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Electron-Transfer Reactions between C_{60} and Radical Ions of Metalloporphyrins and Arenes

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Electron-transfer reactions with C_{60} leading to the singly reduced and oxidized radical ions, $C_{60}^{\bullet-}$ and $C_{60}^{\bullet+}$, have been studied by pulse radiolysis. π-Radical anions of several metalloporphyrins (tetraphenyl- and tetrapyridylporphyrins) reduced C_{60} with rate constants of $(1\text{–}3) \times 10^9$ L mol^{-1} s^{-1}, whereas metalloporphyrins which are reduced at the metal center (Ni^I, Cu^I, Cr^{II}) reacted with C_{60} somewhat more slowly, with rate constants of $(0.7\text{–}2.3) \times 10^8$ L mol^{-1} s^{-1}. $Sb^VOEP^{\bullet-}$ (octaethylporphyrin) did not reduce C_{60} ($k \leq 10^7$ L mol^{-1} s^{-1}) and $Sn^{IV}(Ph)_3(Py)P^{\bullet-}$ reacted in an equilibrium process ($K = 14$). Electron transfer from C_{60} to several aromatic radical cations (derived from naphthalene, biphenyl, *m*-terphenyl, and *trans*-stilbene) also took place rapidly ($k = (2.5\text{–}7.9) \times 10^9$ L mol^{-1} s^{-1}) to produce $C_{60}^{\bullet+}$; the radical cations of anthracene and chrysene, on the other hand, did not exhibit any significant reactivity toward C_{60}.

Introduction

C_{60} undergoes a facile one-electron reduction to yield $C_{60}^{\bullet-}$ radical anions;[2] the reduction potential is −0.44 V vs SCE in CH_2Cl_2.[3] It also undergoes one-electron oxidation to the radical cation $C_{60}^{\bullet+}$;[4–6] the ionization potential for this process is 7.6 eV.[7] One-electron reduction and oxidation of C_{60} have been achieved by electrochemical techniques[3,8] and also by radiolytic methods in solution, where C_{60} is known to react with strongly reducing and oxidizing species.[4,9–11] Pulse radiolysis studies[4,9] permitted recording of the optical absorption spectra of $C_{60}^{\bullet-}$ and $C_{60}^{\bullet+}$ at short times after the pulse and determination of the rate constants leading to the formation of these species. The respective radical ions exhibit strong absorption in the near IR with peaks at 1080 ($C_{60}^{\bullet-}$) and 980 nm ($C_{60}^{\bullet+}$). Reduction could be achieved by solvated electrons, e^-_{sol}, and $(CH_3)_2C^\bullet(OH)$ radicals in 2-propanol and toluene/acetone/2-propanol mixtures with rate constants of $\geq 10^{10}$ and 8.5×10^8 L mool^{-1} s^{-1}, respectively. Oxidation of C_{60} to yield the radical cation through radiation-generated solvent radical cations occurs generally very fast, with rate constants $\geq 10^{10}$ L mol^{-1} s^{-1} (in 1,2-dichloroethane, and dichloro- and dibromomethane, and cyclohexane as solvent). In the present study we examined electron-transfer reactions of C_{60} that have a lower driving force than those reported earlier, and which may therefore provide a quantifiable correlation between the rate constant and the free energy of the reaction. We chose to study the reduction of C_{60} by several metalloporphyrin π-radical anions and metal-reduced metalloporphyrins with wide variations in reduction potentials. In addition, we studied the oxidation of C_{60} by several aromatic π-radical cations. The capacity of C_{60} to serve as a multielectron acceptor, in general, and the moderate redox potential for the first reduction step, in particular, suggest that C_{60} might be successfully employed in solar energy conversion schemes.

