4502 *J. Am. Chem. Soc.* **1996,** *118,* 4502−4503

Direct Observation of Carbon−Carbon Bond Cleavage in Ultrafast Decarboxylations

T. Michael Bockman, Stephan M. Hubig, and Jay K. Kochi*

Department of Chemistry, University of Houston
Houston, Texas, 77204-5641

Received January 16, 1996

We wish to report how the recent developments in time-resolved spectroscopy make it possible to observe the direct scission of a carbon−carbon bond in real time, a process of fundamental importance in organic chemistry.[1,2] We initially focus on the facile C−C bond cleavage in the decarboxylation of labile acyloxy radicals ($R-CO_2^{\bullet}$) since they generally have lifetimes of $\tau < 10^{-9}$ s.[3] In order to generate this reactive precursor, we employ the novel method based on electron-transfer oxidation of carboxylate salts,[4] i.e.

$$R-CO_2^{-},\quad A^{+} \xrightarrow{h\nu_{CT}} A^{\bullet},\quad R-CO_2^{\bullet} \xrightarrow{k_{CC}} R^{\bullet} + CO_2 \quad (1)$$

which circumvents the difficulties encountered in the usual methodology based on bond homolysis.[5] Thus the instantaneous production of the acyloxy radical by oxidation of carboxylate is achieved by charge-transfer excitation ($h\nu_{CT}$)[7] in eq 1 with the aid of a new pump−probe spectrometer based on a 230-fs high-power Ti:sapphire laser[10] which allows the simultaneous spectral detection of the reactive transients over a continuous (350−900 nm) wavelength range.

We find that photoexcitation ($h\nu_{CT}$) according to eq 1 of the colored pyridinium salts of benzilic acid leads to the loss of carbon dioxide from the intermediate acyloxy radical within a picosecond. These ultrafast decarboxylations thus approach barrier-free unimolecular rates to approximate the transition state of C−C bond scission.[11] For example, upon the photoexcitation of the yellow methylviologen salt[12] of benzilic acid at λ_{CT} = 375 nm, the UV absorption band of the reduced methylviologen ($A^{\bullet}$) at λ_{max} = 395 nm[13] is observed immediately (Figure 1). In addition, the transient spectrum shows another visible absorption centered at 600 nm, and the digital deconvolution of the experimental spectrum yields the resolved absorption bands of $MV^{\bullet}$[13] and $Ph_2C^{\bullet}OH$,[14] as illustrated in Figure 1.[15] On the basis of the observation of both transients within 1−2 ps of the laser excitation, we conclude that the photoinduced electron transfer in eq 1 is closely accompanied by decarboxylation, i.e.

$$Ph_2C(OH)CO_2^{-},\quad MV^{+} \xrightarrow{h\nu_{CT}} MV^{\bullet},\quad Ph_2C(OH)CO_2^{\bullet} \xrightarrow{k_{CC}} Ph_2C^{\bullet}OH + CO_2 \quad (2)$$

where MV^{+} and $MV^{\bullet}$ represent methylviologen and reduced methylviologen,[13] respectively. The absorption spectrum of $Ph_2C^{\bullet}OH$ can also be generated without admixture from the $MV^{\bullet}$ spectrum by the charge-transfer photostimulation of the *N*-methyl-4-cyanopyridinium salt, as shown in the inset of Figure 1.[16]

Simultaneous monitoring of the growth of both transients, as illustrated in Figure 2, demonstrates that the formation of $Ph_2C^{\bullet}OH$ is significantly slower (by about 1 ps) than the formation of $MV^{\bullet}$. Reduced methylviologen is thus generated with the same time constant (τ < 700 fs, fwhm) as the instrumental response of the laser system, in accordance with its instantaneous generation in eq 1.[7] On the other hand, the slower rise of the ketyl radical absorption indicates that it is formed

---

(1) (a) Manz, J.; Wöste, L. *Femtosecond Chemistry*; VCH: Weinheim, 1995. (b) Simon, J. D. *Rev. Sci. Instrum.* **1989**, *60*, 3597.

