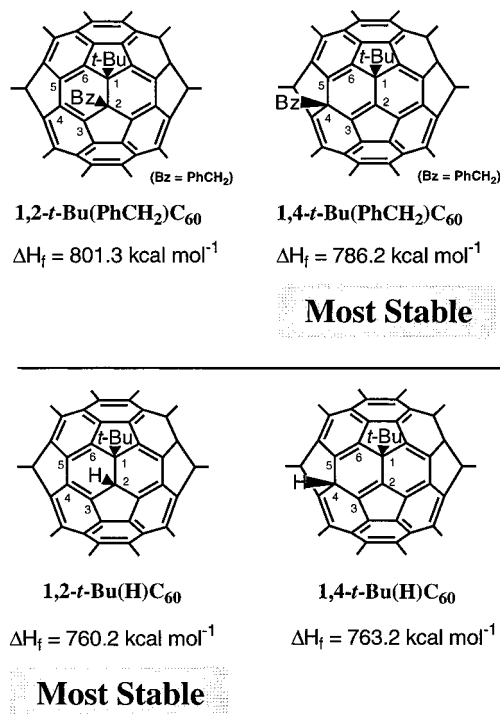


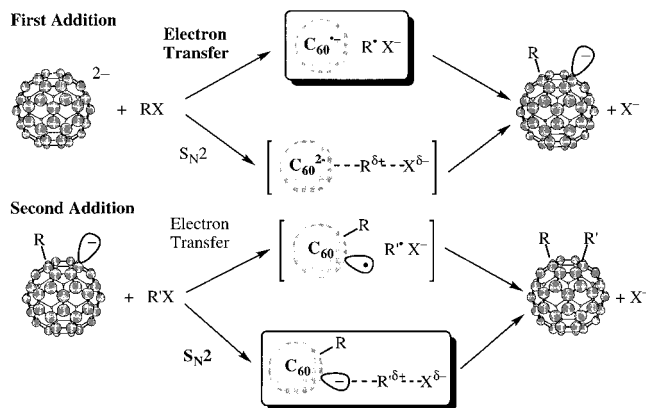
Figure 4. Calculated heats of formation (ΔH_f) for regioisomers of $t\text{-Bu}(\text{PhCH}_2)\text{C}_{60}$ and $t\text{-Bu}(\text{H})\text{C}_{60}$.

Table 1. Reduction Half-Wave Potentials ($E_{1/2}$) for the 1,4- and 1,2-Adducts of C_{60} in PhCN Containing 0.1 M TBAP at 298 K

compd	$E_{1/2}$ vs SCE, V (in PhCN)		
	1st	2nd	3rd
C_{60}	−0.43	−0.87	−1.33
1,4- $t\text{-Bu}(\text{PhCH}_2)\text{C}_{60}$	−0.55	−0.98	−1.51
1,4- $(\text{PhCH}_2)_2\text{C}_{60}$	−0.57 ^a	−0.99 ^a	−1.51 ^a
1,2- <i>o</i> -xylyl- C_{60}	−0.54 ^a	−1.00 ^a	−1.51 ^a
1,2-MeOC(=O)CMe ₂ (H) C_{60}	−0.56 ^b	−0.97 ^b	

^a Taken from ref 10a. ^b Taken from ref 17a.

Scheme 2



addition step of Scheme 2.³³ The addition of a second alkyl group to RC_{60}^- may also proceed via electron transfer from RC_{60}^- to $\text{R}'\text{X}$ to give a radical pair ($\text{RC}_{60}^{\bullet-}\text{R}'\text{X}^-$), followed by fast radical coupling to yield the final product, $\text{R}(\text{R}')\text{C}_{60}$. As

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(33) No homo-coupling products of alkyl radicals were obtained, indicating that no free radicals escaped from the cage to be involved in the electron-transfer pathway.