Experimental Section

The porphyrins were obtained from Midcentury Chemicals, Posen, IL, with purity >99% based on optical absorption spectra, and were used as received. The following abbreviations are used for the porphyrins: TPP (tetraphenylporphyrin), TPyP (tetrapyridylporphyrin), OEP (octaethylporphyrin), MSP (mesoporphyrin-IX), and Ph_3PyP (triphenylmonopyridylporphyrin). The C_{60} was purchased from Kaesdorf (Geräte für Forschung und Industrie, München, Germany). The aromatic compounds were obtained from Aldrich Chemical Co. with ultrahigh purity. All other chemicals were of analytical grade. The solvents were generally redistilled prior to use. Stock solutions of C_{60}($(0.05\text{–}0.5) \times 10^{-3}$ mol L^{-1}), metalloporphyrin ($(0.5\text{–}1.0) \times 10^{-3}$ mol L^{-1}) and arene (0.01×10^{-3} mol L^{-1}) were freshly prepared for each set of experiments. Concentrations of C_{60} were measured by UV/vis spectrophotometry by comparison with authentic samples of known concentration and in reference to published extinction coefficients. The samples were irradiated either under air or, if oxygen had to be avoided, after purging with N_2 or N_2O for ca. 30 min. Pulse radiolysis experiments were performed with the apparatus described before, which utilizes 50-ns pulses of 2-MeV electrons from a Febetron Model 705 pulser.[12] The dose per pulse, determined by KSCN dosimetry, was varied between 7 and 40 Gy, which, in aqueous solutions, corresponds to a 4–24 μmol L^{-1} radical concentration. All experiments were carried out at ambient temperature.

Results and Discussion

One-electron transfer reactions between C_{60} and various reducing and oxidizing species were studied by pulse radiolysis. Two main series of experiments were carried out. In one series, various metalloporphyrins were reduced by a one-electron process and the resulting species subsequently reduced C_{60} to its radical anion. In the other series, aromatic π-radical cations were produced in the first instance and their reactions with C_{60}, to yield $C_{60}^{\bullet+}$, were monitored. In all cases, the reaction rate constants were determined by following the rate of decay of the reducing or oxidizing species as a function of C_{60} concentration. In several cases, the formation of the fullerene radical ions could also be measured directly by monitoring their respective absorptions in the IR region.

Electron Transfer from Metalloporphyrin π-Radical Anions to C_{60}. Metalloporphyrins were reduced by radiolysis in a solvent mixture containing 65 vol % 2-propanol, 25 vol % toluene, and 10 vol % acetone. This solvent mixture has been chosen to achieve optimal solubility for both the porphyrins and C_{60} and because it has been demonstrated previously to be very suitable for the radiolytic reduction of both C_{60}[4,9] and the porphyrin.[13] The reducing species in this solvent mixture is the radical derived from 2-PrOH by H-abstraction, i.e. $(CH_3)_2C^\bullet(OH)$. The same radical is also formed by addition of an electron to acetone and

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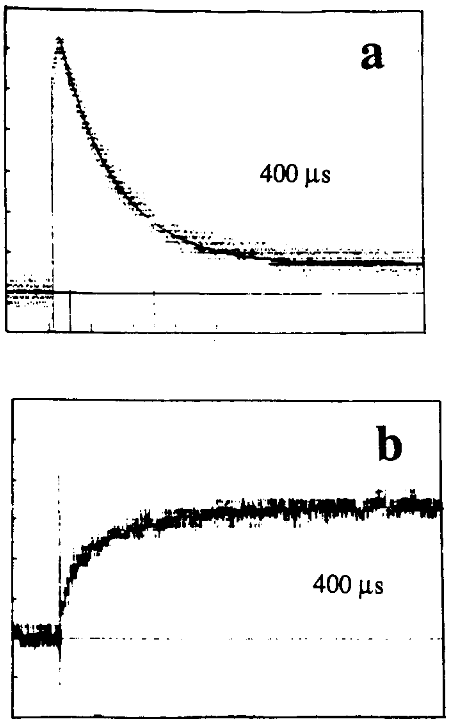


