

Absolute Rate Constant for the Reaction of Diphenylcarbene with C₆₀

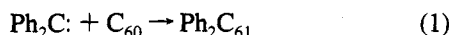
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Recently, in their efforts to develop polymers containing the C₆₀ moiety, Wudl and co-workers¹ have demonstrated that divalent carbon equivalents may be added to fullerene C₆₀ to produce functionalized C₆₁ fulleroids. Specifically, the addition of a diphenylcarbene (Ph₂C:) equivalent to a C₆₀ double bond was accomplished by dipolar addition of diphenyldiazomethane (Ph₂CN₂) followed by N₂ extrusion of the intermediate five-membered-ring heterocycle. The resulting cyclopropyl adduct is then believed to undergo a norcaradiene–cycloheptatriene-like electrocyclic rearrangement and spherically expand to the Ph₂C₆₁ fulleroid product (see Scheme 1). The expanded fullerenes were found to essentially retain the electronic structure of C₆₀.

In the present work, laser flash photolysis (LFP) technique has been used to measure the absolute rate constant for the reaction of Ph₂C: with C₆₀. This reaction represents the overall process of inflation of buckminsterfullerene C₆₀ to fulleroid Ph₂C₆₁.



The experimental difficulties in obtaining absolute kinetics of the reaction of transient intermediates toward C₆₀ by optical spectroscopy have been well documented.² For example, the intense UV absorption bands of C₆₀ often inhibit monitoring of the addition reactions of free radicals to C₆₀ due to spectral overlap with the absorption bands of the free radicals. The intense UV absorption bands of C₆₀ and the facile generation of excited triplet C₆₀ (³C₆₀*) also present difficulties in the selective photoexcitation of free radical precursors using UV excitation. Free radical reactivity toward C₆₀ has been successfully obtained by optical spectroscopy, however, by monitoring growth kinetics of both UV² and IR^{2c} absorption bands of free radical/C₆₀ addition adducts, RC₆₀.

The measurement of the decay kinetics of triplet Ph₂C:, λ_{max} = 310 nm,³ in the presence of C₆₀ was also unsuccessful due to the above limitations. However, a rate constant of 4.0 × 10⁸ M⁻¹ s⁻¹ was obtained for the reaction of Ph₂C: with C₆₀ to form Ph₂C₆₁ due to the following favorable circumstances:

(1) The visible absorption band of Ph₂CN₂ was sufficiently intense to allow selective 532 nm LFP of Ph₂CN₂ over a significant C₆₀ concentration range.

(2) The Ph₂C: addition adduct, Ph₂C₆₁, could be monitored at a wavelength that did not significantly overlap with either Ph₂CN₂ or C₆₀.

(1) (a) Shi, S.; Khemani, K. C.; Li, Q.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 10656–10657. (b) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, O. *Science* **1991**, *254*, 1186–1188. (c) Baum, R. M. *Chem. Eng. News* **1991**, *69* (Dec 16), 17–20. (d) Eiermann, M.; Wudl, F.; Prato, M.; Maggini, M. *J. Am. Chem. Soc.* **1994**, *116*, 8364–8365.

(2) (a) Dimitrijević, N. M.; Kamat, P. V.; Fessenden, R. W. *J. Phys. Chem.* **1993**, *97*, 615–618. (b) Walbinder and Fisher have recently demonstrated that the initial rate constant for the reaction of benzyl radical with C₆₀ of 9.3 × 10⁸ M⁻¹ s⁻¹, as determined by optical spectroscopy,^{2a} was overestimated and have measured a rate constant of 1.4 × 10⁷ M⁻¹ s⁻¹ by time-resolved ESR spectroscopy. Walbinder, M.; Fisher, H. *J. Phys. Chem.* **1993**, *97*, 4880–4881. (c) Guldi, D. M.; Hungerbühler, H.; Janata, E.; Asmus, K.-D. *J. Phys. Chem.* **1993**, *97*, 11258–11264. (d) Dimitrijević, N. M. *Chem. Phys. Lett.* **1992**, *194*, 457–460.

(3) (a) Platz, M. S.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Plenum: New York, 1990; pp 239–352. (b) Scaiano, J. C. In *Chemical Kinetics of Small Organic Radicals*; Alfassi, Z. B., Ed.; CRC Press: Boca Raton, FL, 1988; Vol. III, pp 73–101.

