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Formation of Radical Anions in the Reaction of *p*-Benzoquinone and C_{60} with Alkoxide Ions

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Abstract: Reactions of *p*-benzoquinone and its derivatives with hydroxide and alkoxide ions (RO^-: R = H, Me, Et, *i*-Pr, $PhCH_2$) in acetonitrile (MeCN) result in formation of the corresponding semiquinone radical anions accompanied by the formation of RO-substituted *p*-benzoquinones, which are the oxidized products of *p*-benzoquinones. Detailed product and kinetic analyses of the reactions have demonstrated that the RO-adduct anion of *p*-benzoquinone is a real electron donor and that RO^- is acting as a very strong base or nucleophile rather than a one-electron reductant in an aprotic solvent, such as MeCN. Similarly, the reaction of C_{60} with methoxide anion (MeO^-) in benzonitrile (PhCN) results in formation of $C_{60}^{\bullet-}$. Spectroscopic and kinetic studies also indicate that a methoxy adduct anion of C_{60} is an actual electron donor and that MeO^- is acting as a very strong base or nucleophile rather than an electron donor in PhCN.

Introduction

It has long been known that electron acceptors such as quinones and viologens are reduced in the presence of hydroxide ion (OH^-) to yield the corresponding one-electron reduced radical species, semiquinone radical anions and viologen radical cations, respectively.[1−6] Hydroxide ion may be a much stronger electron donor in an aprotic solvent such as acetonitrile (MeCN) than in water, since the solvation energy for OH^- is much less in an aprotic solvent than in water.[1] Thus, OH^- in aprotic solvents has been reported to act as an electron donor in the one-electron reduction of quinones and other electron acceptors.[1−6] In such cases, the oxidized product of OH^- has been presumed to be H_2O_2 or O_2. However, no oxidized products of OH^- have so far been identified in the one-electron reduction of electron acceptors in the presence of OH^- in an aprotic solvent.

Alkoxide ions such as MeO^- in an aprotic solvent can also induce the one-electron reduction of electron acceptors as does OH^-. In fact, methyl viologen (MV^{2+}) is known to be reduced to $MV^{\bullet+}$ in both alkaline aqueous and methanolic solutions in the absence of air.[7] The MeO^- was regarded as capable of reducing MV^{2+} to $MV^{\bullet+}$.[7] However, a pseudobase produced by the initial attack of OH^- at the 2-position of one of the aromatic rings of MV^{2+} was also suggested to reduce successively 2 equiv of MV^{2+}.[8] In such a case, MV^{2+} but not OH^- or MeO^- would be oxidized in the one-electron reduction of MV^{2+}. Wilson and Wu[9] have also reported that C_{60} is reduced to $C_{60}^{\bullet-}$ by addition of a MeO^- solution to C_{60} in toluene, and this reaction is accompanied by formation of the adduct anions, $C_{60}(OMe)_n^-$ (n = 1, 3, 5, 7). Electron transfer from MeO^- to C_{60} is thought to result in formation of $C_{60}^{\bullet-}$ and the adduct anions.[9] However, the ultimate electron source to reduce C_{60} should be the MeO^- adduct of C_{60}, since C_{60} is oxidized to $C_{60}(OMe)_n^-$. Thus, a mechanism for the one-electron reduction of electron acceptors in the presence of a strong base has not been firmly established and the actual electron source remains to be clarified. Since the redox properties of *p*-benzoquinone[10] are similar to those of C_{60},[11] it is of interest to study the mechanism and products formed in the reactions of C_{60} with a strong base in an aprotic polar solvent for comparison with that of *p*-benzoquinone.

This study reports that various *p*-benzoquinones as well as C_{60} are readily reduced in an aprotic solvent containing OH^- or MeO^- to yield the corresponding radical anions which are

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stable in the absence of oxygen.[12] The semiquinone radical anions are known to be important intermediates in biological redox systems.[10] However, the electronic spectra of semiquinone radical anions, especially in the UV region, have scarcely been studied because of the instability of radicals.[13,14] Thus, the present study provides a convenient method for preparation of these important radicals under stable conditions. Mechanisms for the one-electron reduction of quinones in the presence of OH^- and MeO^- in deaerated MeCN are discussed in comparison with similar reactions involving C_{60} in benzonitrile (PhCN) and provide a more comprehensive understanding of the actual role of the base in electron transfer reactions in aprotic solvents.

Experimental Section

Materials. Most *p*-benzoquinones and the rhodizonic acid disodium salt were obtained commercially and purified by standard methods.[15] Chloro-*p*-benzoquinone and 2,3-dicyano-*p*-benzoquinone were prepared from the corresponding hydroquinones as described in the literature.[16] C_{60} (>99.95% pure) was purchased from Science Laboratories Co., Ltd., Japan, and used as received. Tetramethylammonium hydroxide pentahydrate ($NMe_4OH \cdot 5H_2O$) was obtained from Sigma. A 0.10 M NMe_4OH stock aqueous solution was used for the preparation of various concentrations of NMe_4OH in acetonitrile. Tetra-*n*-butylammonium hydroxide (NBu_4OH) (1.0 M in methanol) was purchased from Aldrich and used as received. Benzonitrile and acetonitrile were purchased from Wako Pure Chemical Ind. Ltd., Japan, and purified by successive distillation over P_2O_5 prior to use.

General Procedure. Since some semiquinone radical anions and $C_{60}^{\bullet -}$ are readily oxidized by oxygen, the reactions were carried out under strictly deaerated conditions. A continuous flow of Ar gas was bubbled through an MeCN or PhCN solution containing *p*-benzoquinone (1.0×10^{-3} M) or C_{60} (2.0×10^{-4} M) in a square quartz cuvette (10 mm i.d.) for 10 min. The neck of the cuvette was then sealed with a rubber septum and Parafilm under Ar in order to ensure that air would not leak into the cuvette. A microsyringe was used to inject 1−10 μL of a stock solution of NMe_4OH or NMe_4OMe (0.10 M), which was also deaerated, into the cuvette, after which the neck of the cuvette was resealed with Parafilm. The UV−visible and near-IR spectra were recorded on a Shimadzu UV-160A spectrophotometer equipped with a Shimadzu TCC-240A thermostated cell holder or a Hewlett-Packard 8452A photodiode array spectrophotometer. ^1H NMR spectra were recorded on a JEOL FT-NMR GSX-400 spectrometer.

ESR spectra were taken on a JEOL JES-RE1XE and were recorded under nonsaturating microwave power conditions. The magnitude of the modulation was chosen to optimize the resolution and the signal-to-noise ratio (S/N) of the observed spectra. The *g* values were calibrated by using a Mn^{2+} marker.

