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Kinetic studies of the photochemical reaction of C_{60} with amine in solution

Keizo Takeda [a], Yoshizumi Kajii [b], Kazuhiko Shibuya [a]

[a] *Department of Chemistry, Tokyo Institute of Technology, 2-12-1 Ohokayama, Meguro, Tokyo 152, Japan*

[b] *Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro, Tokyo 153, Japan*

Abstract

The photochemical reactions of C_{60} with solvated electrons and triethylamine (TEA) were studied by a nanosecond transient absorption method. Transient solvated electrons (e_s^-) were prepared by the 308 nm laser photoionization of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD). The removal rate constant of e_s^- was determined to be $(2.6 \pm 0.4) \times 10^9$ M^{-1} s^{-1} in a mixed solvent consisting of 2-propanol and benzene. The electron capture by C_{60} is responsible for the removal process. The C_{60} molecule in the S_1 state reacts with triethylamine with a rate constant of $(3.3 \pm 0.3) \times 10^9$ M^{-1} s^{-1} to form an exciplex, which generates a stable product.

Keywords: Kinetic studies; Fullerenes; Amines

1. Introduction

Since the discovery of C_{60}, special attention has been paid to its photoinduced reactions, such as charge transfer (CT), electron transfer and energy transfer, because of its unique photochemical and photophysical properties. The quenching rate constants of C_{60} in the triplet state by several amines have been determined [1–4]. The quenching process of C_{60} in the triplet state in polar solvents is explained in terms of electron transfer [1], since a fairly good correlation between the experimental quenching rates and the rates calculated from the Rehm–Weller equation is demonstrated. Fullerenes of C_{60} and C_{70} in the ground state form CT-type complexes with several amines. The photodynamic properties of these CT-type complexes have been investigated [5–8]. The photoexcitation of the CT complex leads to the formation of a geminate ion pair which recombines rapidly within picoseconds. Recently, Park et al. [9] have reported the photoinduced electron transfer from *N,N*-dimethylaniline and 4,4′-methylenebis(*N,N*-dimethylaniline) to C_{60}.

In this paper, we report the reaction of C_{60} with solvated electrons, prepared by the photoionization of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) in a polar solvent, to demonstrate the fundamental electron transfer process from an electron donor to C_{60}. The photoexcitation of C_{60} in the presence of triethylamine (TEA) in toluene was found to give a stable photoproduct [10]. We have investigated the mechanism of this photochemical reaction in more detail by laser flash photolysis and product analysis.

2. Experimental details

Transient absorption spectra were obtained from excimer laser flash photolysis experiments described in detail elsewhere [11]. Briefly, a 308 nm XeCl excimer laser (Lambda Physik LPX 105) was used as a light source. An Xe flash lamp and the excimer laser were fired synchronously. A monochromator/photomultiplier combination was used to observe the transient absorption spectra with a spectral resolution of 2 nm. Transient spectra were measured by digital memory (Iwatsu DM901) on-line with a personal computer and were averaged over a few tens of shots. A flow cuvette was used to avoid the influence of photoproducts. The C_{60}–TMPD solution was thoroughly degassed by freeze–pump–thaw cycling on a vacuum line. The steady state photolysis was performed using a 150 W Xe continuous wave lamp with a combination of cut-off (Toshiba UV300) and water filters to eliminate light in the UV and IR regions. Absorption spectra were measured by a spectrophotometer (Shimadzu UV2200).