Figure 1. Kinetic traces (absorbane vs time), recorded at 720 nm (a), displaying the decay of the ZnTPP$^{\bullet-}$ and, at 970 nm (b), displaying the formation of the $C_{60}^{\bullet-}$ for a pulse-irradiated N_2 saturated solution of 1 × 10^{-4} mol L^{-1} ZnTPP and 8.0 × 10^{-6} mol L^{-1} C_{60} in 65 vol % 2-propanol, 25 vol % toluene, and 10 vol % acetone.

subsequent protonation. This radical is known to reduce a number of metalloporphyrins quite rapidly.[14] Metalloporphyrins with reduction potentials more negative than ca. −1.2 V vs SCE were found to react relatively slowly with $(CH_3)_2C^{\bullet}(OH)$. In such cases, a small concentration of the base $(CH_3)_2CHO^-/Na^+$ was added in order to ionize the $(CH_3)_2C^{\bullet}(OH)$ radical to the stronger reductant $(CH_3)_2C^{\bullet}O^-$.

Pulse irradiation of deaerated solutions containing (1–5) × 10^{-4} mol L^{-1} of certain metalloporphyrins (MP) resulted in the formation of broad absorptions in the 600–800-nm range. This absorption is ascribed to the π-radical anion, the product of reduction of the porphyrin ligand, as discussed in a number of previous studies.[14,15]

$$(CH_3)_2C^{\bullet}(OH) + MP \rightarrow (CH_3)_2CO + H^+ + MP^{\bullet-} \qquad (1)$$

$$(CH_3)_2C^{\bullet}O^- + MP \rightarrow (CH_3)_2CO + MP^{\bullet-} \qquad (2)$$

In the absence of other electron acceptors the π-radical anion decays via disproportionation and protonation

$$2\,MP^{\bullet-} + H^+ \rightarrow MPH^- + MP \qquad (3)$$

The lifetime of the π-radical anion has been shown to depend strongly on the medium and on the reduction potential of the metalloporphyrin.[15] Thus, ZnTPP$^{\bullet-}$ decayed within several milliseconds, while $Sn(Ph)_3(Py)P^{\bullet-}$ remained unchanged over this period.

Addition of various concentrations of C_{60} in the range of (0.2–5) × 10^{-5} mol L^{-1} resulted in an accelerated decay of the π-radical anion, as demonstrated in the kinetic trace of Figure 1a. The observed rate ($k_{obs} = \ln 2/t_{1/2}$) was linearly dependent (Figure 2a) on the C_{60} concentration, indicating that the underlying process has to be attributed to a reaction with C_{60}, most probably an electron transfer.

$$C_{60} + MP^{\bullet-} \rightarrow C_{60}^{\bullet-} + MP \qquad (4)$$

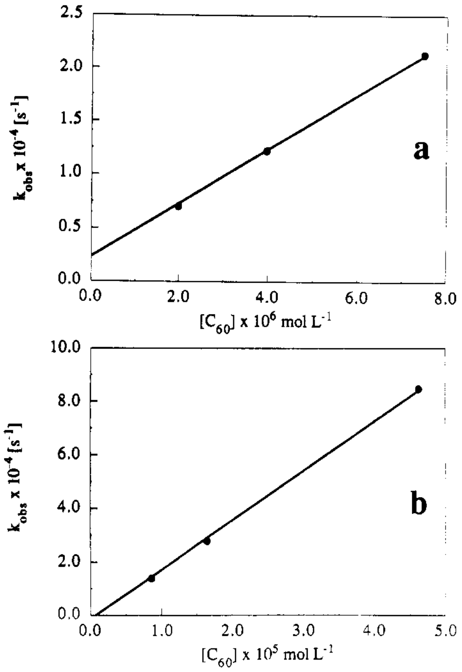


Figure 2. Plot of k_{obs} vs [C_{60}] at 720 nm (a) and 970 nm (b) for the reduction of C_{60} by ZnTPP$^{\bullet-}$ in 2-propanol/toluene/acetone solvent mixture.