Electrospray ionization mass spectrometry (ESI-MS) was carried out on a sector type mass spectrometer (JEOL-D300) connected with a homemade ESI (electrospray ionization) interface. The interface is similar to that of the ESI ion source designed by Fenn.[17] All spectra were obtained by infusing the sample solution directly into the ESI chamber by a syringe pump.

Product Analysis. The reaction of *p*-benzoquinone (5.0×10^{-2} M) with NMe_4OH (2.0×10^{-2} M) in deaerated MeCN was carried out by using a cuvette which was filled with nitrogen (1.6 mL). The products in the gas phase were analyzed by GC with use of a molecular sieve 13 X column, when He was used as a carrier gas for the detection of oxygen. Although tiny leaks of oxygen are inevitable in this analysis, the amount of O_2 detected was less than 1% of the initial amount of NMe_4OH. The GC analysis of the product solution confirmed that no succinonitrile was formed in the reaction of *p*-benzoquinone with NMe_4OH.

The known concentration of H_2O_2 (1.0×10^{-2} M) was treated with triphenylphosphine (1.0×10^{-2} M). The amount of triphenylphosphine oxide formed by reaction of triphenylphosphine with H_2O_2 was analyzed by GC using a OV-17 column. In 40 min, triphenylphosphine was quantitatively converted to triphenylphosphine oxide. The product mixture after reaction of *p*-benzoquinone (2.0×10^{-2} M) with NMe_4OH (2.0×10^{-2} M) was also treated with triphenylphosphine (1.0×10^{-2} M) in deaerated MeCN. No appreciable amounts of triphenylphosphine oxide were detected in 40 min, indicating that no H_2O_2 was formed in the reaction of *p*-benzoquinone with NMe_4OH.

The reduced product of *p*-benzoquinone in the reaction of *p*-benzoquinone (0.10 M) with NMe_4OH in deaerated [$^2H_3$]acetonitrile (CD_3CN) was examined by ^1H NMR spectroscopy. The semiquinone radical anion formed in the reaction was converted to hydroquinone and *p*-benzoquinone by a disproportionation reaction in the presence of excess $HClO_4$, and the only signals other than those of hydroquinone and *p*-benzoquinone which were observed in the ^1H NMR spectrum were $HClO_4$ and NMe_4ClO_4. However, the total amount of hydroquinone and *p*-benzoquinone was only 90% of the initial amount of *p*-benzoquinone (0.20 M), indicating that 10% of the *p*-benzoquinone was oxidized to a species in which all the ring protons were removed, i.e., the rhodizonate dianion.

The yield of rhodizonate dianion was determined by comparing a diluted aqueous solution (×10) of the product mixture formed after reaction of *p*-benzoquinone (2.0×10^{-3} M) with NMe_4OH (3.0×10^{-3} M) in MeCN with the characteristic absorption spectrum of an authentic sample under the same experimental conditions ($\lambda_{max} = 483$ nm, $\epsilon_{max} = 1.5 \times 10^4$ M^{-1} cm^{-1}).[18] By dilution with water, the semiquinone radical anion was converted to hydroquinone and *p*-benzoquinone by the disproportionation reaction, when the yield of rhodizonate dianion was determined accurately. The absorbance due to the rhodizonate dianion disappeared with addition of an excess amount of $HClO_4$ to the diluted aqueous solution in accordance with the known protonation and hydration equilibrium for rhodizonate dianion.[18]

A CD_3CN solution (0.60 mL) containing *p*-benzoquinone (2.0×10^{-2} M) in an NMR tube sealed with a rubber septum was deaerated by bubbling with argon gas through a stainless steel needle for 7 min and resealed with Parafilm. A stock solution of tetramethylammonium methoxide (1.0 M) was obtained by adding MeOH (4×10^{-3} mol) to a CD_3CN suspension (1.0 mL) of tetramethylammonium hydroxide ($NMe_4OH \cdot 5H_2O$) (1×10^{-3} mol) in a sample tube, which was also deaerated by bubbling with argon gas through a Teflon tube for 7 min and sealed with a rubber septum and Parafilm. The reaction was started by adding 6 μL of the stock NMe_4OMe solution to the solution of *p*-benzoquinone by means of a microsyringe and this solution was mixed for 1 h. The products were analyzed by ^1H NMR spectroscopy after addition of $HClO_4$ (0.03 M) to avoid the line broadening due to the *p*-benzosemiquinone radical anion. ^1H NMR (CD_3CN): methoxy-*p*-benzoquinone δ 3.79 (s, 3H), 5.98 (d, $J = 1.95$ Hz, 1H), 6.65−7.71 (m, 2H); 2,5-dimethoxy-*p*-benzoquinone δ 3.79 (s, 6H), 5.89 (s, 2H); 2,6-dimethoxy-*p*-benzoquinone δ 3.82 (s, 6H), 5.89 (s, 2H).

Cyclic Voltammetry. Cyclic voltammetry measurements were performed on a BAS 100B electrochemical analyzer in deaerated PhCN containing 0.10 M tetra-*n*-butylammonium perchlorate (NBu_4ClO_4) as supporting electrolyte. The Pt working electrode (BAS) was polished with a BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/$AgNO_3$ (0.01 M) reference electrode and converted to values vs SCE by adding 0.29

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V.[19] All electrochemical measurements were carried out at 298 K under an atmospheric pressure of argon.

Kinetic Measurements. Kinetic measurements were performed under deaerated conditions with a Union RA-103 stopped flow spectrophotometer or Hewlett-Packard 8452A diode array spectrophotometer, which was thermostated at 298 K. A typical procedure for kinetic measurements of the thermal reactions of *p*-benzoquinone with methoxide ion is as follows: a solution of *p*-benzoquinone (5×10^{-4} to 7.5×10^{-3} M) in MeCN (3 mL) in a 10-mm quartz cuvette was deaerated by bubbling with argon gas for 10 min, after which it was placed in a cell holder of a Hewlett-Packard 8452A diode array spectrophotometer with a magnetic stirrer. Rates for the reduction of *p*-benzoquinone were followed by monitoring the increase in absorbance due to *p*-benzosemiquinone radical anion ($\lambda_{max} = 422$ nm). The pseudo-first-order plots were linear for 3 or more half-lives with a correlation coefficient $\rho > 0.999$. Initial rates (R_i) of the formation of $C_{60}^{\bullet -}$ in the reaction of C_{60} with MeO^- in PhCN at 298 K were monitored by following an increase in the absorbance due to $C_{60}^{\bullet -}$ ($\lambda_{max} = 1080$ nm)[20] in the presence of various concentrations of MeO^- (3.3×10^{-5} to 4.3×10^{-4} M).