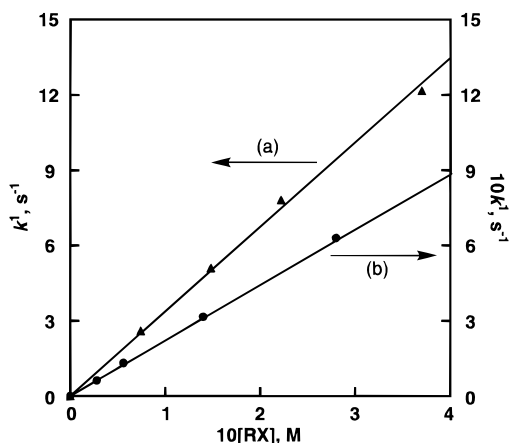


Figure 5. Plots of pseudo-first-order rate constants (k^1) vs $[RX]$ for the reactions of C_{60}^{2-} (2.8×10^{-4} M) with (a) $Me_2C=CHCH_2Br$ and (b) $CH_2=CHCH_2Br$.

Table 2. Observed (k_{obs1}) and Theoretical Rate Constants (in Parentheses) for the First Addition of RX to C_{60}^{2-} and Rate Constants of Electron Transfer from $Me_4Q^{\cdot-}$ to RX (k_{et}) in PhCN at 298 K

no.	RX	$k_{obs1},^a M^{-1} s^{-1}$	$k_{et}, M^{-1} s^{-1}$
1	CCl_4	1.3×10^2 (6.8×10^2)	5.8×10^2
2	$CH_2=CHCH_2I$	5.0×10	5.5×10
3	$Me_2C=CHCH_2Br$	3.2×10	1.9×10
4	$o-C_6H_4(CH_2Br)_2$	8.0	1.4×10
5	$PhCH_2Br$	2.5 (3.0×10^{-1})	2.3
6	$CH_2=CHCH_2Br$	2.2	1.5
7	$Me_2C=CHCH_2Cl$	5.1×10^{-2}	2.4×10^{-1}
8	<i>t</i> -BuI	4.7×10^{-2}	2.6×10^{-1}
9	MeI	3.5×10^{-2}	7.5×10^{-2}
10	<i>s</i> -BuI	2.2×10^{-2} (7.1×10^{-1})	8.3×10^{-2}
11	<i>i</i> -PrI	1.2×10^{-2} (2.0×10^{-3})	5.5×10^{-2}
12	EtI	1.2×10^{-2} (5.9×10^{-3})	3.3×10^{-2}
13	<i>n</i> -PrI	7.3×10^{-3}	
14	<i>n</i> -BuI	4.5×10^{-3} (2.0×10^{-3})	1.7×10^{-2}
15	$PhCH_2Cl$	2.3×10^{-3} (2.6×10^{-3})	5.0×10^{-3}

^a Theoretical values in parentheses are evaluated on the basis of the Marcus theory by using eqs 7 and 8, see text.

shown in Scheme 2, the electron transfer and S_N2 pathways in each step would give the same products. In such a case, the operating mechanism can only be distinguished by evaluating the reactivity of RX in each step. Thus, we examined the rates of both the first and second alkyl group addition to C_{60}^{2-} and compared these data with rates of authentic electron transfer and S_N2 reactions (*vide infra*).

Evaluation of the Electron-Transfer Pathway. The rates of C_{60}^{2-} disappearance in the reaction with RX were determined by monitoring both the decrease in C_{60}^{2-} absorbance and the increase in RC_{60}^- absorbance (see Figure 1 for the case of R = *t*-Bu). The rates obey pseudo-first-order kinetics under experimental conditions where the RX concentration is greater than 10-fold excess of the C_{60}^{2-} concentration. The pseudo-first-order rate constants increase proportionally with the RX concentration as shown in Figure 5 for the case of $Me_2C=CHCH_2Br$ and $CH_2=CHCH_2Br$, where the second-order rate constants (k_{obs1}) in eq 5 are obtained from the slopes of the plots.