TABLE 1: Rate Constants for Reduction of C_{60} by Reduced Metalloporphyrins[a]

reducing species	λ, nm	k, L mol^{-1} s^{-1}
$Zn^{II}TPP^{\bullet-}$ [b]	720	(2.6 ± 1.0) × 10^9
$Zn^{II}TPyP^{\bullet-}$	700	(1.1 ± 1.0) × 10^9
$In^{III}TPP^{\bullet-}$	700	(2.6 ± 1.0) × 10^9
$Ge^{IV}TPP^{\bullet-}$	700	(2.2 ± 1.0) × 10^9
$Al^{III}TPyP^{\bullet-}$	700	(2.0 ± 1.0) × 10^9
$Ga^{III}TPP^{\bullet-}$	720	(2.0 ± 1.0) × 10^9
$Sn^{IV}(Ph)_3(Py)P^{\bullet-}$	700	(3.2 ± 1.0) × 10^9
$Sb^{V}OEP^{\bullet-}$	700	<10^7
$Ni^{I}TPP$ [b]	500	(1.3 ± 1.0) × 10^8
$Cu^{I}TPP$ [b]	490	(2.4 ± 1.0) × 10^8
$Cr^{II}MSP$ [b]	490	(6.8 ± 2.0) × 10^7

[a] Determined by following the rate of decay of the reducing species at the wavelength indicated as a function of C_{60} concentration ((0.1–2) × 10^{-5} mol L^{-1}). [b] In the presence of 4 mmol L^{-1} $(CH_3)_2CHO^-$.

To confirm this reaction, we also monitored the formation of the characteristic $C_{60}^{\bullet-}$ absorption in the IR (λ_{max} = 1080 nm) where the MP$^{\bullet-}$ does not absorb significantly (Figure 1b). The rate of formation of the absorption at various wavelengths in the 980-1060-nm range was similar to the rate of decay of the MP$^{\bullet-}$ absorption at 650–750 nm (Figure 2b). For example, in the case of ZnTPP$^{\bullet-}$, we derived a rate constant of (2.5 ± 1.0) × 10^9 L mol^{-1} s^{-1} from the decay at 720 nm and (1.4 ± 1.0) × 10^9 L mol^{-1} s^{-1} from the formation at 970 nm. These two values are in reasonable agreement, considering the large error margins in the kinetic measurements, particularly for the weak IR signal.

The rate constants for electron transfer from various metalloporphyrin π-radical anions to C_{60} (Table 1) are found to be in the range of (1–3) × 10^9 L mol^{-1} s^{-1} in most cases studied, despite the fact that the one-electron reduction potentials for the metalloporphyrins examined cover a range of 0.55 V ($E_{ZnTPP/ZnTPP^{\bullet-}}$ = −1.35 V, $E_{Sn(Ph)_3(Py)P/Sn(Ph)_3(Py)P^{\bullet-}}$ = −0.8 V vs SCE[16]). This lack of dependence of the rate constant on the driving force for the reaction probably reflects the fact that the reduction potentials for these porphyrins are considerably more negative than that of C_{60} so that all these reactions are nearly diffusion-controlled.[17] Only in the case of $Sb^{V}OEP^{\bullet-}$ is the electron transfer to C_{60} too slow to be measured under our conditions; in this case the reduction

