

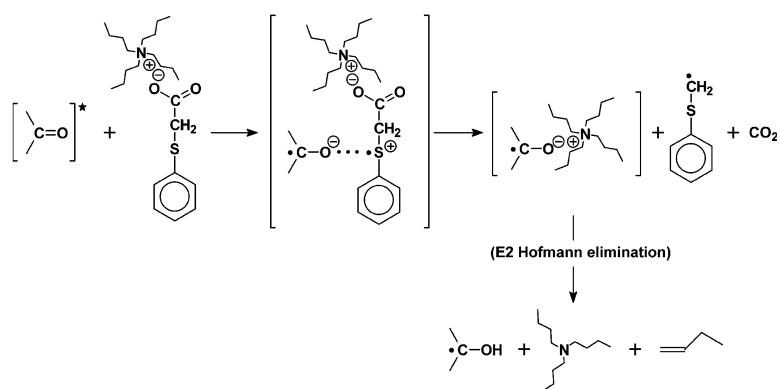
Communication

Unexpected Hofmann Elimination in the Benzophenone–(Phenylthio)acetic Tetrabutylammonium Salt Photoredox System

Andrzej Wrzyszczycki, Marek Pietrzak, Jarogniew Bartoszewicz, Halina Kozubek, Gordon L. Hug, Bronislaw Marciniak, and Jerzy Pa#czkowski

J. Am. Chem. Soc., **2003**, 125 (37), 11182-11183 • DOI: 10.1021/ja036196v • Publication Date (Web): 20 August 2003

Downloaded from <http://pubs.acs.org> on March 29, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Unexpected Hofmann Elimination in the Benzophenone–(Phenylthio)acetic Tetrabutylammonium Salt Photoredox System

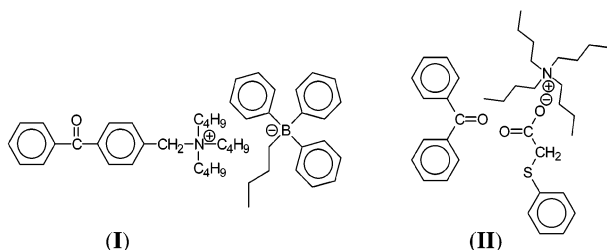
Andrzej Wrzyszczyński,[†] Marek Pietrzak,[†] Jarogniew Bartoszewicz,[‡] Halina Kozubek,[‡] Gordon L. Hug,^{*,§} Bronislaw Marciniak,^{*,‡} and Jerzy Pączkowski^{*,†}

Faculty of Chemical Technology and Engineering, University of Technology and Agriculture, Bydgoszcz, Poland, Faculty of Chemistry, A. Mickiewicz University, Poznań, Poland, and Radiation Laboratory, University of Notre Dame, Indiana 46556

Received May 16, 2003; E-mail: hug.1@nd.edu; marcinia@amu.edu.pl; paczek@atr.bydgoszcz.pl

Photoinduced electron transfer has features that make it attractive in initiating free-radical polymerizations.¹ It is generally a fast process, and it leads directly to radical ions that often fragment to form a variety of secondary radicals that are, themselves, useful polymerization initiators. Electron donors, such as thioethers, are of interest as potential co-initiators because of the tendency of their sulfur-centered radical cations to fragment,² giving the radicals that can start free radical polymerization.³

Radical cations from sulfur-containing aromatic carboxylic acids (SCCA) are good candidates as co-initiators of photopolymerizations. They are susceptible to decarboxylation and deprotonations, leading to carbon-centered radicals that are efficient initiators of free-radical polymerization. For such a co-initiator to be soluble in nonpolar and medium polar monomers, it is prudent to introduce the SCCA as its organic salt. The co-initiator system under study in this work consists of the SCCA's tetraalkylammonium salt plus a photosensitizer that should, itself, be a good electron acceptor, as well as being an efficient light absorber. Such a system is reminiscent of photoinitiators studied by Neckers et al.⁴ (see I).



There are two significant structural differences between the main system under study in the current work (II) and (I). First the tertiary amine group is not covalently attached to a chromophore in our system, and second we use the (phenylthio)acetate anion as the electron donor, instead of a *n*-butyltriphenylborate anion.

The photoreduction of benzophenone (BP) by Ph–S–CH₂–COOH and Ph–S–CH₂–COO[−]N⁺(C₄H₉)₄ was studied by transient nanosecond laser flash spectroscopy⁵ and steady-state photolysis. Laser flash excitation (337 nm) of BP (2×10^{-3} M) in the presence of Ph–S–CH₂–COOH (0.02 M) resulted in the appearance of an absorption corresponding to the presence of the benzophenone ketyl radical (BPH•, $\lambda_{\text{max}} = 550$ nm). For Ph–S–CH₂–COO[−]N⁺(C₄H₉)₄ a new absorption band appears in the red region of the transient absorption spectra (see Figure 1).