$$-d[C_{60}^{2-}]/dt = k_{obs1}[C_{60}^{2-}][RX] \quad (5)$$

The k_{obs1} values for the first addition of a series of RX to C_{60}^{2-} in PhCN at 298 K are listed in Table 2 and arranged according to the magnitude of the rate constant, which varies

from $1.3 \times 10^2 M^{-1} s^{-1}$ in the case of CCl_4 (**1**) to $2.3 \times 10^{-3} M^{-1} s^{-1}$ in the case of $PhCH_2Cl$ (**15**). The reactivity of RX toward C_{60}^{2-} is insensitive to the steric hindrance of the alkyl group of RX, being opposite from what is expected for the normal reactivity in S_N2 reactions.²¹ For example, the largest rate constant is seen for sterically hindered CCl_4 , while *t*-BuI (**8**), which is also sterically hindered, has a larger k_{obs} value ($4.7 \times 10^{-2} M^{-1} s^{-1}$) than the much less sterically hindered MeI (**9**: $3.5 \times 10^{-2} M^{-1} s^{-1}$). The k_{obs} values for the reactions with RI (**8–14**) follow the order R = *t*-Bu > Me > *s*-Bu > *i*-Pr = Et > *n*-Pr > *n*-Bu, and such an insensitivity of the rate to the steric hindrance of RX is a known characteristic of electron-transfer reductions of RX.^{34,35}

Dianionic C_{60}^{2-} is expected to act as a strong electron donor judging from its largely negative oxidation potential ($E_{ox}^0 = -0.87$ V vs SCE in PhCN).^{17a,36} The standard free energy change of electron transfer (ΔG_{et}^0) from C_{60}^{2-} to RX can be calculated from the oxidation potential of C_{60}^{2-} and the reduction potential (E_{red}^0) of RX^{34,35} by using eq 6, where F is

$$\Delta G_{et}^0 = F(E_{ox}^0 - E_{red}^0) \quad (6)$$

the Faraday constant. The dependence of the activation free energy of electron transfer (ΔG^\ddagger) on the free energy change of electron transfer (ΔG_{et}^0) is given by the Marcus theory of electron transfer (eq 7),³⁷ where ΔG_0^\ddagger is the intrinsic barrier

$$\Delta G^\ddagger = \Delta G_0^\ddagger(1 + \Delta G_{et}^0/4\Delta G_0^\ddagger)^2 \quad (7)$$

that represents the activation free energy when the driving force of electron transfer is zero, i.e., $\Delta G^\ddagger = \Delta G_0^\ddagger$ at $\Delta G_{et}^0 = 0$.

The ΔG_0^\ddagger values for electron-transfer reduction of a number of RX groups have previously been reported.^{12,34,35} The ΔG^\ddagger values are related to the rate constants of electron transfer (k_{et}) as given by eq 8,

$$\Delta G^\ddagger = 2.3RT \log[Z(k_{et}^{-1} - k_{diff}^{-1})] \quad (8)$$

where Z is the collision frequency that is taken as $10^{11} M^{-1} s^{-1}$ and k_{diff} is the diffusion rate constant that is taken as $5.6 \times 10^9 M^{-1} s^{-1}$.³⁸

Theoretical rate constants for electron transfer from C_{60}^{2-} to various RX in PhCN at 298 K were calculated from the ΔG_{et}^0 and ΔG_0^\ddagger values by using eqs 7 and 8, and these values are listed in parentheses in Table 2 along with the experimentally obtained k_{obs} values. As seen in the table, the theoretical rate constants agree within 1 order of magnitude with the experimentally determined k_{obs} values. Such an agreement indicates that electron transfer from C_{60}^{2-} to RX is the rate-limiting step in the formation of RC_{60}^- .