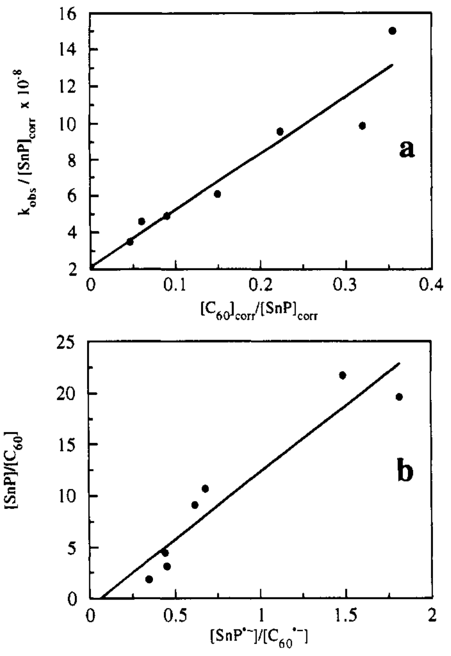


Figure 3. (a) Plot of $k_{obs}/[Sn^{IV}P]_{cor}$ vs $[C_{60}]_{cor}/[Sn^{IV}P]_{cor}$ according to eq 7, and (b) plot of $[Sn^{IV}P][C_{60}]$ vs $[Sn^{IV}P^{\bullet-}][C_{60}^{\bullet-}]$ according to eq 9.

potential of the porphyrin[18] may be very close to or possibly even slightly more positive than that of C_{60}.

Electron Transfer between Sn-Porphyrin and C_{60}. Sn^{IV}-porphyrins are very easily reduced to give long-lived π-radical anions.[15] Because their reduction potential is only slightly more negative than that of C_{60}, it was expected that the electron transfer between these two species, if sufficiently rapid as compared with the decay of the radicals, may lead to observation of equilibrium conditions.

$$Sn^{IV}P^{\bullet-} + C_{60} \rightleftarrows Sn^{IV}P + C_{60}^{\bullet-} \qquad (5)$$

Indeed, we found such an equilibrium with $Sn^{IV}(Ph)_3(Py)P$. Reduction of this porphyrin in the same solvent mixture as above and after addition of 10 vol % pyridine (for the reasoning of this addition see below) resulted in formation of the π-radical anion with absorption in the 700–800-nm range. Upon addition of various C_{60} concentrations, the rate of decay of this π-radical anion increased linearly with $[C_{60}]$, as found with the other metalloporphyrins. However, the rate of decay was also found to increase upon raising the porphyrin concentration at constant $[C_{60}]$. Such a dependence of the rate of reaction upon both concentrations is indicative of an equilibrium process as formulated in reaction 5. To confirm this equilibrium process and to determine the equilibrium constant, we measured the rate constant with a series of different $Sn^{IV}P$ and C_{60} concentrations. The results show the linear dependence as expected from eqs 7 and 9.

$$k_{obs} = k_5[C_{60}] + k_{-5}[Sn^{IV}P] \qquad (6)$$

$$k_{obs}/[Sn^{IV}P]_{cor} = k_5[C_{60}]_{cor}/[Sn^{IV}P]_{cor} + k_{-5} \qquad (7)$$

$$K_5 = k_5/k_{-5} \qquad (8)$$

$$K_5 = [Sn^{IV}P]/[C_{60}] \times [C_{60}^{\bullet-}]/[Sn^{IV}P^{\bullet-}] \qquad (9)$$

(The concentrations of $Sn^{IV}P$ and C_{60} were corrected for the respective fractions that were converted into radicals.) The kinetic plot (Figure 3a) gives $k_5 = 3.2 \times 10^9$, $k_{-5} = 2.1 \times 10^8$ L mol^{-1} s^{-1}, and $K = 15$. In good agreement with this figure, the absorbance plot (Figure 3b) gives $K = 13$. Thus the average equilibrium constant from these plots is $K_5 = 14 \pm 3$, and the reduction potential of this tin porphyrin in this solvent mixture, calculated from this number (eq 10), is 64 mV more negative than that of C_{60}.