At high concentrations of Ph–S–CH₂–COO[−]N⁺(C₄H₉)₄ (0.01 M), such that the triplet state of BP is quenched within a time shorter

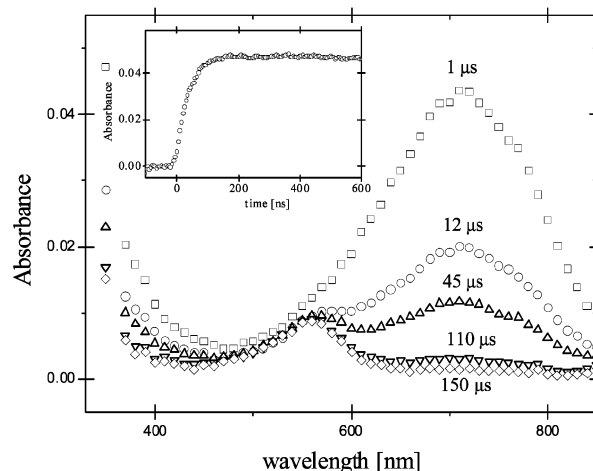


Figure 1. Transient absorption spectra of intermediates following the quenching of benzophenone triplet by Ph–S–CH₂–COO[−]N⁺(C₄H₉)₄ (0.01 M). Inset: kinetic trace at 710 nm.

than 200 ns following the laser pulse, the 710-nm kinetic traces (see inset to Figure 1) clearly indicate the formation of a transient whose growth rate is identical (within experimental error) to the decay rate of the triplet state. This observation suggests that the intermediate absorbing at ab. 710 nm is a primary product from the quenching of the BP triplet by Ph–S–CH₂–COO[−]N⁺(C₄H₉)₄.

There are some observations and facts that are pertinent to an assignment of the 710-nm transient. (i) No 710-nm transients were seen in laser flash experiments performed on either the reaction mixture of BP (0.002 M) – Ph–S–CH₂–COOH (0.02 M) – N(C₄H₉)₄Cl (0.02 M) or in the system containing BP (0.002 M) and Ph–S–CH₂–COOH (0.02 M). However, both of these mixtures yielded the benzophenone ketyl radical (BPH• transient with an absorption maximum at 550 nm). (ii) The 710-nm intermediate cannot be assigned to solvated electrons because any electrons would be scavenged by acetonitrile.⁶ (iii) The benzophenone radical anion (BP^{•−}) in acetonitrile shows a broad band with a maximum around 650–720 nm depending on experimental conditions.⁷ (iv) The formation of a 710-nm transient occurs only when the (phenylthio)acetate anion and the N⁺(C₄H₉)₄ cation are used in experiments as the Ph–S–CH₂–COO[−]N⁺(C₄H₉)₄ salt. Thus, the transient absorption with a maximum at ab. 710 nm can be assigned as the BP^{•−} present in the [BP^{•−}⋯N⁺(C₄H₉)₄] ion pair.^{7b,8}

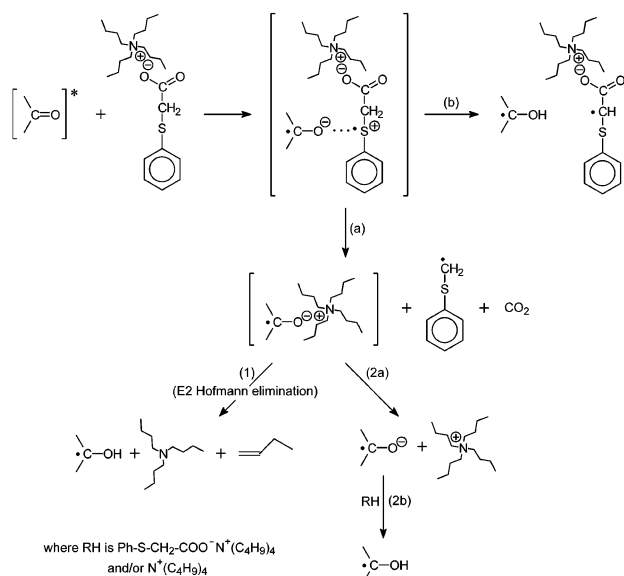
From the photochemical point of view, the most striking feature of the time-resolved transient spectra (Figure 1) is the apparent growth of the long-lived BPH• at the expense of the [BP^{•−}⋯N⁺(C₄H₉)₄] intermediate. This finding suggests that BPH• is formed

[†] Faculty of Chemical Technology and Engineering, University of Technology and Agriculture.

