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Rate Correlation of Photoinduced Electron Transfer to C_{70}

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Quenching rate constants (k_q) of triplet C_{70} by electron donors have been measured by laser flash spectroscopy in benzonitrile and in acetonitrile-benzene (1:4). A plot of k_q values versus free energy change for the electron transfer to $^3C_{70}$ gives a fairly good correlation with rate constants calculated from the Rehm-Weller equation if corrected the diffusion-controlled rates in solvents used.

Photoinduced electron transfers encompass a wide range of processes that are of great importance in chemistry and biology. Extensively studied are electron transfers from various donors to excited aromatic hydrocarbons and ketones.1) Recent interest in fullerenes such as C_{60} and C_{70}2) includes the redox reactions because of their low reduction potentials.3) The formation of C_{60} anion radical and N,N-dimethylaniline cation radical was observed by irradiating the charge transfer complex using a femtosecond laser spectrometer.4) Production of C_{60} radical cation by a photosensitized one electron oxidation has also been reported.5) Recently, Foote et al. have shown that the rate constants of electron transfer from amines to triplet C_{60} are represented as a function of the free energy change (ΔG_0) of the electron transfer.6)

We were interested in the kinetic behavior of photoinduced electron transfers of fullerenes and determined the one-electron transfer rates from donors to triplet C_{60} and C_{70}. Recent communication on the electron transfer to triplet C_{60}6,7) led us to report our kinetic results on the electron transfer to triplet C_{70}. Studies on photoinduced electron-transfer rates are important in exploring the kinetic behavior of excited states of various fullerenes. In particular, the comparison of C_{70} with C_{60} is interesting in order to see the effect of shapes, spheroidal and sphere, on the electron transfer rates. Herein, we wish to report a kinetic study on electron transfers to triplet C_{70}, revealing a good correlation with the Rehm-Weller equation.8)

C_{70} sample was prepared by the method described before.9) Laser flash photolysis (Nd:YAG, 355 nm, 10 ns) of C_{70} in de-oxygenated benzonitrile showed, immediately after the laser pulse, a transient absorption spectrum with λ_{max} of 400 nm assignable to $^3C_{70}$ reported as the T-T absorption in benzene.10) Then, solutions of C_{70} and appropriate donors were irradiated in benzonitrile or in acetonitrile/benzene (1:4) under argon. Typically, the flash photolysis of C_{70} (0.05 mM) and diphenylamine (DPA; 1.5 mM) in benzonitrile showed rapid decay of the absorption of $^3C_{70}$ (λ_{max} = 400 nm) and formation of DPA radical cation (680 nm).[11] Formation of other aromatic amine radical cations was similarly detected in comparison to the reported spectra.[12] It is apparent that the electron transfer quenching of $^3C_{70}$ is quite general for these donors. The second order rate constants (kq) for the quenching of $^3C_{70}$ by various amines were determined from the decay kinetics of $^3C_{70}$ and are summarized in Table 1.

The free energy change for electron transfer from donor D to electron acceptor A is calculated from Eq. 1.[8]

$$\Delta G_0\ (\mathrm{kJ\ mol^{-1}}) = 96.5\ [\ E(D^+/D) - E(A^-/A) - \Delta E_{0,0} - e_0^2/a\varepsilon\ ] \qquad (1)$$

Here, the oxidation potential (E(D$^+$/D)) is $E_{1/2}^{ox}$ and reduction potential E(A$^-$/A) is -0.51 V,[14] the excitation energy of $^3C_{70}$ ($\Delta E_{0,0}$) is 1.53 V[15] and the $e_0^2/a\varepsilon$ value is 0.085 V in benzonitrile.[14] In Table 1 are listed the $E_{1/2}^{ox}$ values of donors and the resulting ΔG_0 values for the electron transfer to $^3C_{70}$.

Table 1. Half-Peak Oxidation Potentials ($E_{1/2}^{ox}$), Free Energy Changes for Electron Transfer (ΔG_0), and Quenching Rate Constants (k_q) of $^3C_{70}$ by Electron Donors in Benzonitrile and in Acetonitrile-Benzene (1:4)

Electron donor	$E_{1/2}^{ox}$ a) V vs. SCE	ΔG_0 b) V vs. SCE	ΔG_0 b) kJ mol^{-1}	$k_q / 10^9\ M^{-1}\ s^{-1}$ c) in PhCN	$k_q / 10^9\ M^{-1}\ s^{-1}$ c) in MeCN-PhH (1:4)
Tetramethylphenylenediamine	0.14	-0.97	-93.1	5.1	4.3
N,N-Diethylaniline	0.64	-0.47	-44.9	7.1	
N,N-Dimethylaniline	0.71	-0.40	-38.1	4.8	
Diphenylamine	0.84	-0.27	-25.6	3.5	
Triphenylamine	0.85	-0.26	-24.6	1.4	0.65
Triethylamine	0.96	-0.15	-14.0	0.95	
Aniline	0.98	-0.13	-12.1	0.15	
Dibutylamine	1.17	0.065	6.3	0.10	0.025
Pyrrole	1.20 d)	0.095	9.2	0.000 0061	
Dipropylamine	1.23	0.13	12.1	0.089	
Diethylamine	1.31	0.21	19.8	0.11	
Dibenzylamine	1.36	0.26	24.6	0.019	0.0045
Pyrene	1.36	0.26	24.6	0.00012	

a) The oxidation potentials are the reported values in CH_3CN. Ref. 6. b) Calculated from Eq. 1 using the values in the Text. c) Observed quenching rate constants, M = mol dm^{-3}. The probable errors were in the range of ± 10 %. d) See, Ref. 13.