$$\Delta G = -nFE = -RT\ln K \qquad (10)$$

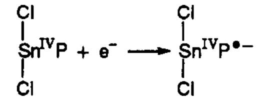
Using the Marcus equations,[19] a value of $\Delta G^{\ddagger} = 8.5$ kJ mol^{-1} for the free energy of activation is derived from the rate constant k_5. From this value and the free energy of the reaction, $\Delta G^0 = -RT\ln K = -6.1$ kJ mol^{-1}, a solvent reorganization energy $\lambda = 47$ kJ mol^{-1} can be calculated via eq 11a. Another possibility to

$$\Delta G^{\ddagger} = \frac{(\Delta G^0 + \lambda)^2}{4\lambda} \qquad (11a)$$

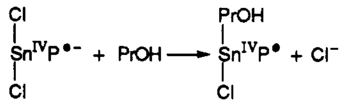
$$\lambda = \left(\frac{1}{2r_1} + \frac{1}{2r_2} + \frac{1}{r_{12}}\right)\left(\frac{1}{n^2} - \frac{1}{\epsilon}\right)(\Delta ze)^2 \qquad (11b)$$

evaluate λ is based on eq 11b (n = refractive index; ϵ = dielectric constant). If we take the diameter of C_{60} ($2r_1 = 7.1$ Å) and the diameter of the porphyrin *planar* π-system ($2r_2 = 8$ Å), we calculate a solvent reorganization energy of 87 kJ mol^{-1} for 2-PrOH, 90 kJ mol^{-1} for acetone, and 4.8 kJ mol^{-1} for toluene. Although the solvent mixture contains only 25% toluene, the reaction between the porphyrin π-radical anion and C_{60} may be viewed as a reaction between one species solvated predominantly by 2-PrOH (MP) and another solvated predominantly by toluene (C_{60}). It is noted that the reorganization energy calculated from the rate constant is nearly the average between the values calculated from the reactant radii and solvent parameters for these two solvents.

Without the addition of pyridine, the spectrum of the initially formed $Sn^{IV}P^{\bullet-}$ changed over 1 ms in a process that can be ascribed to ligand exchange.[20] The original tin porphyrin was in the dichloro form, and the reduced species apparently exchanges a Cl^- for a 2-PrOH molecule from the solvent mixture.

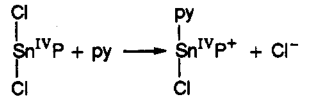


$$\overset{Cl}{\underset{Cl}{Sn^{IV}P}} + e^- \longrightarrow \overset{Cl}{\underset{Cl}{Sn^{IV}P^{\bullet-}}} \qquad (12)$$



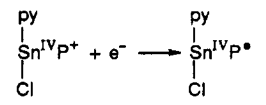
$$\overset{Cl}{\underset{Cl}{Sn^{IV}P^{\bullet-}}} + PrOH \longrightarrow \overset{PrOH}{\underset{Cl}{Sn^{IV}P^{\bullet}}} + Cl^- \qquad (13)$$

To confirm this assignment, we added up to 10 vol % pyridine to the solution to replace the Cl^- axial ligands by pyridine. The absorption peaks of the porphyrin were slightly blue-shifted upon addition of pyridine, indicating that Cl^- ligands were at least partially replaced with the more strongly coordinating pyridine, e.g.,



$$\overset{Cl}{\underset{Cl}{Sn^{IV}P}} + py \longrightarrow \overset{py}{\underset{Cl}{Sn^{IV}P^{+}}} + Cl^- \qquad (14)$$

The radiolysis of $Sn^{IV}P$ in this solvent mixture resulted in reduction of the porphyrin to the π-radical anion (eq 15), with no subsequent spectral changes on the time scale of the pulse radiolysis.



$$\overset{py}{\underset{Cl}{Sn^{IV}P^{+}}} + e^- \longrightarrow \overset{py}{\underset{Cl}{Sn^{IV}P^{\bullet}}} \qquad (15)$$

Electron Transfer from Metalloporphyrins at Low Oxidation States to C_{60}. One-electron reduction of $Cr^{III}MSP$, $Ni^{II}TPP$, and $Cu^{II}TPP$ (under the same experimental conditions as above)

TABLE 2: Rate Constants for Oxidation of C_{60} by Aromatic π-Radical Cations[a]

oxidizing species	IP, eV	λ, nm	k, L mol^{-1} s^{-1}
naphtalene	8.14	400	$(2.5 \pm 1.0) \times 10^9$
m-terphenyl	8.01	410	$(3.8 \pm 2.0) \times 10^9$
biphenyl	7.95	400	$(7.9 \pm 2.0) \times 10^9$
trans-stilbene	7.7	490	$(6.8 \pm 2.0) \times 10^9$
chrysene	7.59	400	$\leq 1 \times 10^9$
anthracene	7.45	430	$\leq 1 \times 10^9$

[a] Determined by following the rate of decay of the oxidizing species at the wavelength indicated as a function of C_{60} concentration ($(0.7-6) \times 10^{-5}$ mol L^{-1}).