Theoretical Calculations. Theoretical calculations were performed with the MOPAC program (version 6) which is incorporated in the MOL-GRAPH program by Daikin Industries, Ltd. The MNDO[21] or PM3[22] Hamiltonian was used for the semiempirical MO calculations. Final geometries and energetics were obtained by optimizing the total molecular energy with respect to all structural variables. Values of the heat of formation (ΔH_f) were calculated with the restricted Hartree–Fock (RHF) formalism by using a key word "PRECISE".

Results and Discussion

Formation of Stable Semiquinone Radical Anions in the Reactions of *p*-Benzoquinones with OH^-. Upon mixing *p*-benzoquinone (Q) with NMe_4OH in deaerated MeCN at 298 K, Q is readily reduced to $Q^{\bullet -}$ ($\lambda_{max} = 422$ nm), the yield of which, based on the amount of OH^-, is 100%. ESR measurements of the deaerated product solution confirm the formation of $Q^{\bullet -}$ ($g = 2.0046$, $a_H = 2.4$ G).[23] The semiquinone radical anion ($Q^{\bullet -}$) is stable in deaerated MeCN at 298 K, but disappears gradually when oxygen is introduced to the deaerated solution to regenerate Q. Similarly, the reaction of various quinones with NMe_4OH in deaerated MeCN yields the corresponding semiquinone radical anions which are also stable in deaerated MeCN. The absorption maxima (λ_{max}) and the extinction coefficients (ϵ_{max}) of various semiquinone radical anions are listed in Table 1.[24] The yields of most of the investigated semiquinone radical anions are high except for those derived from tetrasubstituted *p*-benzoquinone derivatives such as tetramethyl-*p*-benzoquinone, *p*-chloranil, *p*-bromanil, and *p*-fluoranil, and in these cases the yields are significantly smaller than those of the other quinones as shown in Table 2.

Table 1. Absorption Maxima (λ_{max}) and the Extinction Coefficients (ϵ_{max}) of Semiquinone Radical Anions Formed in the Reaction of Various Quinones with NMe_4OH in MeCN

quinone	λ_{max}, nm ($10^{-4}\epsilon_{max}$, M^{-1} cm^{-1})
2-methyl-1,4-naphthoquinone (vitamin K_3)	300 (1.6), 400 (1.0)
2,3-dimethoxy-5-methyl-*p*-benzoquinone (coenzyme Q_0)	320 (2.0), 438 (0.9)
2,5-dimethyl-*p*-benzoquinone	324 (1.6), 436 (0.7)
methyl-*p*-benzoquinone	324 (1.4), 422 (0.6)
p-benzoquinone	324 (1.5), 422 (0.6)
chloro-*p*-benzoquinone	324 (1.6), 440 (0.6)
2,6-dichloro-*p*-benzoquinone	324 (1.0), 432 (0.6)
2,3-dicyano-*p*-benzoquinone	340 (0.9), 440 (0.5), 554 (0.3)

Table 2. Yields of Semiquinone Radical Anions in the Reactions of Various Quinones (1.0×10^{-3} M) with NMe_4OH (6.0×10^{-4} M) in Deaerated MeCN

quinone	product (yield, %)[a]
2-methyl-1,4-naphthoquinone (VK_3)	$VK_3^{\bullet -}$ (59)
2,3-dimethoxy-5-methyl-*p*-benzoquinone (CoQ_0)	$CoQ_0^{\bullet -}$ (63)
tetramethyl-*p*-benzoquinone (Me_4Q)	$Me_4Q^{\bullet -}$ (12)
2,5-dimethyl-*p*-benzoquinone (Me_2Q)	$Me_2Q^{\bullet -}$ (98)
methyl-*p*-benzoquinone (MeQ)	$MeQ^{\bullet -}$ (100)
p-benzoquinone (Q)	$Q^{\bullet -}$ (100)
chloro-*p*-benzoquinone (ClQ)	$ClQ^{\bullet -}$ (90)
2,6-dichloro-*p*-benzoquinone (Cl_2Q)	$Cl_2Q^{\bullet -}$ (65)
p-chloranil (Cl_4Q)	$Cl_4Q^{\bullet -}$ (7)
p-bromanil (Br_4Q)	$Br_4Q^{\bullet -}$ (7)
p-fluoranil (F_4Q)	$F_4Q^{\bullet -}$ (6)
2,3-dicyano-*p*-benzoquinone (DCQ)	$DCQ^{\bullet -}$ (100)

[a] Based on NMe_4OH.

No oxidized products of OH^- (H_2O_2 or O_2) were detected in the one-electron reduction of Q in the presence of OH^- in deaerated MeCN (see Experimental Section). H_2O_2 has been reported to decompose in the presence of OH^- to yield water and oxygen or acetamide and oxygen.[4] In any case, the oxidized product of OH^- should be oxygen which was not detected under our experimental conditions. Control experiments have also established that H_2O_2 in the presence of NMe_4OH in MeCN can oxidize triphenylphosphine to yield triphenylphosphine oxide. However, no triphenylphosphine oxide was detected after addition of triphenylphosphine to the product mixture (see Experimental Section). In addition, semiquinone radical anions disappear instantly upon addition of H_2O_2 to the MeCN solution. Thus, it is certain that no oxidized product of OH^- is produced in the reaction of Q with OH^-. Oxidized products derived from the solvent (e.g., succinonitrile)[25] are also not formed in the reaction with OH^-, either (see Experimental Section). No ESR spectra other than those of semiquinone radical anions have been observed by using the rapid mixing flow system, which has previously been applied to detect cyanomethyl radical ($^{\bullet}CH_2CN$) formed by the reaction of $OH^{\bullet}$ with MeCN.[26] Therefore, the question arises as to what is really oxidized in the one-electron reduction of Q in the presence of OH^- in MeCN. A scrutiny of the detailed stoichiometry of the reaction in Figure 1 reveals that a slight excess of OH^- is required to complete the reaction. The oxidized product is found to be derived from *p*-benzoquinone itself, rhodizonate dianion (**1**: $\lambda_{max} = 483$ nm)[17] that is the ten-electron oxidized product of *p*-benzoquinone (see Experimental Section). Under such conditions, the stoichiometry of the reaction is given by eq 1, where the one-electron

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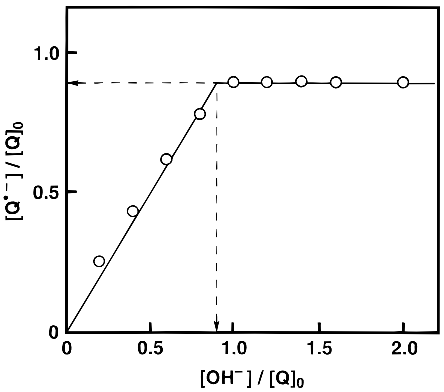
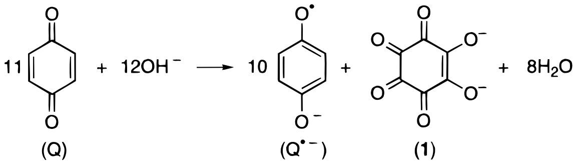


Figure 1. Plot of the ratio of the $Q^{\bullet -}$ concentration formed in the reduction of Q (1.0×10^{-3} M) in the presence of NMe_4OH to the initial concentration of Q in deaerated MeCN, $[Q^{\bullet -}]/[Q]_0$ vs $[OH^-]/[Q]_0$.

reduction of ten Q molecules is accompanied by the ten-electron oxidation of one Q molecule. Thus, OH^- is not an electron donor, but instead *p*-benzoquinone itself acts as an electron donor which is oxidized to the 10-electron oxidized species (**1**) in the presence of OH^- in MeCN to reduce 10 equiv of Q, yielding $Q^{\bullet -}$ (eq 1).