(2) (a) Kliner, D. A. V.; Alfano, J. C.; Barbara, P. F. *J. Chem. Phys.* **1993**, *98*, 5375. (b) Sension, R. J.; Repinec, S. T.; Szarka, A. Z.; Hochstrasser, R. M. *J. Chem. Phys.* **1993**, *98*, 6291. (c) Joly, A. G.; Nelson, K. A. *Chem. Phys.* **1991**, *152*, 69. (d) Schwartz, B. J.; Peteanu, L. A.; Harris, C. B. *J. Phys. Chem.* **1992**, *96*, 3591. (e) Schoenlein, R. W.; Peteanu, L. A.; Wang, Q.; Mathies, R. A.; Shank, C. V. *J. Phys. Chem.* **1993**, *97*, 12087. (f) Laermer, F.; Elsaesser, T.; Kaiser, W. *Chem. Phys. Lett.* **1988**, *148*, 119. (g) Lenderink, E.; Duppen, K.; Wiersma, D. A. *Chem. Phys. Lett.* **1993**, *211*, 503. (h) Sakata, Y.; Tsue, H.; Oneil, M. P.; Wiederrecht, G. P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1994**, *116*, 6904.

(3) (a) Braun, W.; Rajbenbach, L.; Eirich, F. R. *J. Phys. Chem.* **1962**, *66*, 1591. (b) Kaptein, R.; Brokken-Zijp, J.; de Kanter, F. J. J. *J. Am. Chem. Soc.* **1972**, *94*, 6280. (c) Falvey, D. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 7419. (d) Hilborn, J. W.; Pincock, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2683. (e) Budac, D.; Wan, P. *J. Photochem. Photobiol. A* **1992**, *67*, 135.

(4) See: (a) Barnett, J. R.; Hopkins, A. S.; Ledwith, A. *J. Chem. Soc. Perkin Trans. 2* **1973**, 80. (b) Deronzier, A.; Esposito, F. *Nouv. J. Chem.* **1983**, *7*, 15. (c) Jones, G., II; Zisk, M. B. *J. Org. Chem.* **1986**, *51*, 947. (d) Mandler, D.; Willner, I. *J. Chem. Soc. Perkin Trans. 2* **1988**, 997.

(5) Bond homolysis by the direct photoexcitation of precursors such as peroxides,[3c,6] esters,[3d] etc. involves excited states, the temporal relaxation of which leads to the acyloxy radical on the same time scale as the cleavage process itself. The overall kinetics of the photodecarboxylation is thus a convolution of the formation as well as the decomposition of the acyloxy radical, and rate constants (k_{CC}) on the picosecond time scale cannot be readily extracted. For a discussion of this problem in the context of peroxide decomposition, see ref 3c.

(6) Pacansky, J.; Brown, D. W. *J. Phys. Chem.* **1983**, *87*, 1553. See also: Sheldon, R. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 5175.

(7) Time-resolved spectroscopy by Mataga, Hochstrasser, and co-workers[8] has established charge-transfer excitation to effect the transfer of an electron from the donor to the acceptor within 500 fs. The radical−ion pair is thus already present in its ground state prior to the time window of our experiments, in accord with Mulliken theory.[9]

(8) (a) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 4147. (b) Wynne, K.; Galli, C.; Hochstrasser, R. M. *J. Chem. Phys.* **1994**, *100*, 4797. See also: (c) Hilinski, E. F.; Masnovi, J. M.; Amatore, C.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6167. (d) Hilinski, E. F.; Masnovi, J. M.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 8071.

(9) (a) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811. (b) Mulliken, R. S.; Person, W. B. *Molecular Complexes: A Lecture and Reprint Volume*; Wiley: New York, 1969. (c) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 600.

(10) The laser spectrometer consists of a Ti:sapphire oscillator and two amplifiers. The oscillator is pumped by an argon ion laser to generate 110-fs pulses tunable between 720 and 920 nm. These pulses are amplified sequentially by a regenerative amplifier and a linear (multipass) amplifier, both of which are pumped by the frequency-doubled output of a (10 Hz) Q-switched Nd:YAG laser. The laser system produces 230-fs pulses with energies up to 10 mJ which are frequency-doubled (360−460 nm) for excitation.

(11) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley: New York, 1981; p 173.

(12) (a) Ebbesen, T. W.; Ferraudi, G. *J. Phys. Chem.* **1983**, *87*, 3717. (b) Ebbesen, T. W.; Manring, L. E.; Peters, K. S. *J. Am. Chem. Soc.* **1984**, *106*, 7400. (c) Hubig, S. M. *J. Phys. Chem.* **1992**, *96*, 2903. (d) Hubig, S. M.; Kochi, J. K. *J. Phys. Chem.* **1995**, *99*, 17578.