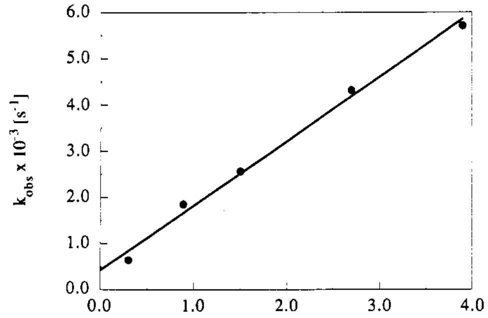


Figure 4. Plot of k_{obs} vs $[C_{60}]$ at 500 nm for the reduction of C_{60} by Ni^{I}TPP in 2-propanol/toluene/acetone solvent mixture.

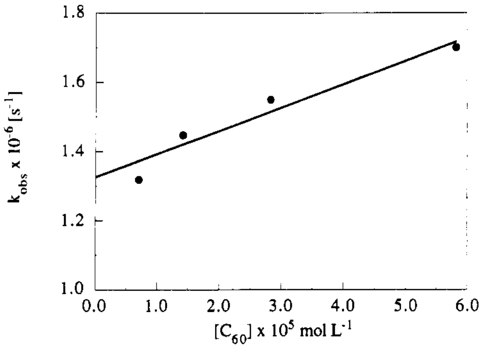


Figure 5. Plot of k_{obs} vs $[C_{60}]$ at 410 nm for the oxidation of C_{60} by (terphenyl)$^{\bullet+}$ in dichloromethane.

is known to occur at the metal center to yield Cr^{II}MSP, Ni^{I}TPP, and Cu^{I}TPP.[21] This reduction path results in only minor spectral changes and lacks, in particular, the intense absorption in the 600–800-nm range. The decay of these species upon reaction with C_{60} was monitored in the 500-nm range, where the reduced metalloporphyrin absorbs more intensely than the parent compound. The rate constants for these reactions (Table 1) were derived from the linear dependence of the decay rate upon C_{60} concentration (Figure 4).

$$\mathrm{Cr^{II}MSP} + C_{60} \rightarrow \mathrm{Cr^{III}MSP} + C_{60}^{\bullet-} \qquad (16)$$

These rate constants are substantially lower than those measured for the reduction by the π-radical anions (reaction 4) despite the similarity in the reduction potentials ($E_{\mathrm{Cr^{III}MSP/Cr^{II}MSP}} = -1.14$ V, $E_{\mathrm{Ni^{II}TPP/Ni^{I}TPP}} = -1.18$ V, $E_{\mathrm{Cu^{II}TPP/Cu^{I}TPP}} = -1.2$ V vs SCE[16]). Possibly, the small size of the reactive metal center, vs the large size of that in the porphyrin π-radical anions, i.e. geometric constraints, may be the cause for the decreased rate constants.

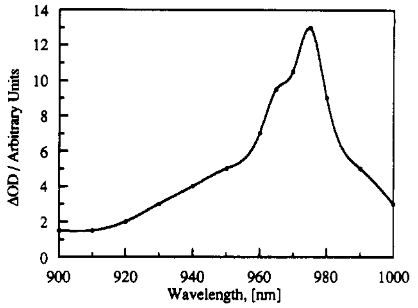


Figure 6. IR spectrum of the $C_{60}^{\bullet+}$ radical cation, recorded ~5 μs after the pulse, following oxidation of C_{60} by (terphenyl)$^{\bullet+}$ in dichloromethane solution containing 0.01 mol L^{-1} *m*-terphenyl and 3.8×10^{-5} mol L^{-1} C_{60}.