The C_{60} sample was purchased from MER and purified by high performance liquid chromatography (HPLC) (model LC-908 with JAIGEL 1H, 2H, Japan Analytical Industry Co.). Toluene, benzene and 2-propanol (Cica Merck, GR)

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were used without further purification. TEA (Kanto, thin layer chromatography (TLC) grade) was distilled in a high vacuum line, and TMPD (Aldrich) was purified by recrystallization in *n*-hexane. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Electron attachment from solvated electron to C_{60}

The photoejection of an electron from TMPD in polar solvents has been examined extensively by many researchers. Photoexcitation of TMPD causes ionization, yielding a geminate electron–ion pair ($TMPD^+$–e^-), which undergoes rapid recombination to recover to the ground state of TMPD. A certain number of ion–electron pairs escape recombination and are separated into the free cation ($TMPD^+$), and a solvated electron (e_s^-) [12,13]. As a result, the transient solvated electron can be prepared together with $TMPD^+$ and TMPD in the triplet state ($^3TMPD^*$). Both $TMPD^+$ and $^3TMPD^*$ absorb light at wavelengths shorter than approximately 600 nm, but do not interfere with the analysis of the decay of e_s^- monitored at wavelengths longer than 650 nm.

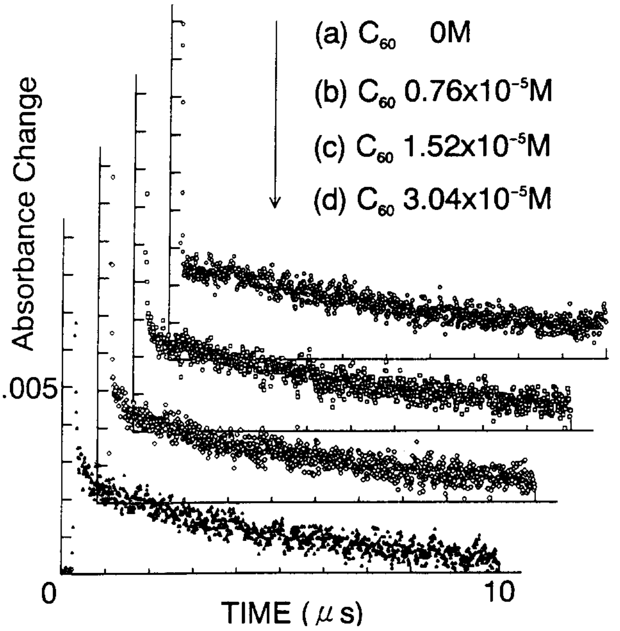


Fig. 1. Time evolution of the transient absorption of the TMPD–C_{60} ([TMPD] = 1.0 M; [C_{60}] = 1.92×10^{-5} M) system in a mixed solvent of 2-propanol and benzene (9:1).

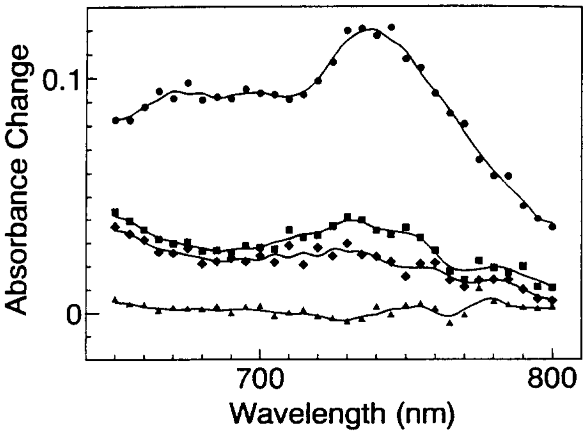
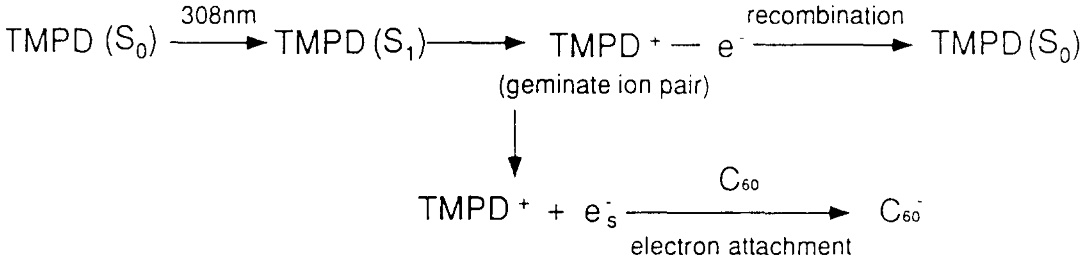


Fig. 2. Transient absorption spectra of the TMPD–C_{60} system. Measured at 0 ns (●), 100 ns (■), 200 ns (◆) and 9.0 μs (▲) after 308 nm excitation.