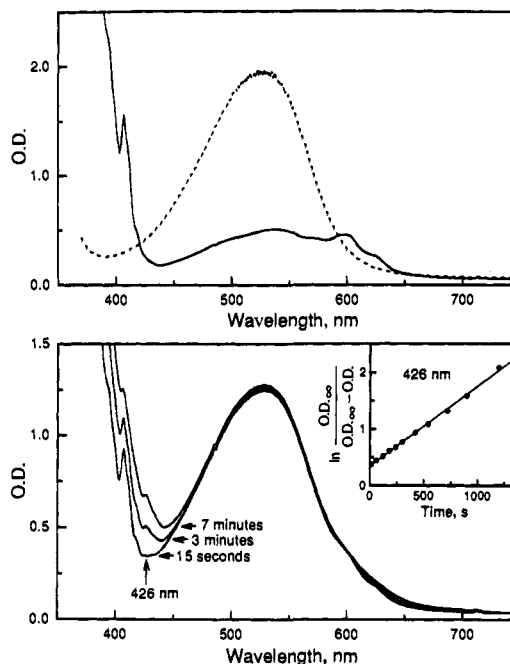
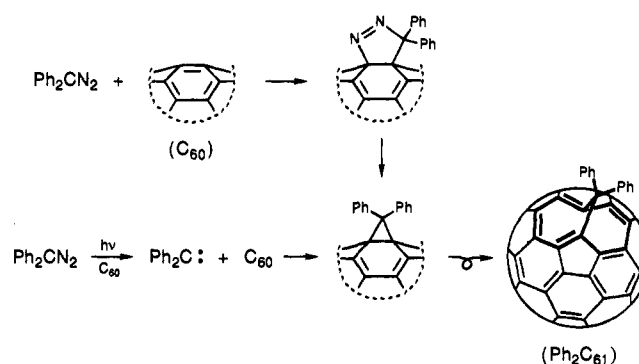


Figure 1. Top: Comparison of the UV–visible absorption spectra of 1 × 10⁻³ M C₆₀ (—); and 3.5 × 10⁻² M Ph₂CN₂ (---). Bottom: Absorption spectra observed 15 s and 3 and 7 min following addition of Ph₂CN₂ to a 5 × 10⁻⁴ M C₆₀ benzene solution; see text. Inset: Time dependence of production of the 426 nm product.

Scheme 1



(3) Rapid mixing procedures allowed for kinetic measurements to be obtained prior to significant thermal reactivity of Ph₂CN₂ with C₆₀.

(4) Triplet ³C₆₀* was found to react rapidly with Ph₂CN₂ at 4.1 × 10⁸ M⁻¹ s⁻¹. Therefore, at high quenching concentrations of C₆₀, when some C₆₀ excitation did occur, the ³C₆₀* lifetime was short compared to Ph₂C₆₁ formation⁴ and did not interfere in obtaining Ph₂C₆₁ growth kinetics. The details of the experimental results are described below.

Figure 1 (top) contains a comparison of the UV–visible absorption spectra⁵ of 1 × 10⁻³ M C₆₀ and 3.5 × 10⁻² M Ph₂CN₂ in benzene solution⁶ measured in 6 mm Suprasil quartz LFP cells. In a typical experiment two LFP cells were prepared and thoroughly deaerated with argon, with one containing 1.0

(4) The similarities in *k*_{bi} for Ph₂C₆₁ production (420 nm) and ³C₆₀* quenching (750 nm) by Ph₂CN₂ suggest a mechanism for direct Ph₂C₆₁ production from ³C₆₀*. However, when the 750 nm decay and the 420 nm growth at [C₆₀] = 1 × 10⁻⁴ M and [Ph₂CN₂] = 1.75 × 10⁻² M were monitored, *k*_{ob} = 5 × 10⁶ s⁻¹ and 8 × 10⁴ s⁻¹, respectively, were obtained, which clearly demonstrates that the decay and growth are not concurrent.

(5) SLM-Aminco Spectronic 3000 array spectrophotometer.

(6) C₆₀ (SES Research, Inc., 99.9%) was used as received; Ph₂CN₂ was prepared according to a previously described procedure;⁷ benzene (Aldrich, spectranalyzed) was freshly distilled from calcium hydride prior to use; and cyclohexane (Fisher, HPLC grade) was used as received.