One-Electron Oxidation of C_{60} by Aromatic π-Radical Cations. Oxidative electron transfer from C_{60} to various organic radical cations was studied in CH_2Cl_2 as solvent. Radiolysis of this solvent, and other halogenated solvents, is known to lead to oxidation of many organic compounds.[22-24] Several studies have been carried out with aromatic hydrocarbons for which the formation of the arene π-radical cations has been demonstrated.[22,23] For example,

$$CH_2Cl_2^{\bullet+} + \text{terphenyl} \rightarrow CH_2Cl_2 + \text{terphenyl}^{\bullet+} \qquad (17)$$

To study the electron transfer from C_{60} to the terphenyl radical cation, i.e.

$$\text{terphenyl}^{\bullet+} + C_{60} \rightarrow \text{terphenyl} + C_{60}^{\bullet+} \qquad (18)$$

we irradiated CH_2Cl_2 solutions containing 10^{-2} mol L^{-1} of terphenyl in the presence of various C_{60} concentrations, $(0.7-6) \times 10^{-5}$ mol L^{-1}. Similar experiments were conducted with several other arenes. The respective arene radical cations exhibited quite different lifetimes; some of them decayed within several microseconds, which restricted the ability to measure their reaction with C_{60}. In a number of cases, however, the addition of C_{60} resulted in a measurable increase of the first-order decay rate, showing a linear dependence on the C_{60} concentration. To confirm the formation of $C_{60}^{\bullet+}$ in reaction 17 and analogous processes with other arenes, we measured its absorption in the near-IR region ($\lambda_{max} = 980$ nm[4,6,9]). The differential absorption spectrum recorded with a CH_2Cl_2 solution containing 10^{-2} mol L^{-1} *m*-terphenyl and 2×10^{-5} mol L^{-1} C_{60}, about 5 μs after the pulse (Figure 6), is in good agreement with that found upon direct oxidation of C_{60} in various halogenated hydrocarbons.[7] The kinetic traces in the IR region did not permit determination of exact rate constants for the formation of $C_{60}^{\bullet+}$ because the signals were too weak. It was clear, however, that the time scale for the formation of $C_{60}^{\bullet+}$ monitored in the IR region was similar to that of the decay of the (arene)$^{\bullet+}$ monitored in the visible region.

The rate constants measured for the different arenes are summarized in Table 2. Among the compounds studied, only biphenyl has been shown to oxidize C_{60} in an earlier photooxidation study.[6] The rate constant for this reaction, 7.9×10^9 L mol^{-1} s^{-1}, is close to the diffusion-controlled limit (in CH_2Cl_2 the calculated value is $k_{diff} = 1.3 \times 10^{10}$ L mol^{-1} s^{-1}). The rate constants for *trans*-stilbene, *m*-terphenyl, and naphthalene vary between 2.5 $\times 10^9$ and 6.8×10^9 L mol^{-1} s^{-1}, and the variations show little correlation with the ionization potentials of these compounds. The reactions between C_{60} and the radical cations of chrysene and anthracene could not be observed under our pulse radiolysis conditions. These reactions probably do not take place since the ionization potentials for these arenes are lower than that of C_{60}.

Conclusion

In conclusion, C_{60} undergoes one-electron reduction and oxidation by π-radical anions and cations, respectively, with rate constants that are very close to the diffusion-controlled limit, even when the driving force for the reaction (the difference in reduction potentials) is relatively small. This suggests a very high self-exchange rate between C_{60} and its radical ions, probably due to the high degree of delocalization of the unpaired electron and the unchanged geometry upon electron transfer. Reducing species which are not delocalized π-radical anions, such as the low oxidation state metalloporphyrins, reacted with C_{60} somewhat more slowly.

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