[‡] Faculty of Chemistry, A. Mickiewicz University.

[§] Radiation Laboratory, University of Notre Dame.

Scheme 1



directly from BP^{•-} within the [BP^{•-}...N⁺(C₄H₉)₄] ion pair. Assuming that the decay of the [BP^{•-}...N⁺(C₄H₉)₄] ion pair intermediate leads exclusively to the BPH[•] radical, one can estimate the molar absorption coefficient of the ion pair at 710 nm as $\epsilon_{710} = 18000 \text{ M}^{-1} \text{ cm}^{-1}$ taking the value of $\epsilon_{550} = 3400 \text{ M}^{-1} \text{ cm}^{-1}$ as the molar absorption coefficient of the ketyl radical in acetonitrile.⁵ Furthermore, by applying experimental conditions described in ref 5, one can establish the quantum yield of [BP^{•-}...N⁺(C₄H₉)₄] formation, as equal to 0.35 ± 0.05 . This value, based on our mechanistic assumption, also corresponds to the benzophenone ketyl radical quantum yield.

Steady-state irradiation of the BP/Ph-S-CH₂-COO⁻ N⁺(C₄H₉)₄ photoredox system in MeCN gives CO₂ ($\Phi_{\text{CO}_2} = 0.45 \pm 0.09$), benzopinacole, thioanisole, 1,2-bis(phenylthio)ethane, and two unexpected products, i.e., butene-1 ($\Phi \approx 0.26$) and tributylamine ($\Phi \approx 0.20$). In addition, during the steady-state irradiation, the quantum yield for BP consumption was determined to be $\Phi_{\text{BP}} = 0.42 \pm 0.05$.⁹ The equality of Φ_{CO_2} and Φ_{BP} is evidence that the potential formation of BPH[•] via reaction b can be neglected (Scheme 1) because reaction b does not lead to the formation of CO₂. From comparisons of the quantum yield of [BP^{•-}...N⁺(C₄H₉)₄] formation, the quantum yield of decarboxylation, and the quantum yield of BP consumption, one can conclude that the benzophenone ketyl radical can only be formed from [BP^{•-}...N⁺(C₄H₉)₄].

On the basis of the known photochemistry of sulfur-containing aromatic carboxylic acids^{2,3} and the experimental data, we propose the mechanism in Scheme 1 that is consistent with the observations described above.

In this scheme, electron transfer from the sulfur of the Ph-S-CH₂-COO⁻ N⁺(C₄H₉)₄ gives the benzophenone radical anion and the sulfur-centered radical cation Ph-S^{•+}-CH₂-COO⁻ N⁺(C₄H₉)₄. Experimental data suggests that the electron transfer is followed by decarboxylation that occurs on the nanosecond time scale.¹⁰ Decarboxylation yields an α -alkylthio-type radical (R-S-CH₂•) that escapes from the cage leaving a BP^{•-} forming the ion pair with the tetrabutylammonium cation. The [BP^{•-}...N⁺(C₄H₉)₄] ion pair remaining in the solvent cage is organized and stabilized by electrostatic interaction of the BP^{•-} and the tetrabutylammonium cation. This interaction is probably responsible for the specific properties of the benzophenone radical anions in the ion pair. In addition, since BP^{•-} can be considered as a base, the close proximity

of BP^{•-} and N⁺(C₄H₉)₄ may result in an effective proton abstraction from the β carbon to the nitrogen, yielding butene-1 and tributylamine as products. This reaction is quite analogous to the Hofmann elimination observed in quaternary ammonium ions.¹¹

The earlier mentioned photoinitiating systems, studied by Neckers et al.⁴ (I) behave quite differently. In those systems, electron transfer from borate anions to the BP triplet state gives the (benzophenonylmethyl)-tri-*n*-butylammonium radical anion (not seen on the nanosecond time scale). A further sequence of reactions yields the 4-benzoylbenzyl radical. In our supporting experiments with the *n*-butyltriphenylborate tetrabutylammonium salt as the electron donor, the laser flash photolysis studies clearly show again the formation of a long-lived benzophenone radical anion. This observation indicates that the observed phenomena are general and that the mechanism of the reaction likely applies to other electron donors that can exist as ion pairs in solution.

In summary, we have demonstrated a specific sequence of photoinitiated reactions involving the Hofmann elimination, yielding typical products for this type of elimination. We have also shown that this type of reaction requires the presence of substrates in a specific form, namely the electron donor is present as the (phenylthio)acetic tetrabutylammonium salt instead of as the carboxylic acid.