(13) (a) Michaelis, L. *Biochem. Z.* **1932**, *250*, 564. (b) Michaelis, L.; Hill, E. S. *J. Gen. Physiol.* **1933**, *16*, 859. (c) Bockman, T. M.; Kochi, J. K. *J. Org. Chem.* **1990**, *55*, 4127. (d) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

(14) (a) Johnston, L. J.; Lougnot, D. L.; Wintgens, V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 518. (b) Nagarajan, V.; Fessenden, R. W. *Chem. Phys. Lett.* **1984**, *112*, 207.

(15) (a) The derived spectrum of the ketyl radical (− − −) is obtained by subtraction of the authentic spectrum of reduced methylviologen (···) from the composite absorption band (—). The derived extinction coefficient of ϵ_{530} = 6200 L mol^{-1} cm^{-1} for $Ph_2C^{\bullet}OH$ (based on its equimolar formation with $MV^{\bullet}$ in eq 2) is in reasonable agreement with the reported value[15b] of ϵ_{530} = 5500 L mol^{-1} cm^{-1}. Since the experimental spectrum in Figure 1 is unchanged over a period of more than 50 ps, correction for group velocity dispersion is unnecessary. (b) Hayon, E.; Ibata, T.; Lichtin, N. N.; Simic, M. *J. Phys. Chem.* **1972**, *76*, 2072.

(16) (a) The authentic spectrum of the ketyl radical ($Ph_2C^{\bullet}OH$) in the inset of Figure 1 was obtained by picosecond charge-transfer excitation of the ion pair formed from *N*-methyl-4-cyanopyridinium (NCP^{+}) and benzilate and is identical with the spectrum of $Ph_2C^{\bullet}OH$ generated by pulse-radiolysis.[15b] (b) Note that the absorption spectrum (λ_{max} = 390 nm) of the reduced *N*-methyl-4-cyanopyridinyl radical ($NCP^{\bullet}$) is strongly blue-shifted away from the absorption band of the ketyl radical. See: Itoh, M.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 369.

(17) (a) The transient absorbance of reduced methylviologen is simulated simply as the integral over time of the laser profile. (b) The rise of the 530-nm absorbance is simulated by the combination of the instantaneous[7] rise of the $MV^{\bullet}$ absorbance and the (slower) first-order rise of the absorbance of the ketyl radical, $Ph_2C^{\bullet}OH$, with a rate constant of $k_{CC} = 8 \times 10^{11}$ s^{-1}. The ratio of the two components is based on the extinction coefficients of $MV^{\bullet}$ (ϵ_{530} = 3200 M^{-1} cm^{-1})[13d] and $Ph_2C^{\bullet}OH$ (ϵ_{530} = 5500 M^{-1} cm^{-1}).[15b] (c) The kinetic trace of the ketyl radical in Figure 2 is displaced by 0.4 ps to accommodate the difference in the group velocity dispersion of the 530-nm monitoring wavelength relative to that at 605 nm. [Note that the later rise of the 530-nm absorbance is opposite to that based on the consideration of group velocity dispersion and thus cannot be due to an instrumental artifact ("chirp"). See: Sharma, D. K.; Yip, R. W.; Williams, D. F.; Sugamori, S. E.; Bradley, L. L. T. *Chem. Phys. Lett.* **1976**, *41*, 460. For an example of chirp-induced spectral distortion, see: Miyasaka, H.; Ojima, S.; Mataga, N. *J. Phys. Chem.* **1989**, *93*, 3380. Yip, R. W.; Korppi-Tommola, J. *Rev. Chem. Intermed.* **1985**, *6*, 33.]

S0002-7863(96)00112-6 CCC: $12.00

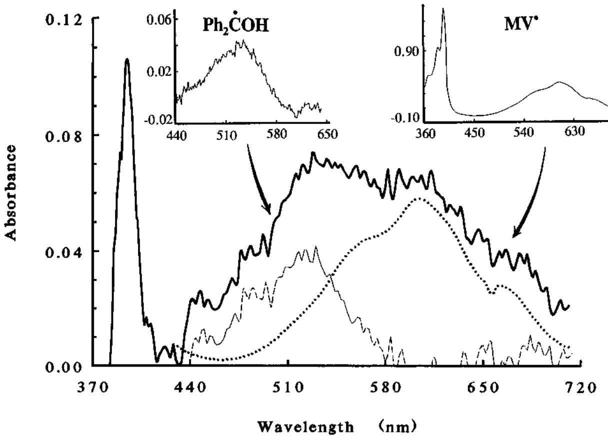

Figure 1. Transient absorption spectrum obtained at 1.0 ps following the 375-nm charge-transfer excitation of the [MV$^+$, benzilate$^-$] salt in water at 25 °C. Inset: (left) Authentic spectrum of the ketyl radical (Ph$_2$C$^\bullet$OH) in ref 16 and (right) the spectrum of reduced methylviologen (MV$^\bullet$) in ref 13c. Digital deconvolution of the broad absorption band (440−740 nm) in the experimental spectrum is shown as the composite of the spectra of Ph$_2$C$^\bullet$OH (− − −) and MV$^\bullet$ (···), as described in footnote 15.