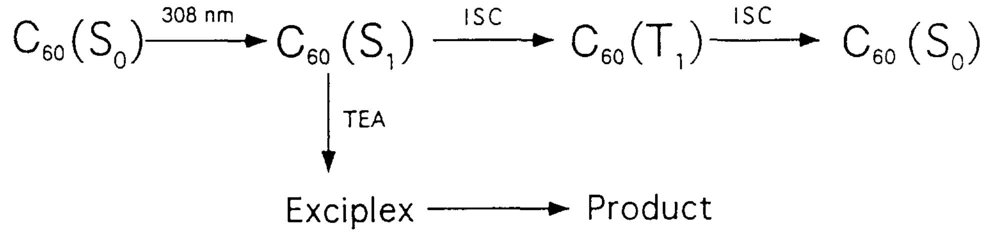
Trace (a) in Fig. 1 shows the time evolution of the transient absorption measured at 690 nm during the 308 nm photoionization of TMPD in the absence of C_{60}. This decay curve has two distinct components: one decays very rapidly within the laser duration (approximately 20 ns), and the other decays exponentially with a lifetime of 8.1 μs. The faster component is attributed to the decay of $TMPD^+$–e^-. The slower component is due to the decay of e_s^-. Fig. 1 also shows the temporal profiles during the photoionization of TMPD measured at several C_{60} concentrations: (b) 0.76×10^{-5} M; (c) 1.52×10^{-5} M; (d) 3.04×10^{-5} M. In these decay curves, a third decaying component with a lifetime of approximately 300 ns appears immediately after geminate recombination.

To assign the species responsible for this third component, the transient absorption spectra were measured for the TMPD–C_{60} system (Fig. 2). A broad peak can be recognized at 750 nm in addition to the broad absorption band due to $TMPD^+$–e^-. Both C_{60} and TMPD absorb 308 nm light, and XeCl laser excitation generates both the triplet state of C_{60} and $TMPD^+$–e^-. Since the triplet–triplet (T–T) absorption of C_{60} in benzene has a peak at 750 nm [14], the transient absorption spectrum (delay time, 0 ns) obtained immediately after laser excitation of the C_{60}–TMPD system is considered to be due to the superposition of the spectra of $TMPD^+$–e^- and C_{60} in the triplet state. The triplet state of C_{60} in this system decays with a lifetime of approximately 300 ns (see Fig. 1), which is much shorter than that in benzene [14]. TMPD has been reported to quench C_{60} in the triplet state at diffusion-controlled rates in benzonitrile [1]. The effective quenching of C_{60} in the triplet state by TMPD accounts for the short lifetime of C_{60} in the triplet state observed in this study.

As shown in Fig. 1, the decay rate of the solvated electron is accelerated by increasing the C_{60} concentration, which implies that the solvated electron may react with C_{60} in the ground state. The decay rates measured at several concentrations of C_{60} are plotted in Fig. 3, which exhibits a straight line. Hence the reaction rate constant of the transient solvated electron with C_{60} can be determined to be $(2.6 \pm 0.4) \times 10^9$ M^{-1} s^{-1}. This large rate constant suggests that the reaction between the solvated electron and C_{60} is a diffusion-controlled process. Judging from the large electron affinity of C_{60}, it is probable that this reaction may be electron attachment from the solvated electron to C_{60}. Scheme I summarizes the overall reaction mechanism discussed above.



Scheme I. Reaction scheme of the C_{60}–TMPD system.



Scheme II. Reaction scheme of the C_{60}–TEA system.