(Q) ($Q^{\bullet -}$) (**1**)

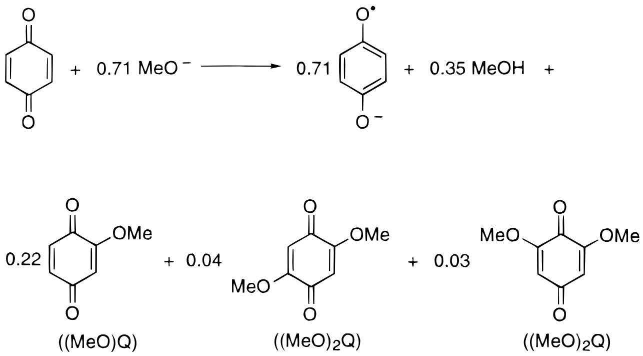
(1)

When OH^- is added to *p*-benzoquinone, the adduct anion can act as an electron donor toward *p*-benzoquinone as shown in Scheme 1. There are three possible forms of the OH^- adduct of *p*-benzoquinone; the first is the OH^- adduct on the carbonyl carbon of the quinone, the second is that on the carbonyl oxygen, and the last is that on the carbon next to the carbonyl group. The first one has so far been simply assumed to be formed.[4] An MO calculation with the MNDO method[21] was carried out for these possible OH^- adducts of *p*-benzoquinone, methyl-*p*-benzoquinone, and chloro-*p*-benzoquinone and reveals that the OH^- adduct attached on the carbon next to the carbonyl group is most stable for each quinone as shown in Table 3. An electron transfer from the adduct anion to Q may occur accompanied by deprotonation to yield the OH-substituted semiquinone radical anion and $Q^{\bullet -}$. A subsequent electron transfer from the OH-substituted semiquinone radical anion to Q may rapidly occur to yield the OH-substituted quinone and $Q^{\bullet -}$. Thus, the one-substitution of Q by OH, which corresponds to the two-electron oxidation of Q, results in the one-electron reduction of two equivalent Q to yield two $Q^{\bullet -}$. As a consequence, the successive substitution of Q by OH finally results in the formation of the ten-electron oxidized species (**1**), accompanied by a one-electron reduction of 10 equiv Q to yield 10 $Q^{\bullet -}$ as shown in Scheme 1. This novel disproportionation of *p*-benzoquinone, in which the quinone itself acts as a ten-electron donor in the presence of OH^-, is responsible for the apparently quantitative formation of semiquinone radical anion (eq 1).

In the case of tetrasubstituted *p*-benzoquinone derivatives, the formation of an OH^- adduct may be prohibited due to the steric effects. Even if the adduct is formed, no deprotonation of the OH^- adduct would occur. This may be the reason the yields of semiquinone radical anions derived from the tetrasubstituted *p*-benzoquinone derivatives (X_4Q) are extremely small as compared with the quinones which contain ring protons (Table 2). The formation of small amounts of semiquinone radical anions may be ascribed to the known substitution reaction of OH^- with X_4Q to yield dihydroxy-substituted quinones.[27]

Reactions of *p*-Benzoquinone Derivatives with Alkoxide Ions. Upon mixing of *p*-benzoquinone (Q) with methoxide ion (MeO^-) produced by the reaction of methanol with NMe_4OH in deaerated MeCN, Q is also reduced to semiquinone radical anion ($\lambda_{max} = 422$ nm) as is the case for the reaction with OH^-. Similarly, the reactions of methoxide ion and ethoxide ion with various *p*-benzoquinone derivatives except for tetrasubstituted *p*-benzoquinone derivatives such as duroquinone (Me_4Q), *p*-chloranil (Cl_4Q), and *p*-bromanil (Br_4Q) yield the corresponding semiquinone radical anions.

The product analysis other than $Q^{\bullet -}$ was performed by ^1H NMR, when $Q^{\bullet -}$ was converted to QH_2 and Q by the disproportionation of $Q^{\bullet -}$ in the presence of perchloric acid in CD_3CN.[28] In the reaction of MeO^- (0.01 M) with Q (0.02 M), 22% of methoxy-*p*-benzoquinone, 4% of 2,5-dimethoxy-*p*-benzoquinone, and 3% of 2,6-dimethoxy-*p*-benzoquinone are formed based on the initial amount of Q. The disproportionation reaction results in formation of the same amounts of hydroquinone (36%) and of Q (36%). The stoichiometry of the reaction of MeO^- with Q before adding $HClO_4$ is thereby given by eq 2, where no oxidation of MeO^- occurs but instead a part of Q acts as an electron source to reduce the other Q to the corresponding semiquinone radical anion $Q^{\bullet -}$. Methoxide ion is converted to MeOH and methoxy-substituted *p*-benzoquinones ((MeO)Q and $(MeO)_2Q$). Thus, MeO^- acts as a strong base or nucleophile rather than as an electron source when *p*-benzoquinone itself is oxidized to the methoxy-substituted *p*-benzoquinones, (MeO)Q and $(MeO)_2Q$, in the presence of MeO^-. In such a case, the reaction mechanism for formation of $Q^{\bullet -}$ may be essentially the same as reported for the reaction of OH^- with Q in Scheme 1, which is rewritten as shown in Scheme 2.