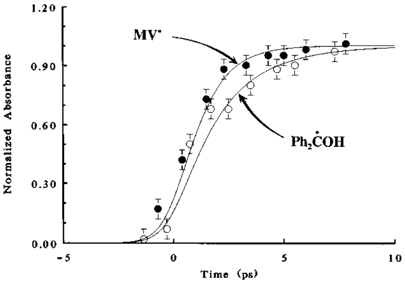

Figure 2. Kinetic (fs/ps) traces of the formation of MV$^\bullet$ (●) and Ph$_2$C$^\bullet$OH (○) monitored at 605 and 530 nm, respectively. The smooth curves represent (a) the rise of MV$^\bullet$ simulated by taking into account the instrumental response time of 700 fs (fwhm, see footnote 17a) and (b) the rise of Ph$_2$C$^\bullet$OH simulated by the convolution of the instrumental response time and the decarboxylation rate constant of $k_{CC} = 8 \times 10^{11}$ s^{-1} (see footnote 17b). The error bars reflect an uncertainty of ±0.005 absorbance units in the spectroscopic measurements.

Table 1. Rate Constants for Decarboxylation and Back Electron Transfer in Methylviologen/Benzilate Radical−Ion Pairs[a]

benzilate donor (RCO$_2^-$)	k_{bet}[b] (10^{11} s^{-1})	k_{CC}[c] (10^{11} s^{-1})
unsubstituted	2	8[d]
4,4′-dimethyl	5	5
4-methoxy	3	1
4,4′-dimethoxy	8	2
2,2′,5,5′-tetramethoxy	8	0.4

[a] Benziloxy radicals generated by charge-transfer irradiation of [MV$^+$, RCO$_2^-$] with the 230-fs (fwhm) laser pulse at $\lambda_{exc} = 375$ or 400 nm in aqueous solution at 23 °C. [b] Rate constant (±5%) for back electron transfer in eq 3. [c] Rate constant (±5% unless indicated otherwise) for decarboxylation of the acyloxy radical derived from the benzilate anion in eq 3. [d] Rate constant (±10%) for benziloxy only.

from the short-lived benziloxy precursor. Simulation and comparison of the kinetic traces in Figure 2 allow the extraction of the first-order rate constant for the formation of the ketyl radical, and thus k_{CC} in eq 2 is 8×10^{11} s^{-1}.[17]

Polar (substituent) effects on the C−C bond cleavage are examined in the series of methylviologen salts of methyl- and methoxy-substituted benzilates. The kinetic traces show partial decay of the spectral transients to a nonzero residual absorbance, the value of which varies with the particular benzilate anion. The complex transient kinetics can be analyzed in terms of a competition between C−C bond cleavage (eq 2) and back electron transfer (k_{bet}) to restore the original viologen salt, i.e.

$$R-CO_2^-, \quad A^+ \xleftarrow{k_{bet}} A^\bullet, \quad R-CO_2^\bullet \xrightarrow{k_{CC}} R^\bullet + CO_2 \qquad (3)$$

Simulation of the rise and decay of MV$^\bullet$, combined with quantitative analysis of the fractional residual absorbance, allows the separation of the rate constants k_{CC} and k_{bet} for the systems listed in Table 1.[18]

The ultrafast C−CO$_2$ bond scission in acyloxy radicals that are derived from benzilates, with first-order rate constants k_{CC} in the range of $10^{11}-10^{12}$ s^{-1}, stands in marked contrast to the much slower rates measured for alkyl- and aryl-substituted acetyloxy radicals, with $k_{CC} \approx 10^9-10^{10}$ s^{-1}.[3] (Rate constants for the decarboxylation of these acyloxy radicals determined by our method agree well with those reported earlier.[19]) These rapid rates reflect the very low energies of the transition state (relative to the acyloxy reactant), which in turn are a consequence of the high degree of stabilization of the ketyl radical, Ar$_2$C$^\bullet$OH, as the product of decarboxylation.[6]