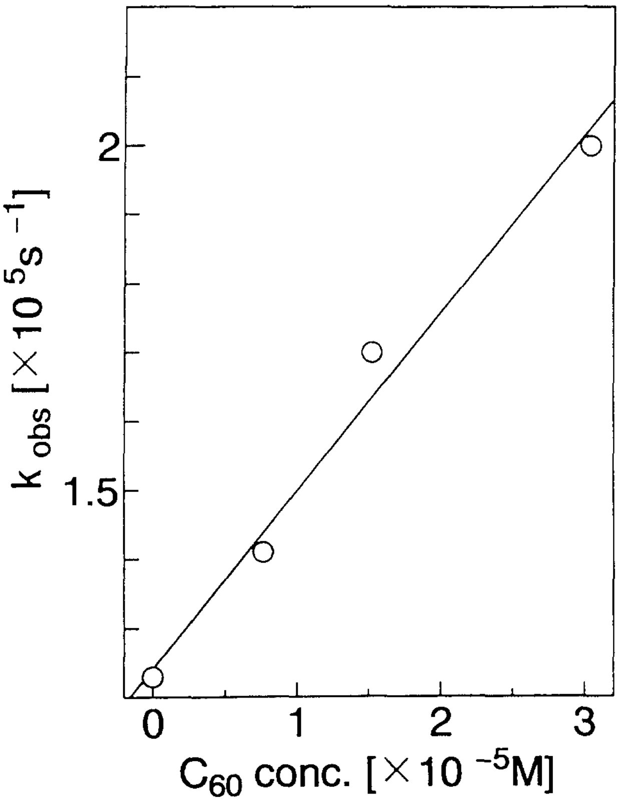


Fig. 3. Stern–Volmer plot to determine the reaction rate constant of the solvated electron with $C_{60}(S_0)$.

3.2. Reaction of $C_{60}(S_1)$ and TEA

The laser flash photolysis method was applied to the C_{60}–TEA system in toluene. The spectral change after laser excitation is shown in Fig. 4. The bleaching due to the depletion of C_{60} and the transient absorption similar to the T–T absorption of C_{60} are recognized immediately after laser excitation. However, the red absorption band around 720 nm is much wider than that of the T–T absorption of C_{60} at 750 nm. Furthermore, the absorption intensity decreases with increasing delay time, which is accompanied by a shift of the maximum from 720 nm (at 0 ns) to 750 nm (at 700 ns), as shown in Fig. 4. The spectral feature in the red region becomes similar to that due to the T–T absorption of C_{60}. The bleaching intensity around 330 nm, which is weaker than that measured in the C_{60}–benzene system [14], becomes stronger after long delay times. At 8 μs, the spectrum exhibits a residual absorption in the region below 500 nm. This final spectrum resembles that observed during steady state photolysis [10].

Fig. 5 shows the time evolution of the absorbance measured at 330, 450 and 750 nm. Two exponential components can be recognized by the nanosecond transient absorption experiment monitored at 330 and 750 nm. The faster component has a lifetime of approximately 200 ns and the slower component has a lifetime of about 4 μs. The bleaching at 330 nm becomes deeper during the initial decay time of 200 ns and then recovers with a time constant of approximately 4 μs. The bleaching does not recover completely; this implies that

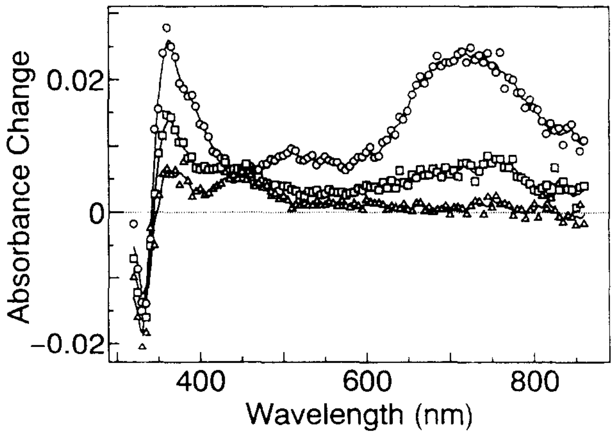


Fig. 4. Transient absorption spectra obtained by laser flash photolysis of the C_{60}–TEA ([TEA] = 1.0 M) system in toluene solution: 0 ns (○), 700 ns (□) and 8.0 μs (△) after 308 nm excitation.