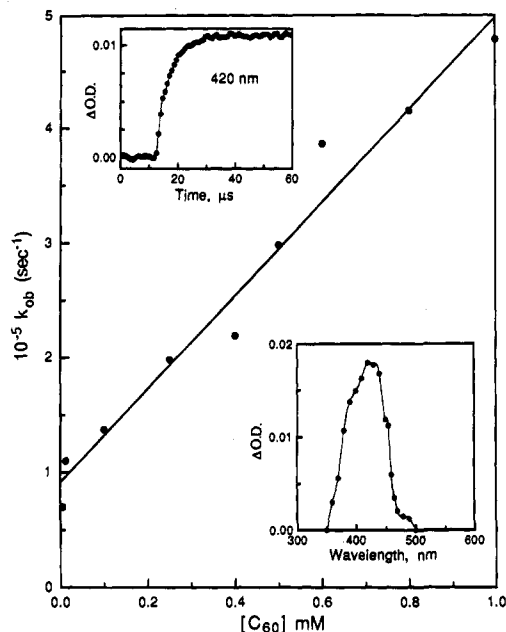


Figure 2. Dependence of k_{ob} measured at 420 nm on C_{60} concentration. Top inset: Absorption signal observed containing 5×10^{-4} M C_{60} . Bottom inset: Absorption spectrum observed following LFP of Ph_2CN_2 in the presence of C_{60} .

mL of a known concentration of C_{60} and the other containing a Ph_2CN_2 solution adjusted to an optical density (OD) of 2.0 at the 532 nm laser excitation⁸ wavelength. Immediately prior to an experiment 1.0 mL of Ph_2CN_2 solution was transferred to the LFP cell containing the C_{60} solution via syringe under a nitrogen atmosphere and vigorously shaken prior to laser excitation. Mixing, LFP, and collection of data were accomplished within ca. 15–30 s. This procedure was also used to monitor the thermal reaction of Ph_2CN_2 with C_{60} . Figure 1 (bottom) contains UV–visible spectra taken at 15 s, 3 min, and 7 min following the procedure described using a 5×10^{-4} M C_{60} solution. Product formation is clearly observed. As mentioned, Ph_2C_{61} retains much of the electronic nature¹ of C_{60} ; however, Ph_2C_{61} also possesses visible absorption bands^{1b} that are distinctive to Ph_2C_{61} . The absorption band at 426 nm (Figure 1, bottom) was also observed in the reaction of Ph_2CN_2 with C_{60} in cyclohexane and corresponds to the 429 nm band reported for isolated Ph_2C_{61} in cyclohexane.^{1b} The production of the 426 nm band in benzene was monitored over a 30 min period, and a plot of $\ln \text{OD}_\infty / (\text{OD}_\infty - \text{OD})^9$ versus time (Figure 1, inset) indicates that formation of Ph_2C_{61} occurs with overall first-order kinetics with an apparent rate constant of $1.4 \times 10^{-3} \text{ s}^{-1}$.

The combination of the distinctive 426 nm absorption band of Ph_2C_{61} and the relatively slow reactivity of Ph_2CN_2 with C_{60} allowed for determination of an absolute bimolecular rate constant, k_{bi} , for the reaction of Ph_2C with C_{60} . LFP (532 nm) of Ph_2CN_2 in deaerated benzene in the absence of C_{60} resulted in no detectable product absorption signals. Ph_2C generation was verified, however, by detection of the formation

(7) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928–3937.

(8) Quanta Ray DCR-1 Nd:YAG (~10 mJ pulse width ~6 ns). The LFP apparatus is described elsewhere. Fessenden, R. W.; Nagarajan, V. *J. Phys. Chem.* **1985**, *89*, 2330–2335.