The occurrence of a rate-determining electron transfer from C_{60}^{2-} to RX was further confirmed by comparison between the observed rate constants (k_{obs1}) for formation of RC_{60}^- and the rate constants (k_{et}) of electron transfer from tetramethylseminquinone radical anion ($Me_4Q^{\cdot-}$) to the same series of RX. These k_{et} values are also listed in Table 2. The radical anion $Me_4Q^{\cdot-}$

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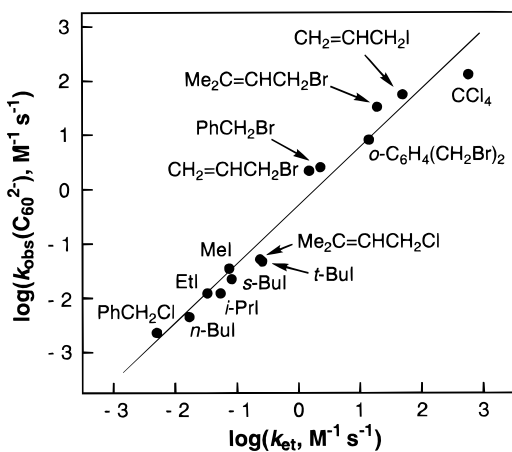


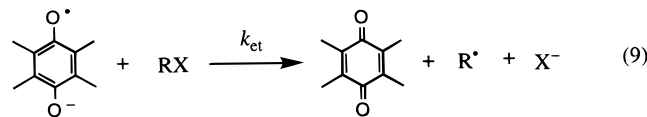
Figure 6. Correlation between $\log k_{\text{obs}}$ for the reaction of C_{60}^{2-} ($2.8 \times 10^{-4} \text{ M}$) with various alkyl halides and $\log k_{\text{et}}$ for the electron-transfer reaction of $\text{Me}_4\text{Q}^{\bullet-}$ ($3.7 \times 10^{-4} \text{ M}$) with various alkyl halides in deaerated PhCN at 298 K.

Table 3. Rate Constants for Addition of RX to $t\text{-BuC}_{60}^-$ ($k_{\text{obs}2}$) and CoTPP^- ($k_{\text{S}_{\text{N}2}}$) in PhCN at 298 K

no.	compd	$k_{\text{obs}2}, \text{M}^{-1} \text{s}^{-1}$	$k_{\text{S}_{\text{N}2}}, \text{M}^{-1} \text{s}^{-1}$
3	$\text{Me}_2\text{C}=\text{CHCH}_2\text{Br}$	4.2×10^{-2}	4.7×10^5
2	$\text{CH}_2=\text{CHCH}_2\text{I}$	2.7×10^{-2}	2.2×10^5
6	$\text{CH}_2=\text{CHCH}_2\text{Br}$	4.0×10^{-3}	4.3×10^4
5	PhCH_2Br	2.9×10^{-3}	1.9×10^5
9	MeI	1.5×10^{-3}	2.1×10^4
12	EtI	9.7×10^{-5}	8.6×10^2
13	<i>n</i> -PrI	7.4×10^{-5}	1.1×10^3 ^a
14	<i>n</i> -BuI	4.6×10^{-5}	2.6×10^3
1	CCl_4	3.0×10^{-5}	4.5×10^2
10	<i>s</i> -BuI	0	3.6×10^4
8	<i>t</i> -BuI	0	0

^a Taken from ref 21.

was chosen to model the electron-transfer reactions of C_{60}^{2-} with RX (eq 9), since $\text{Me}_4\text{Q}^{\bullet-}$ has nearly the same oxidation



potential ($E_{1/2} = -0.84 \text{ V}$ vs SCE in MeCN)³⁹ as that of C_{60}^{2-} ($E_{1/2} = -0.87 \text{ V}$ vs SCE in PhCN).^{17a,36} The plot between the experimentally determined $\log k_{\text{obs}}$ and $\log k_{\text{et}}$ values (Figure 6) shows a linear correlation with a slope of unity, thus demonstrating clearly that the activation barrier for the first-step reaction of C_{60}^{2-} with RX is essentially the same as that for the electron-transfer reaction of $\text{Me}_4\text{Q}^{\bullet-}$ with the same series of RX.