((MeO)Q) ((MeO)₂Q) ((MeO)₂Q)

(2)

First, the addition of MeO^- to Q may produce a methoxy adduct anion, which can transfer an electron to Q to give a methoxy adduct radical and $Q^{\bullet -}$. Then, a deprotonation of the methoxy adduct radical with MeO^- gives MeOH and the methoxy-substituted semiquinone radical anion which is a stronger electron donor than $Q^{\bullet -}$ and can transfer an electron to Q to yield the methoxy-substituted quinone and $Q^{\bullet -}$. According to Scheme 2, the stoichiometry of the reaction is given by eq 3, where Q reacts with $^2/_3$ MeO^- to yield $^2/_3$ $Q^{\bullet -}$,

$$Q + {}^2/_3MeO^- \rightarrow {}^2/_3Q^{\bullet -} + {}^1/_3MeOH + {}^1/_3(MeO)Q \quad (3)$$

$^1/_3$ MeOH, and $^1/_3$ (MeO)Q. Since dimethoxy-substituted

Scheme 1

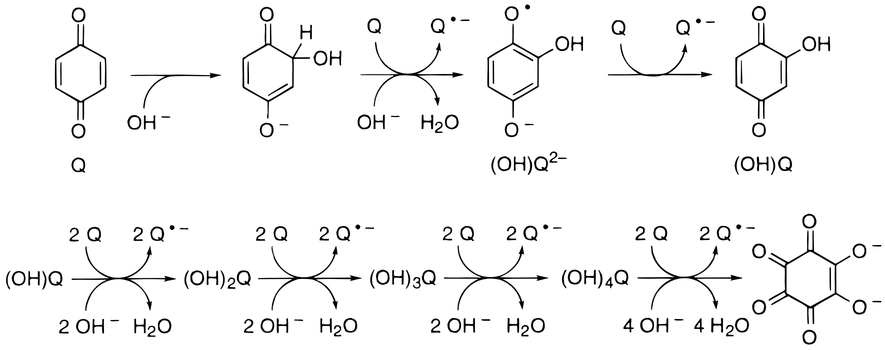
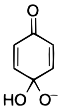
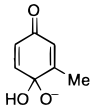
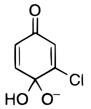
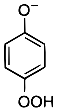
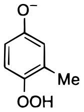
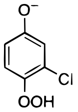
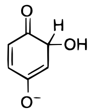
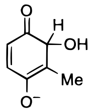
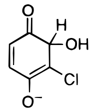
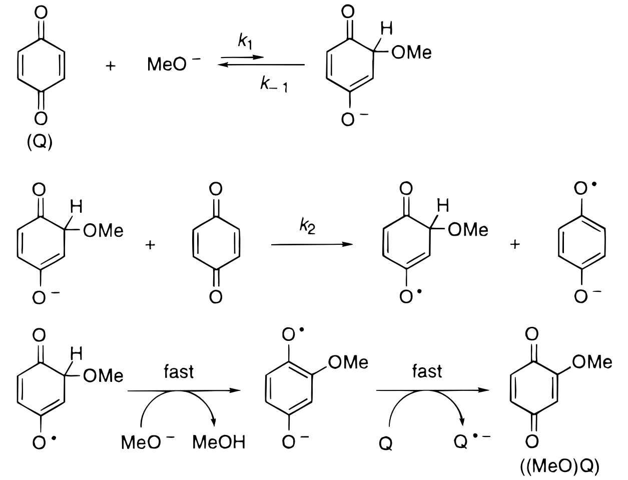


Table 3. Heats of Formation (ΔH_f, kcal mol^{-1}) of OH^- Adducts of *p*-Benzoquinones Calculated by Using the MNDO Method[a]

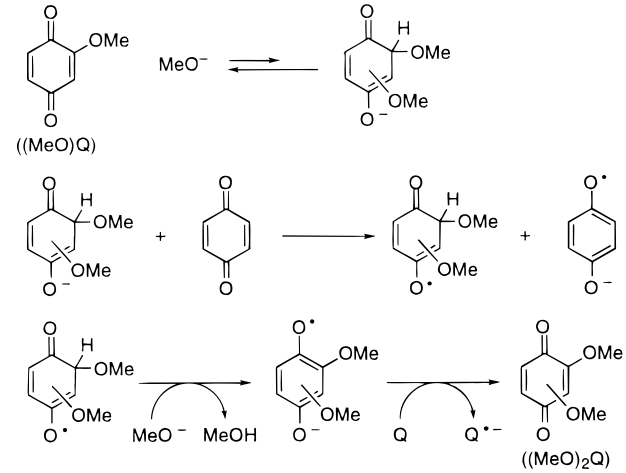
Q	ΔH_f, kcal mol^{-1}	MeQ	ΔH_f, kcal mol^{-1}	ClQ	ΔH_f, kcal mol^{-1}
	−103		−109		−115
	−72		−77		−86
	−118		−127		−134

[a] Geometrical parameters being optimized.

Scheme 2



Scheme 3



quinones are also produced in the reaction of MeO^- with Q, the reaction sequence in Scheme 2 may also hold for methoxy-substituted *p*-benzoquinone ((MeO)Q) to yield dimethoxy-substituted *p*-benzoquinones ($(MeO)_2Q$) as shown in Scheme 3. According to Scheme 3, the stoichiometry of the reaction of MeO^- with (MeO)Q and Q is given by eq 4, where (MeO)Q reacts with 2 Q and 2 MeO^- to yield 2 $Q^{\bullet -}$, MeOH, and $(MeO)_2Q$. The observed stoichiometry in eq 2 can be explained by combining eqs 3 and 4 provided that 24% of (MeO)Q undergoes the subsequent reaction in Scheme 3.[29]

$$(MeO)Q + 2Q + 2MeO^- \rightarrow 2Q^{\bullet -} + MeOH + (MeO)_2Q \tag{4}$$

There are three possible forms of the RO^- adducts of *p*-benzoquinones; the first is where RO^- is added to the carbonyl carbon of quinone, the second is on the carbonyl oxygen, and the last is on the carbon next to the carbonyl group. MO calculations with the PM3 method were performed for three possible RO^- (R = H, Me, Et, *i*-Pr, $PhCH_2$) adduct anions of Q[22] and the calculated heats of formation (ΔH_f) are listed in Table 4. In each case, the alkoxy anion adduct attached on the carbon next to the carbonyl group shown in Scheme 2 is most stable judging from the most negative ΔH_f values.

The rates of formation of semiquinone radical anion $Q^{\bullet -}$ in the reactions of RO^- (R = Me, Et, *i*-Pr) with a large excess of Q obey the pseudo-first-order kinetics and the observed pseudo-first-order rate constant (k_{obs}) increases linearly with an increase in the Q concentration as shown in Figure 2. However, when Q is replaced by methyl-*p*-benzoquinone (MeQ) and 2,6-dimethyl-*p*-benzoquinone (Me_2Q), the k_{obs} increases parabolically with increase in [MeQ] and [Me_2Q] as shown in Figure 3.