Acknowledgment. This work was supported by the State Committee for Scientific Research (Grant 4T09A 051 22 and BW-20/01), the A. Mickiewicz University, and the Office of Basic Energy Sciences of the U.S. Department of Energy. This is Document No. NDRL-4450 from the ND Radiation Laboratory.

References

- (1) (a) Oster, G. *Nature* **1954**, 173, 300. (b) Pączkowski, J.; Neckers, D. C. Photoinduced Electron-Transfer Initiating Systems for Free Radical Polymerization, in *Electron Transfer*; Gould, I. R., Ed.; Wiley-VCH: New York, 2001; Vol. 5, pp 516–585.
- (2) (a) Bobrowski, K.; Marciniak, B.; Hug, G. L. *J. Am. Chem. Soc.* **1992**, 114, 10279. (b) Marciniak, B.; Bobrowski, K.; Hug, G. L.; Rozwadowski, J. *J. Phys. Chem.* **1994**, 98, 4854. (c) Bobrowski, K.; Hug, G. L.; Marciniak, B.; Schöneich, C.; Wiśniowski, P. *Res. Chem. Intermed.* **1999**, 25, 285.
- (3) Wrzyszczyński, A.; Filipiak, P.; Hug, G. L.; Marciniak, B.; Pączkowski, J. *Macromolecules* **2000**, 33, 1577.
- (4) Hassoon, S.; Sarker, A.; Rodgers, M. A. J.; Neckers, D. C. *J. Am. Chem. Soc.* **1995**, 117, 11369.
- (5) Experimental conditions of nanosecond flash photolysis: 337 nm nitrogen laser excitation, [BP] = 2 mM, [Ph-S-CH₂-COO⁻ N⁺(C₄H₉)₄] = 10 mM, argon saturated solutions; quantum yields of [BP^{•-}...N⁺(C₄H₉)₄] and of BPH[•] formation were determined using external actinometry: benzophenone triplet state in acetonitrile $\epsilon_{520} = 6500 \text{ M}^{-1} \text{ cm}^{-1}$ (Baral-Tosh, S.; Chattopadhyay, S. K.; Das, P. K. *J. Phys. Chem.* **1984**, 88, 1404) and taking molar absorption coefficients of [BP^{•-}...N⁺(C₄H₉)₄] as $\epsilon_{710} = 18000 \text{ M}^{-1} \text{ cm}^{-1}$ and of BPH[•] as $\epsilon_{550} = 3400 \text{ M}^{-1} \text{ cm}^{-1}$ of the ketyl radical in acetonitrile (Sudhindra, N.; Bhattacharyya, N.; Das, P. K. *J. Chem. Soc., Faraday Trans. 2* **1984**, 80, 1107).
- (6) (a) Singh, A.; Gesser, H. D.; Scott, A. R. *Chem. Phys. Lett.* **1968**, 2, 271. (b) Bell, I. P.; Rodgers, M. A. J.; Burrows, H. D. *J. Chem. Soc., Faraday Trans. 1* **1977**, 73, 315. (c) Burrows, H. D.; Kosower, E. M. *J. Phys. Chem.* **1974**, 78, 112.
- (7) (a) Das, P. K.; Bobrowski, K. *J. Chem. Soc., Faraday Trans. 2* **1981**, 77, 1009. (b) Peters, K. S.; Lee, J. *J. Phys. Chem.* **1993**, 97, 3761 and references therein.
- (8) (a) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, 103, 6403. (b) Mataga, N.; Miyasaka, H. *Prog. React. Kinetics* **1994**, 19, pp 317–430.
- (9) The steady-state measurement conditions: $\lambda_{\text{ir}} = 365 \text{ nm}$; light intensity $I_0 = 1.76 \times 10^{-4} \text{ einstein dm}^{-3} \text{ min}^{-1}$ measured using benzophenone-benzhydrol actinometry (see: Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993), concentrations of BP and Ph-S-CH₂-COO⁻ N⁺(C₄H₉)₄ were equal to 4.0 and 4.8 mM, respectively. Stable products were analyzed by GC and HPLC methods.
- (10) (a) Su, Z.; Mariano, P. S.; Falvey, D. E.; Yoon, U. C.; Oh, S. W. *J. Am. Chem. Soc.* **1998**, 120, 10676. (b) Korzeniowska-Sobczuk, A.; Hug, G. L.; Carmichael, I.; Bobrowski, K. *J. Phys. Chem. A* **2002**, 106, 9251.
- (11) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 4th ed.; Allyn and Bacon: Boston, 1983.

JA036196V