Evaluation of the $\text{S}_{\text{N}2}$ Pathway. Values of second-order rate constants ($k_{\text{obs}2}$) for addition of each alkyl group to $t\text{-BuC}_{60}^-$ are given in Table 3 and arranged according to the order of magnitude of the rate constant. These rates were determined by monitoring the disappearance of the 660 nm absorption band due to $t\text{-BuC}_{60}^-$ as seen in Figure 3 for PhCH_2Br . The rates obey pseudo-first-order kinetics under experimental conditions where the RX concentration is greater than 10-fold excess of the $t\text{-BuC}_{60}^-$ concentration. The pseudo-first-order rate constants (k^1) are in all cases proportional to the RX concentration as shown in Figure 7 for the case of RX = $\text{CH}_2=\text{CHCH}_2\text{I}$, $\text{Me}_2\text{C}=\text{CHCH}_2\text{Br}$, and MeI. The second-order kinetics shows

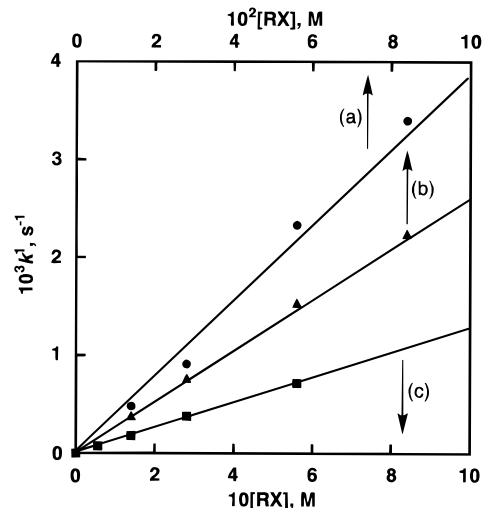
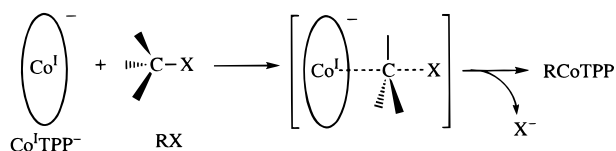


Figure 7. Plots of pseudo-first-order rate constants (k^1) vs $[\text{RX}]$ for the reactions of $t\text{-BuC}_{60}^-$ ($2.8 \times 10^{-4} \text{ M}$) with (a) $\text{CH}_2=\text{CHCH}_2\text{I}$, (b) $\text{Me}_2\text{C}=\text{CHCH}_2\text{Br}$, and (c) MeI.

Scheme 3



a first-order dependence on each reactant (eq 10), thus indicating that there is no contribution of an $\text{S}_{\text{N}1}$ reaction pathway where the dissociation of RX to R^+ and X^- is the rate-determining step.⁴⁰

$$-\frac{d[t\text{-BuC}_{60}^-]}{dt} = k_{\text{obs}2}[t\text{-BuC}_{60}^-][\text{RX}] \quad (10)$$

The reactivity order of RX for the second step addition in Table 3 is quite different from that for the first step addition in Table 2. For example, CCl_4 (**1**), is the most reactive RX group in the first step addition, but it is much less reactive in the second step addition and has a $k_{\text{obs}2}$ value of $3.0 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, which is 3 orders of magnitude smaller than the most reactive $\text{Me}_2\text{C}=\text{CHCH}_2\text{Br}$ (**3**: $4.2 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$). The sterically hindered *t*-BuI (**8**) and *s*-BuI (**10**) both have a good reactivity in the first R group addition, but show no reactivity at all in the second R group addition. Such sensitivity to the steric hindrance of the alkyl group of RX is characteristic of $\text{S}_{\text{N}2}$ reactions involving RX and nucleophiles, a typical example of which is the conversion of cobalt(I) tetraphenylporphyrin anion, $\text{Co}^{\text{I}}\text{TPP}^-$, to the σ -bonded complex, RCoTPP , as shown in Scheme 3.^{21,41}

The $\text{S}_{\text{N}2}$ reactions of alkyl halides at a tetrahedral carbon center with low-valent metal porphyrins such as Co(I), Fe(I), and Rh(I) porphyrins have been well-established to yield σ -bonded organometallic porphyrins.^{42,43} Thus, the second-

(40) In this case the rate would be zeroth-order with respect to $[t\text{-BuC}_{60}^-]$, which is clearly distinguished from the kinetic formulation in eq 10 observed under the present experimental conditions. Even if R^+ is formed by an $\text{S}_{\text{N}1}$ reaction pathway, R^+ would be immediately trapped by a base that is present in a solution of naphthalene radical anion used for generation of C_{60}^{2-} .