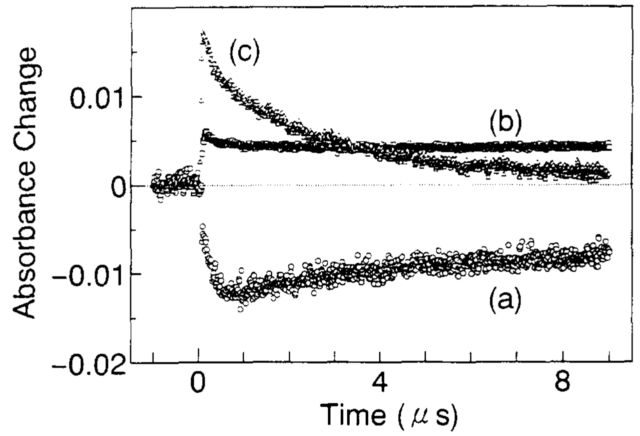


Fig. 5. Time evolution of the transient absorption. Monitored at 330 nm (a), 450 nm (b) and 750 nm (c) during the flash photolysis of the C_{60}–TEA ($[C_{60}] = 1.5 \times 10^{-5}$ M; [TEA] = 1.0 M) system in toluene solution at 308 nm.

the parent C_{60} molecules are consumed as a result of the photochemical reaction. At 330 nm, the faster and slower components are also determined to have lifetimes of approximately 200 ns and 4 μs respectively. Only the faster decay of about 200 ns can be recognized at 450 nm and the residual absorption remains.

Thus three chemical species seem to contribute to the transient absorption spectra measured in this photochemical C_{60}–TEA–toluene system. One species decays rapidly with a lifetime of approximately 200 ns, and exhibits a transient absorption similar to, but broader than, the T–T absorption of C_{60}. This species is formed immediately after laser excitation as shown in Fig. 4, and seems to be generated through the quenching process of C_{60} in the S_1 state by TEA. Therefore an exciplex, radical anion (C_{60}^{-}) and ion pair (C_{60}^{-}–TEA^{+}) are considered as candidates for this short-lived species. The transient absorption band around 720 nm cannot be ascribed to C_{60}^{-} or the ion pair, because the radical anion is reported to have characteristic absorption bands at 925 and 1076 nm but no band is observed around 720 nm [15]. Therefore we tentatively assign this short-lived species to the exciplex formed by C_{60} in the S_1 state with TEA. Another species decays slowly, and can be assigned to C_{60} in the triplet state. The last species is the photoproduct which absorbs light at wavelengths shorter than 500 nm.

The transient absorbance due to T–T absorption in the red region is reduced on addition of TEA. Therefore we measured the initial triplet absorbance at several TEA concentrations by analysing the decay curves monitored at 750 nm as a double exponential function. Stern–Volmer analysis gives the quenching rate constant of C_{60} in the S_1 state by TEA to be $(3.3 \pm 0.3) \times 10^9\ M^{-1}\ s^{-1}$, using the reported S_1 lifetime of 1.2 ns [16]. This large rate constant suggests that the quenching of the S_1 state by TEA is less than that in a diffusion-controlled process. Recently, a similar value of the rate constant ($2.9 \times 10^9\ M^{-1}\ s^{-1}$) has been reported by Sun et al. [17].

In the fast atom bombardment (FAB) mass spectrum of the photoproduct, a strong peak was detected at $m/z = 410.3$ corresponding to C_{60}–TEA^{2+}, although a peak at $m/z = 821.1$ for C_{60}–TEA^{+} was not measured. The photoproduct contains an ethyl group judging from the proton nuclear magnetic resonance (^{1}H NMR) spectrum. We could not confirm conclusively that the photoproduct was the adduct of C_{60} with TEA. Scheme II summarizes the overall reaction mechanism discussed above.

Acknowledgments

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