(9) OD_∞ represents the last data point taken from the “growth” of the 426 nm band.

of diphenylcarbonyl oxide³ in O_2 -saturated benzene solution following 532 nm laser excitation.¹⁰ LFP of Ph_2CN_2 in the presence of C_{60} resulted in formation of product possessing an apparent absorption maximum at 420 nm (Figure 2, bottom). Observed rate constants, k_{ob} , for formation of this product were measured at 420 nm (Figure 2, top) over a C_{60} concentration range^{11,12} of 5×10^{-6} to 1×10^{-3} M. A bimolecular rate constant,¹³ $k_{\text{bi}} = 4.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, was obtained from the results presented in Figure 2 and $k_{\text{ob}} = k_0 + k_{\text{bi}}[\text{C}_{60}]$, where k_0 represents the rate constant for decay of Ph_2C : in the absence of C_{60} . At the highest C_{60} concentrations used in Figure 2 ($> 5 \times 10^{-4}$ M) some photoexcitation of C_{60} was observed at 420 nm. Fortunately, the amplitude and lifetime of the $^3\text{C}_{60}^*$ absorption signal did not interfere with the measurement of the growth kinetics of the Ph_2C_{61} product since $^3\text{C}_{60}^*$ was found to rapidly decay in the presence of Ph_2CN_2 .^{14,15} The rate constant for reaction of $^3\text{C}_{60}^*$ with Ph_2CN_2 ($4.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) was independently determined by excitation of 1×10^{-3} M C_{60} and selective measurement of $^3\text{C}_{60}^*$ decay kinetics at 750 nm over a Ph_2CN_2 concentration range of 5×10^{-4} to 2.7×10^{-2} M.

In summary, it should be noted that it is possible that the absorption signal observed following LFP of Ph_2CN_2 in the presence of C_{60} is due to the initial cyclopropane adduct formed by carbene addition; however, the typical instability of norcaradienes¹⁸ and the spectral similarities with the thermally generated product of Ph_2CN_2 and C_{60} strongly suggest that the absorption signal observed following LFP is that of the fulleroid Ph_2C_{61} .

Acknowledgment. The work described herein was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. This is Contribution No. NDRL-3722 from the Notre Dame Radiation Laboratory.

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(10) Photodecomposition of Ph_2CN_2 using visible light has been previously reported. Li, Y.-Z.; Schuster, G. B. *J. Org. Chem.* **1987**, *52*, 4460–4464.

(11) The solubility limit of C_{60} in benzene is 1.7 mg/mL. Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. *J. Phys. Chem.* **1993**, *97*, 3379–3383.

(12) Attempts to use either 308 or 337 nm laser excitation were unsuccessful due to significant C_{60} excitation and a limited $[\text{C}_{60}]$ range, approximately 5×10^{-6} to 5×10^{-5} M.

(13) k_{bi} represents all modes of Ph_2C : reactivity with C_{60} , since $k_{\text{ob}} = k_{\text{T}} + Kk_{\text{S}}$, where k_{T} and k_{S} are the triplet and singlet rate constants, respectively, and K is the singlet/triplet equilibrium constant.

(14) Triplet energy transfer is a likely mechanism for the observed reactivity.¹⁵ Direct production of triplet carbenes by sensitization is a common means of investigation of carbene state selective reactivity. See: March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1992; pp 195–197. Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, 1978; pp 552–556. For triplet-sensitized decomposition of Ph_2CN_2 see, for example: Eisenthal, K. B.; Turro, N. J.; Sitzmann, E. V.; Gould, I. R.; Hefferon, G.; Langan, J.; Cha, Y. *Tetrahedron* **1985**, *41*, 1543–1554.

(15) A triplet energy (E_{T}) of Ph_2CN_2 comparable to or lower than that of C_{60} ($E_{\text{T}} = 36 \text{ kcal/mol}$)¹⁶ would support a triplet energy transfer mechanism; however, the E_{T} of Ph_2CN_2 is not available in the literature. Therefore, triplet anthracene (42.5 kcal/mol), 1,6-diphenylhexatriene (35.6 kcal/mol), and tetracene (29.3 kcal/mol) have been generated by LFP and $k_{\text{bi}} = 2.0 \times 10^9$, 1.9×10^7 , and $< 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, respectively, were obtained using Ph_2CN_2 as the quenching substrate. These results indicate that the E_{T} of Ph_2CN_2 is lower than that of C_{60} and fully supports a triplet sensitization mechanism.¹⁷ The results are also inconsistent with an electron transfer mechanism.

(16) E_{T} values were obtained from the following: Morov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker, Inc.: New York, 1993.

(17) (a) Koizumi, M.; Kato, S.; Mataga, N.; Matsoura, T.; Usui, Y. *Photosensitized Reactions*; Kagakudojin Publishing: Kyoto, 1978. (b) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1973; pp 53–63.

(18) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1992; p 869.