(41) Three-electron $\text{S}_{\text{N}2}$ reactions are known to exhibit greatly diminished steric effects. Even in such cases, however, the *Me/t*-Bu ratio for the rate of three-electron $\text{S}_{\text{N}2}$ reaction of 1,1-diphenyl-2-alkylcyclopropane radical cations with methanol is still 31. (a) Dinocenzo, J. P.; Lieberman, D. R.; Simpson, T. R. *J. Am. Chem. Soc.* **1993**, *115*, 366. (b) Dinocenzo, J. P.; Todd, W. P.; Simpson, T. R.; Gould, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 2462.

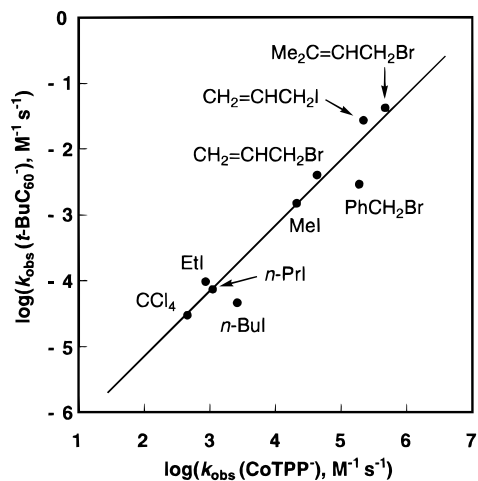


Figure 8. Plot of $\log k_{\text{obs}}$ for the reaction of $t\text{-BuC}_{60}^{2-}$ (2.8×10^{-4} M) with various alkyl halides (1.4×10^{-2} to 5.6×10^{-1} M) vs $\log k_{\text{obs}}$ for the $\text{S}_{\text{N}}2$ reaction of CoTPP^- (5.0×10^{-5} M) with the same series of alkyl halides in deaerated PhCN at 298 K.

order rate constants ($k_{\text{S}_{\text{N}}2}$) for the $\text{S}_{\text{N}}2$ reactions of $\text{Co}^{\text{I}}\text{TPP}^-$ with the same series of RX as employed for the reactions of $t\text{-BuC}_{60}^{2-}$ were determined in the present study by monitoring the appearance of the RCoTPP 406 nm absorption band upon the reaction with RX. These rate constants range from $4.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Me}_2\text{C}=\text{CHCH}_2\text{Br}$ to 0 for $t\text{-BuI}$ (see Table 3).

As seen in Figure 8, a linear correlation with a slope of unity is observed between $\log k_{\text{obs}2}$ of $t\text{-BuC}_{60}^{2-}$ and $\log k_{\text{S}_{\text{N}}2}$ of CoTPP^- . In contrast, no correlation is seen between $\log k_{\text{obs}2}$ or $\log k_{\text{S}_{\text{N}}2}$ vs $\log k_{\text{et}}$ for the data in Table 2. The linear correlation in Figure 8 thus clearly indicates that the alkylation of $t\text{-BuC}_{60}^{2-}$ with RX proceeds via an $\text{S}_{\text{N}}2$ pathway rather than via an electron-transfer pathway.

One question that must be addressed is why the reactions of C_{60}^{2-} and $t\text{-BuC}_{60}^{2-}$ with RX proceed via different mechanisms: an electron transfer and an $\text{S}_{\text{N}}2$, respectively. There is a high delocalization of negative charge on the C_{60} skeleton and the most negative charge at a C_{60}^{2-} carbon atom is only -0.06 .^{10a} It is therefore not surprising that C_{60}^{2-} , with such a small negative charge at each carbon, cannot act as an effective nucleophile in the reaction with RX. In such a case, an electron-transfer pathway is the only choice for the reaction to occur.