The trend in the rates of carbon−carbon bond cleavage show a consistent decrease as more methyl and methoxy substituents are added to the benzilate anions.[20] As a result, the decarboxylation is most rapid for the benziloxy radical (Ph$_2$C(OH)CO$_2^\bullet$), for which the electron-deficiency (hole) of the photooxidized anion is less effectively ameliorated by the electron-poor phenyl moiety relative to the tolyl and anisyl analogues. Furthermore, the opposite substituent effect is expected for the stabilization of the electron-rich product (Ar$_2$C$^\bullet$OH) radicals.[21] Consequently, electron-donating substituents can stabilize the acyloxy reactant as well as destabilize the ketyl product, and thus the Me- and MeO-substituted benziloxy radicals suffer decreased rates of decarboxylation. On the other hand, the rates for back electron transfer (k_{bet}) in Table 1 increase as the aromatic systems become more electron-rich. This trend is in accord with Marcus theory,[22] which predicts such an increase in k_{bet} as the exergonicity of the electron transfer decreases.[23]

We believe that the ultrafast bond cleavages exemplified by decarboxylation of the acyloxy radicals derived from benzilates do not represent limiting cases with respect to the ultimate stability of the product radical. Since increased stabilization of R$^\bullet$ in eq 2 leads to more rapid rates of R−CO$_2^\bullet$ scission, we hope to design carboxylate anions that lose an electron and cleave the C−C bond in a single step. Real-time monitoring of these concerted reactions will thus constitute the direct observation of the transition state[24] for the breaking of a C−C bond.

Acknowledgment. We thank Photonics Industries for technical assistance in the construction of the femtosecond laser system, and the National Science Foundation, the Robert A. Welch Foundation, and the Texas Advanced Research Program for financial support.

JA960112J

---

(18) (a) The quantitative analysis of the rate constants of the two competing processes for the benzilates in Table 1 except Ph$_2$C(OH)CO$_2^-$ is based on the following: $\Phi_{MV} = k_{CC}/(k_{CC} + k_{bet}) = k_{CC}\tau_{MV}$. The lifetime of reduced MV (τ_{MV}) is obtained from the fs/ps kinetics, and the transient quantum yield (Φ_{MV}) of residual MV$^\bullet$ is obtained by nanosecond laser photolysis using benzophenone triplet as actinometer. See: Hurley, J. K.; Sinai, N.; Linshitz, H. *Photochem. Photobiol.* **1983**, *38*, 9. The escape of the radicals out of the solvent cage is not included in the femtosecond kinetics, since it occurs on much slower time scales. See: Scott, T. W.; Liu, S. N. *J. Phys. Chem.* **1989**, *93*, 1393. (b) For Ph$_2$C(OH)CO$_2^-$, the value of k_{CC} was directly obtained from the rise of the ketyl radical (see Figure 2), since back electron transfer is negligible as described in ref 17.

(19) Earlier observations were mostly obtained by indirect methods[3d] calibrated by a single direct measurement[3c] on the picosecond time scale.

(20) The effects of electron-withdrawing substituents such as chloro could not be examined, since the charge-transfer absorption band of the [MV$^+$, 4,4-dichlorobenzilate] ion pair was blue-shifted to $\lambda_{CT} < 360$ nm and thus could not be excited with the Ti:sapphire laser system (see footnote 10).

(21) Ketyl radicals are electron-rich by virtue of their very low oxidation potentials[21a] and ease of oxidation in solution. See: (a) Baumann, H.; Merckel, C.; Timpe, H.-J.; Graness, A.; Kleinschmidt, J.; Gould, I. R.; Turro, N. J. *Chem. Phys. Lett.* **1984**, *103*, 497. (b) Kemp, T. J.; Martins, L. J. A. *J. Chem. Soc. Perkin Trans. 2* **1980**, 1708. (c) Engel, P. S.; Wu, W. X. *J. Am. Chem. Soc.* **1989**, *111*, 1830.

(22) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679. (c) Marcus, R. A. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 7. (d) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.

(23) (a) This trend in k_{bet} is termed "inverted" to contrast with the "normal" behavior of increasing reaction rate with increasing thermodynamic driving force. Inverted driving-force dependence of k_{bet} has been observed with methylviologen complexes[12c,d] and with a variety of other electron donor−acceptor complexes.[23b] (b) Asahi, T.; Ohkohchi, M.; Mataga, N. *J. Phys. Chem.* **1993**, *97*, 13132 and references therein.

(24) Polanyi, J. C.; Zewail, A. H. *Acc. Chem. Res.* **1995**, *28*, 119.