According to Scheme 2, the rate of $Me_nQ^{\bullet -}$ formation (n = 0, 1, 2) in the presence of a large excess of Me_nQ is given by eq 5, from which the pseudo-first-order rate constant k_{obs} in the presence of a large excess of Me_nQ is expressed by eq 6. The first-order dependence of k_{obs} on [Q] for the reactions of Q with

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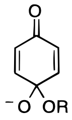
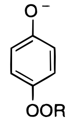
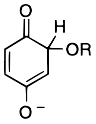
(27) (a) Hancock, J. W.; Morrell, C. E.; Rhum, D. *Tetrahedron Lett.* **1962**, 987. (b) Bishop, C. A.; Tong, L. K. J. *J. Am. Chem. Soc.* **1965**, *87*, 501.

(28) Fukuzumi, S.; Nishizawa, N.; Tanaka, T. *J. Org. Chem.* **1984**, *49*, 3571.

(29) The stoichiometry in eq 2 can be derived by eq 3 + (0.24/3) × eq 4.

Table 4. The Heats of Formation (ΔH_f) of Alkoxy Adducts of *p*-Benzoquinones Calculated by the PM3 Method

R	ΔH_f, kcal mol^{-1}		
			
H	−104	−83	−121
Me	−100	−86	−111
Et	−107	−92	−117
i-Pr	−109	−97	−123
PhCH$_2$	−78	−62	−86

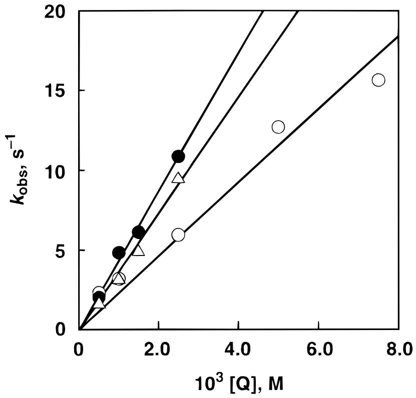


Figure 2. Dependence of the pseudo-first-order rate constant, k_{obs}, on [Q] for the reaction of Q with RO$^-$ (1.0×10^{-4} M: MeO$^-$ (○), EtO$^-$ (●), *i*-PrO$^-$ (△)) in MeCN at 298 K.

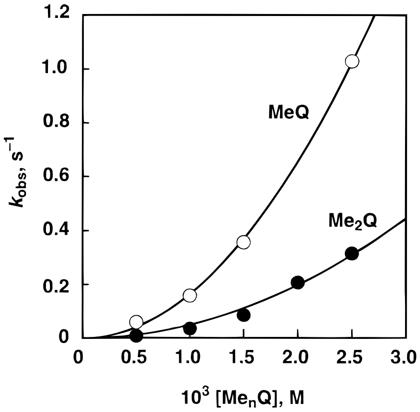


Figure 3. Dependence of the pseudo-first-order rate constant, k_{obs}, on [Me$_n$Q] (n = 1, 2) for the reaction of *i*-PrO$^-$ (1.0×10^{-4} M) with MeQ (○) and Me$_2$Q (●) in MeCN at 298 K.

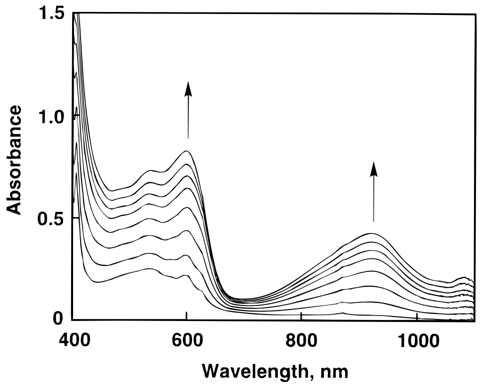


Figure 4. Visible-near-IR spectra observed after the reaction of C$_{60}$ (2.0×10^{-4} M) with MeO$^-$ (0, 3.3×10^{-5}, 6.7×10^{-5}, 1.0×10^{-4}, 1.3×10^{-4}, 1.7×10^{-4}, 2.0×10^{-4}, 2.3×10^{-4} M) in deaerated PhCN at 298 K.

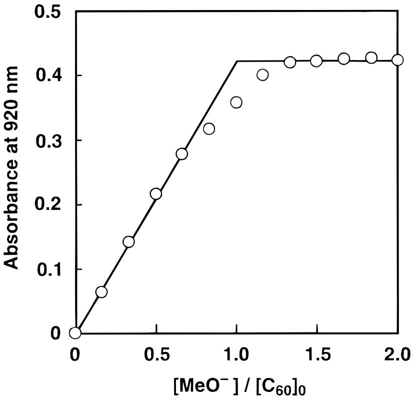


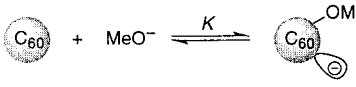
Figure 5. Plot of the absorbance at 920 nm after the reaction between C$_{60}$ and MeO$^-$ in deaerated PhCN at 298 K vs the concentration ratio of MeO$^-$ to C$_{60}$ (2.0×10^{-4} M), [MeO$^-$]/[C$_{60}$]$_0$.

$$d[\mathrm{Me}_n\mathrm{Q}^{\bullet-}]/dt = 2k_1k_2[\mathrm{Me}_n\mathrm{Q}]^2[\mathrm{RO}^-]/(k_{-1} + k_2[\mathrm{Me}_n\mathrm{Q}]) \quad (5)$$

$$k_{obs} = 2k_1k_2[\mathrm{Me}_n\mathrm{Q}]^2/(k_{-1} + k_2[\mathrm{Me}_n\mathrm{Q}]) \quad (6)$$

RO$^-$ in Figure 2 and the second-order dependence of k_{obs} on [MeQ] or [Me$_2$Q] for the reactions with MeO$^-$ in Figure 3 can be well understood by eq 6 (vide infra). In the former case, an electron transfer from the alkoxy adduct anion to Q (k_2) may be much faster than dissociation of the adduct anion to Q and RO$^-$ (k_{-1}), when the dependence of k_{obs} on [Q] should be first order as observed in Figure 2 ($k_{-1} \ll k_2$[Q], $k_{obs} = 2k_1$[Me$_n$Q]). When Q is replaced by MeQ or Me$_2$Q, which is more difficult to reduce than Q, electron transfer from methoxy adduct anion to MeQ or Me$_2$Q may be much slower than dissociation of the adduct anion and the rate of dissociation may then be enhanced by the electron-donating substituent (Me). In such a case, the dependence of k_{obs} on [Me$_n$Q] should be second order as observed in Figure 3 ($k_{-1} \gg k_2$[Q], $k_{obs} = 2k_1k_2$[Me$_n$Q]^2/k_{-1}).