In general, a nucleophile, which is also an electron donor, is forced to undergo an electron-transfer pathway when steric hindrance at the reaction center prevents the nucleophile from interacting strongly enough to undergo an $\text{S}_{\text{N}}2$ reaction.^{12,44} Thus, the $\text{C}_{60}^{2-}/\text{RX}$ system provides a unique example for an electron-transfer pathway of a nucleophile which has a highly delocalized negative charge. In contrast, the negative charge on $t\text{-BuC}_{60}^{2-}$ becomes significantly localized at the C(2) position (-0.33) as well as at the C(4) and C(11) positions (-0.15).^{31a} Addition at the C(2) position may be difficult because of steric

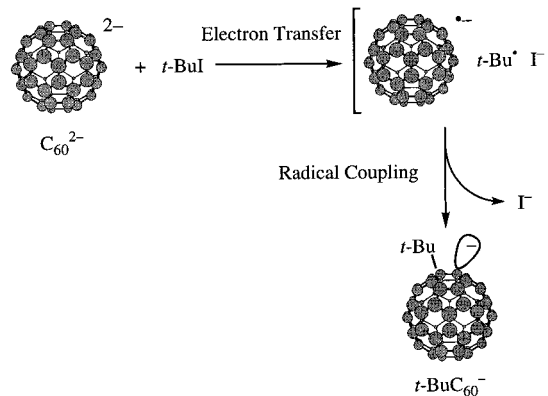
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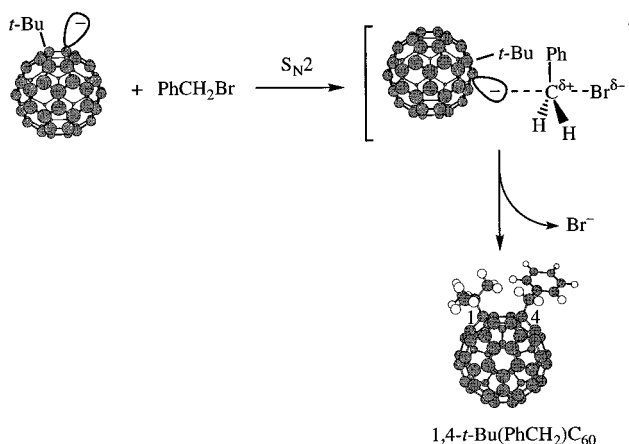
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Scheme 4

First Addition



Second Addition



repulsion between the proximate $t\text{-Bu}$ and benzyl groups, and the nucleophilic addition of RX may then occur at the C(4) or C(11) positions, where the negative charge is the second largest.

In conclusion, the drastic difference in charge distribution between C_{60}^{2-} and $t\text{-BuC}_{60}^{2-}$ causes significant differences in their nucleophilic reactivities so that the reactions of C_{60}^{2-} and $t\text{-BuC}_{60}^{2-}$ with RX proceed via different pathways, i.e., an electron transfer in the first step and an $\text{S}_{\text{N}}2$ pathway in the second step. A summary of the mechanism is shown in Scheme 4 for the formation of $t\text{-Bu}(\text{PhCH}_2)\text{C}_{60}$ as a typical example. The initial electron transfer from C_{60}^{2-} to $t\text{-BuI}$ gives the $\text{C}_{60}^{\bullet-}/t\text{-Bu}^{\bullet}$ radical pair following an instantaneous cleavage of the C-I bond upon the dissociative electron-transfer reduction of $t\text{-BuI}$. A fast radical coupling between $\text{C}_{60}^{\bullet-}$ and $t\text{-Bu}^{\bullet}$ occurs in the radical pair to produce the monoadduct anion, $t\text{-BuC}_{60}^{\bullet-}$, which then undergoes an $\text{S}_{\text{N}}2$ reaction with PhCH_2Br to yield the final product with two different alkyl groups such as $t\text{-Bu}(\text{PhCH}_2)\text{C}_{60}$.

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