The plot of k_q values vs. ΔG_0 is shown in Fig. 1, where the solid line is the calculated rate curve from the Rehm-Weller equation.[8] As shown, the k_q values seem to give qualitatively a good correlation with the equation. However, the k_q values at $\Delta G_0 < -20$ kJ mol^{-1} are significantly smaller compared with the Rehm-Weller rate in acetonitrile, i.e., the diffusion rate constant of 2×10^{10} M^{-1} s^{-1}. The diffusion rate constant in benzonitrile can be estimated from the Stokes-Einstein equation to be $\approx 5.6 \times 10^9$ M^{-1} s^{-1},[16] and the dotted line in Fig. 1 was calculated from the Rehm-Weller equation using the diffusion rate constant of 5.6×10^9 M^{-1} s^{-1}, affording a fairly good correlation as shown.

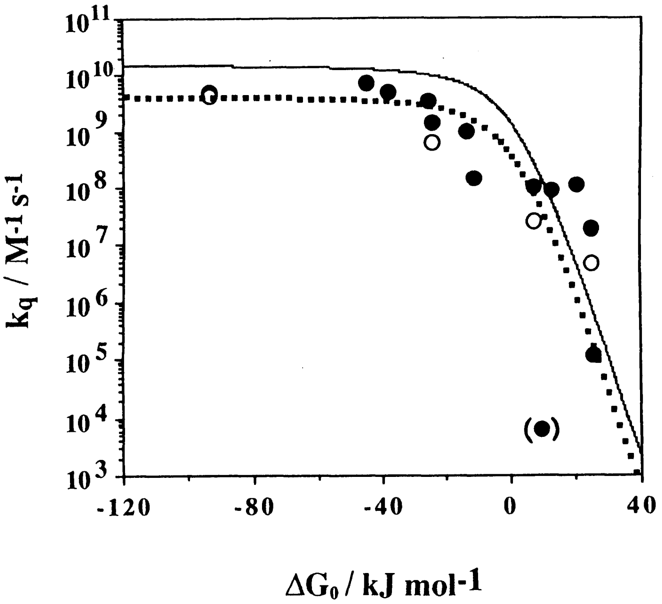

Fig. 1. Correlation of quenching rate constants (k_q) of triplet C_{70} by donors with free energy changes (ΔG_0) for the electron transfer, see Table 1 for rate constants; ●: kq in benzonitrile,○: kq in acetonitrile-benzene (1:4). The solid line was calculated from the Rehm-Weller equation,[8] and the dotted line was calculated using the diffusion rate constant of 5.6×10^9 M^{-1} s^{-1} in benzonitrile. For the ΔG_0 value of pyrrole (i. e., (●)), see Ref. 13.

The k_q values for $^3C_{70}$ are thus shown to be correlated with the Rehm-Weller equation and are practically identical to those for triplet C_{60}.[6,7] It has been reported that the photophysical properties of C_{70} resemble those of C_{60} but differ in some respects;[10,17] for example, a weak fluorescence can be observed from photoexcited C_{70} and the lifetime of $^3C_{70}$ ($\tau_T \approx 130$ µs) is longer than that of $^3C_{60}$ ($\tau_T \approx 40$ µs). However, thermodynamic factors of C_{70} for photo-induced electron transfers are similar to those of C_{60}, that is, the triplet energy and reduction potential of 1.53 V and -0.33 V vs. Ag/AgCl are practically the same with those of C_{60}.[3,6,15] The present quenching study on $^3C_{70}$ revealed again that the kinetic behavior was quite similar to that of $^3C_{60}$.

To investigate the solvent effect, the laser flash photolysis of C_{70} in the presence of representative amines was carried out in acetonitrile/benzene (1:4).[18] As shown in Table 1, the quenching rates in the mixed solvent were significantly small in comparison with those in benzonitrile. Since the viscosity of the mixed solvent (i.e., $\eta = 0.59$ m Pa s) is lower than that of benzonitrile (1.4 m Pa s),[19] it is apparent that the quenching rates are not controlled by diffusion rates or solvent viscosities. The much lower rates in the less polar mixed solvent (dielectric constant $\varepsilon = 9.3$) than those in benzonitrile ($\varepsilon = 25.2$) suggest the importance of polar effect of solvents for the electron transfer to $^3C_{70}$.

In conclusion, the present study revealed that $^3C_{70}$ can accept, in spite of significant difference in shape and photophysical properties, one-electron from donors just as $^3C_{60}$. The result seems to suggest that the electron transfer rates of fullerenes generally depend on the free energy changes as the case for other organic compounds.

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14) The reduction potential of C_{70} is practically the same with that of C_{60}, 3) hence, -0.51 V vs. SCE in acetonitrile is used. 6) The value for $e_0^2/a\varepsilon$ in benzonitrile is 0.085 eV, Ref. 6.

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