Addition of MeO$^-$ to C$_{60}$. The reaction of C$_{60}$ with MeO$^-$ produced in a reaction between MeOH and tetra-*n*-butylammonium hydroxide (NBu$_4$OH) in PhCN was investigated for comparison with the reactions involving *p*-benzoquinones and RO$^-$ in MeCN. When the amount of MeO$^-$ is less than that of C$_{60}$, new absorption bands at 536, 598, and 920 nm increased upon mixing C$_{60}$ (2.0×10^{-4} M) with MeO$^-$ in deaerated PhCN at 298 K as shown in Figure 4. Under these conditions, little formation of the one-electron reduced product of C$_{60}$ (C$_{60}^{\bullet-}$) having a characteristic absorption band at 1080 nm[20] was observed. On the basis of these spectral changes, a detailed spectral titration for the reaction of C$_{60}$ with MeO$^-$ was carried out at λ = 920 nm. The result of this titration is shown in Figure 5 and indicates that the mono-methoxy adduct anion of C$_{60}$ ((MeO)C$_{60}^-$) is formed (eq 7). The formation constant (K) of (MeO)C$_{60}^-$ from C$_{60}$ and MeO$^-$ is estimated as 4.3×10^5



(7)

M^{-1} with eq 8,[30] where [MeO$^-$]$_0$ and [C$_{60}$]$_0$ are the initial

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[30] Fukuzumi, S.; Kondo, Y.; Mochizuki, S.; Tanaka, T. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1753.

$$(\alpha^{-1} - 1)^{-1} = K([\mathrm{MeO}^-]_0 - \alpha[\mathrm{C}_{60}]_0),\quad \alpha = (A - A_0)/(A_\infty - A_0) \tag{8}$$

concentrations of MeO^- and C_{60}, respectively, and *A* is the absorbance at 920 nm due to the $(MeO)C_{60}^-$. The formation of $(MeO)C_{60}^-$ was confirmed by using electrospray ionization mass spectroscopy (ESI-MS).[17,31] When a PhCN/MeCN (1:1 v/v) solution containing C_{60} (1.0×10^{-4} M) and MeO^- (4.0×10^{-4} M) was injected into the ESI-MS, a major peak due to an anionic species corresponding to $(MeO)C_{60}^-$ ($m/z = 751$) was obtained together with a small peak due to $C_{60}^{\bullet-}$ ($m/z = 720$) as shown in Figure 6. No multi-methoxy adduct species, $(MeO)_nC_{60}^{n-}$ ($n \geq 2$) were observed under these experimental conditions.[32]

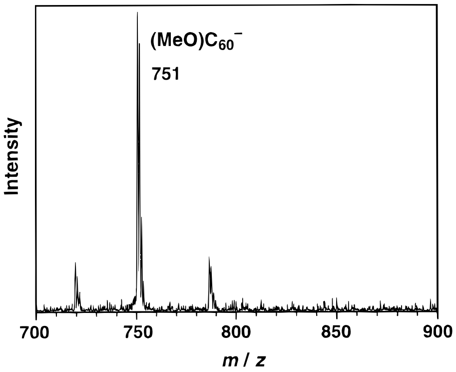

Figure 6. Negative ion ESI-MS spectrum of the reaction mixture of C_{60} (1.0×10^{-4} M) and MeO^- (4.0×10^{-4} M) in deaerated PhCN/MeCN (1:1 v/v).

Formation of $C_{60}^{\bullet-}$ in the Reaction of C_{60} with an Excess Amount of MeO^-. When an excess amount of MeO^- was mixed with the deaerated PhCN solution of C_{60}, the absorption band due to $(MeO)C_{60}^-$ was initially observed, after which a characteristic band at 1080 nm due to $C_{60}^{\bullet-}$ increased gradually, accompanied by a decrease in the band due to $(MeO)C_{60}^-$ as shown in Figure 7. The formation of $C_{60}^{\bullet-}$ was also confirmed by ESR spectroscopy after the reaction of C_{60} with an excess amount of MeO^-. A characteristic broad signal at $g = 2.0000$ is observed together with a sharp spike signal, which is always observed in the ESR spectrum of $C_{60}^{\bullet-}$.[33] In this case as well, no oxidized product of MeO^-, i.e., formaldehyde, was detected from the reaction mixture.

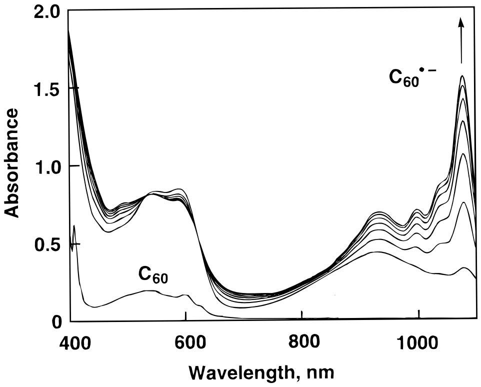

Figure 7. Spectral changes during the reaction between C_{60} (2.0×10^{-4} M) and an excess amount of MeO^- (3.0×10^{-4} M) in deaerated PhCN at 298 K. Interval 120 s.

The dependence of the initial rate of $C_{60}^{\bullet-}$ formation (R_i) on the amount of MeO^- was examined in the reaction between C_{60} and MeO^- in deaerated PhCN. This result is shown in Figure 8, where a sharp volcano-type dependence is observed. When the amount of MeO^- is less than that of C_{60}, the R_i value is nearly zero. However, the R_i value increases drastically with increase in the concentration of MeO^- and reaches a maximum at $[MeO^-]/[C_{60}]_0$ of ca. 1.7. Further increases in the amount of MeO^- result in a sharp drop of the rate. This result indicates that there is an optimum concentration of MeO^- for the formation of $C_{60}^{\bullet-}$ in the reaction of C_{60} with MeO^-.

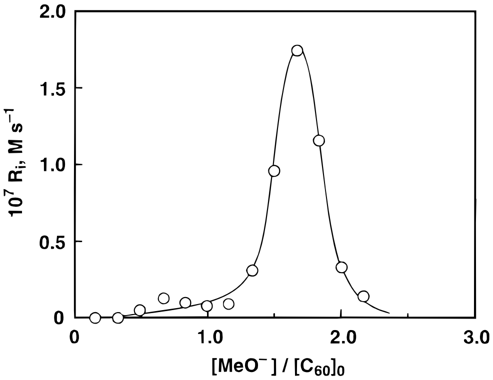

Figure 8. Plot of the initial rate (R_i) of $C_{60}^{\bullet-}$ formation vs the ratio of MeO^- concentration to the initial concentration of C_{60} in the reaction of C_{60} with MeO^- in deaerated PhCN at 298 K.

A mechanism similar to that for *p*-benzoquinone in Scheme 2 may be applied for the reaction of C_{60} with MeO^- as shown in Scheme 4, which includes the calculated heats of formation (ΔH_f) for each species with use of the PM3 semiempirical MO method. The main difference between *p*-benzoquinone and C_{60} is the large formation constant for the methoxide ion adduct of C_{60}, $(MeO)C_{60}^-$ ($K = 4.3 \times 10^5$ M^{-1}), as compared with the case of *p*-benzoquinone in Scheme 2 where the equilibrium lies far to the left. This is also consistent with the highly negative $\Delta\Delta H_f$ value (-86.9 kcal mol^{-1}) for addition of MeO^- to C_{60}.

To estimate the oxidation potential of $(MeO)C_{60}^-$, the cyclic voltammogram of $(MeO)C_{60}^-$ was measured in comparison with that of C_{60}. The addition of NBuOMe (4.0×10^{-4} M) to a deaerated PhCN solution of C_{60} (2.0×10^{-4} M) and NBu_4ClO_4 (0.10 M) results in a drastic negative shift of the oxidation peak potential from $+1.82$ V vs SCE ($C_{60}^{\bullet+}/C_{60}$)[34] to $+0.14$ V vs SCE ($(MeO)C_{60}^{\bullet}/(MeO)C_{60}^-$) at the scan rate of 100 mV s^{-1}. Thus, $(MeO)C_{60}^-$ becomes a much stronger reductant than the parent C_{60} once the methoxide ion adduct is formed. An electron transfer from $(MeO)C_{60}^-$ to C_{60} may then occur to give a methoxy adduct radical of C_{60} ($(MeO)C_{60}^{\bullet}$) and $C_{60}^{\bullet-}$. Although the electron transfer from $(MeO)C_{60}^-$ ($E^p_{ox} = 0.14$ V) to C_{60} ($E^0_{red} = -0.43$ V) is thermodynamically unfavorable as indicated by the difference in redox potentials as well as the positive $\Delta\Delta H_f$ value (33.7 kcal mol^{-1}), the follow-up reaction,

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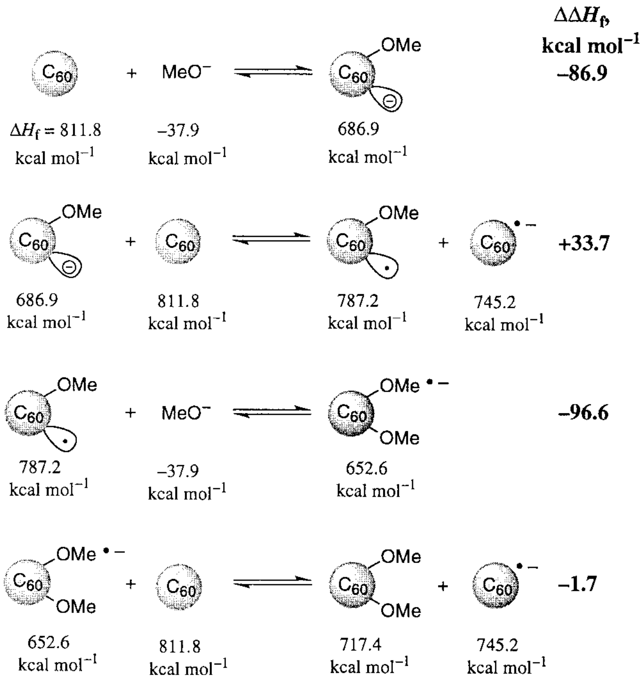
[31] (a) Fenn, J. B.; Mann, M.; Meng, C. K.; Wong, S. F.; Whitehouse, C. M. *Science* **1989**, *246*, 64. (b) Chait, B. T.; Kent, S. B. H. *Science* **1992**, *257*, 1885. (c) Loo, J. A.; Loo, R. R. O.; Light, K. J.; Edmonds, C. G.; Smith, R. D. *Anal. Chem.* **1992**, *64*, 81.

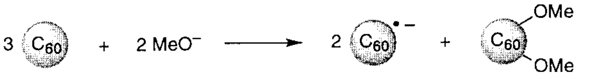
[32] Wilson et al.[9] reported that multi-methoxy adduct anions of C_{60} ($(MeO)_nC_{60}^-$, $n = 1, 3, 5, 7$) are formed in the reaction of C_{60} with large excess MeONa (270 equiv) in 1:1 toluene/methanol.

[33] (a) Allemand, P.-M.; Srdanov, G.; Koch, A.; Khemani, K.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 2780. (b) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364. (c) Stinchcombe, J.; Pénicaud, A.; Bhyrappa, P.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 5212. (d) Boulas, P.; Jones, M. T.; Kadish, K. M.; Ruoff, R. S.; Lorents, D. C.; Tse, D. S. *J. Am. Chem. Soc.* **1994**, *116*, 9393. (e) Boyd, P. D. W.; Bhyrppa, P.; Paul, P.; Stinchcombe, J.; Bolskar, R. D.; Sun, Y.; Reed, C. A. *J. Am. Chem. Soc.* **1995**, *117*, 2907. (f) Subramanian, R.; Kadish, K. M.; Vijayashree, M. N.; Gao, X.; Jones, M. T.; Miller, M. D.; Krause, K. L.; Suenobu, T.; Fukuzumi, S. *J. Phys. Chem.* **1996**, *100*, 16327.

Scheme 4



which involves addition of a second MeO$^-$ to (MeO)$C_{60}^{\bullet}$, is a largely exothermic process (ΔΔH_f = −96.6 kcal mol^{-1}) to give (MeO)$_2C_{60}^{\bullet-}$. Since (MeO)$_2C_{60}^{\bullet-}$ is a much stronger electron donor than the parent $C_{60}^{\bullet-}$, an electron transfer from (MeO)$_2C_{60}^{\bullet-}$ to C_{60} should occur to yield the dimethoxy adduct of C_{60} [(MeO)$_2C_{60}$] and $C_{60}^{\bullet-}$. The overall reaction (eq 9) is thermodynamically favorable.



(9)

The bizarre volcano-type dependence on the formation rate of $C_{60}^{\bullet-}$ with the amount of MeO$^-$ (Figure 8) can also be explained by Scheme 4 (vide infra). When the amount of MeO$^-$ is less than that of C_{60}, almost all of the MeO$^-$ anions are consumed in the reaction with C_{60} to yield (MeO)C_{60}^- and little MeO$^-$ is left to add to (MeO)$C_{60}^{\bullet}$ (the third reaction in Scheme 4). On the other hand, in the presence of excess MeO$^-$, there remains little C_{60} to be reduced by (MeO)C_{60}^- in the second step of Scheme 4. This may be the reason an optimum concentration of MeO$^-$ is required for the formation of $C_{60}^{\bullet-}$.

In conclusion, MeO$^-$ acts as a strong base or nucleophile in an aprotic solvent, which can induce the disproportionation of C_{60} as well as *p*-benzoquinone to yield the corresponding radical anion.

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