to rationalize pattern ii, as far as ^1H and ^{13}C are concerned, in terms of an effect operating much more strongly in one solvent set than in the other, and manifested to a greater extent at the hydrogens than at the carbons; such an effect might be the solvent anisotropy effect which is believed to be prominent in aromatic solvents.[11] However, it seems likely (though by no means certain) that the greater sensitivity of $\Delta\sigma_{Si}$ than $\Delta\sigma_C$ to changing R from C_6H_{11} to C_6H_5 is due to an influence other than solvent anisotropy, perhaps dispersion effects. More detailed interpretations into the nature of these interactions will be discussed in connection with a more comprehensive experimental study.

Acknowledgment. The authors gratefully acknowledge the support of the National Science Foundation. They also thank the staff of the Molecular Biodynamics Laboratory (University of California, Berkeley) for their cooperation and use of the 220-MHz spectrometer.

(11) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

(12) To whom correspondence should be sent at Department of Chemistry, Colorado State University, Fort Collins, Colo. 80521.

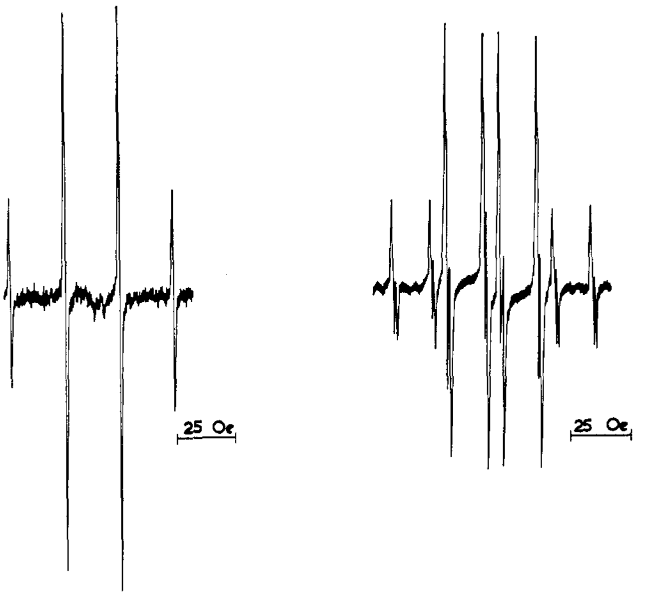
M. Bacon, G. E. Maciel,*[12] W. K. Musker, R. Scholl
Department of Chemistry, University of California
Davis, California 95616

Received February 8, 1971

Optical and Electron Spin Resonance Detection of Radical Intermediates in the Photooxidation of Organic Molecules in Solution by Transition Metal Ions

Sir:

Although the thermal oxidations of a great many organic substrates by transition metal ions are believed to involve free-radical intermediates, the evidence for these transient species has rested chiefly on the nature of the products of reaction and on induced effects such as polymerization, sensitivity to molecular oxygen, etc.[1-3] Direct spectroscopic evidence for radicals in solution has been forthcoming only in a few specialized cases, such as the oxidation of phenols by Ce^{IV} in a flow system, which produces phenoxyl radicals detectable by electron spin resonance (esr) spectroscopy.[4] The interrelation between thermal and photochemical redox processes, which has been discussed by Kochi[3] and Adamson, *et al.*,[5] has prompted us to attempt to characterize spectroscopically radical intermediates in the photooxidations of organic molecules in solution by transition metal ions (abundant evidence for such intermediates in photooxidations of carboxylic acids having been secured by product studies[3]). Our aim has been accomplished for both alkyl and aromatic radicals in the photooxidations of simple organic substrates, such as alkanols and benzilic acid, by a number of transition metal ions including Ce^{IV}, U^{VI}, Cu^{II}, Fe^{III}, and V^{V}. The characterization is by esr for the alkyl radicals and by both optical and esr spectroscopy for the $Ph_2\dot{C}OH$ radical. Details of typical experiments are as follows.



(a) (b)

Figure 1. Esr spectra obtained by photolyzing ($\lambda > 300$ nm) solutions in ethanol at $5 \times 10^{-3} M$ concentrations of (a) ceric ammonium nitrate and (b) uranyl perchlorate.

(i) When 5×10^{-3} *M* solutions in neat degassed ethanol of, first, ceric ammonium nitrate and, secondly, uranyl perchlorate are flowed under pressure at 185°K through a flat cell cooled by cold nitrogen gas and situated in the cavity of an esr spectrometer while under filtered irradiation ($\lambda > 300$ nm) from a focused 1-kW xenon point source,[6,7] then the spectra illustrated in Figures 1a and b, respectively, are obtained. Clearly the ethanol complex of U^{VI} decomposes to give $CH_3\dot{C}HOH$ with $a_{CH} = 15.8$, $a_{OH} = 1.56$, and $a_{CH_3} = 22.9$ Oe while the Ce^{IV} complex gives $CH_3\cdot$ by a C–C cleavage mechanism ($a_H = 22.8$ Oe). Ceric perchlorate gave the same result as the ceric ammonium nitrate solution, indicating that $NO_2\cdot$ or $NO_3\cdot$ is not significantly affecting the photochemistry; the behavior of Ce^{IV} at 185°K, however, contrasts strongly with that observed at 77°K[8] when the radical produced almost exclusively is $CH_3\dot{C}HOH$. Other alcohols RCH_2OH (R = C_2H_5, *n*-C_3H_7) yield the well-resolved esr spectra of R· on photooxidation with Ce^{IV} at 185°K, although the radical at 77°K is predominantly $R\dot{C}HOH$.

(ii) When a solution in ethanol of benzilic acid (10^{-2} *M*) and ferric perchlorate (10^{-3} *M*) is photolyzed at 185°K in conjunction with the same esr technique, a complex spectrum is produced which is analyzed as that of the benzophenone ketyl radical $Ph_2\dot{C}OH$ in terms of the coupling constants $a_{2,6,2',6'} = 3.24$, $a_{3,5,3',5'} = 1.24$, $a_{4,4'} = 3.70$, $a_{OH} = 2.32$ Oe (all ±0.01 Oe); these are in good agreement with those of Wilson[9] who examined $Ph_2\dot{C}OH$ by photolyzing benzophenone in various solvents with a similar irradiation facility.

---

(1) K. B. Wiberg, Ed., "Oxidation in Organic Chemistry, Part A," Academic Press, New York, N. Y., 1965.

(2) W. S. Trahanovsky, P. J. Flash, and L. M. Smith, *J. Amer. Chem. Soc.*, **91**, 5068 (1969), and preceding papers in this series.

(3) R. A. Sheldon and J. K. Kochi, *ibid.*, **90**, 6688 (1968), and references cited therein.

(4) T. J. Stone and W. A. Waters, *Proc. Chem. Soc. London*, 253 (1962).

(5) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

(6) R. S. Davidson and R. Wilson, *J. Chem. Soc. B*, 71 (1970).

(7) R. Livingston and H. Zeldes, *J. Chem. Phys.*, **53**, 1406 (1970), and preceding papers in this series.

(8) D. Greatorex and T. J. Kemp, *Trans. Faraday Soc.*, **67**, 56 (1971).

(9) R. Wilson, *J. Chem. Soc. B*, 84 (1968).

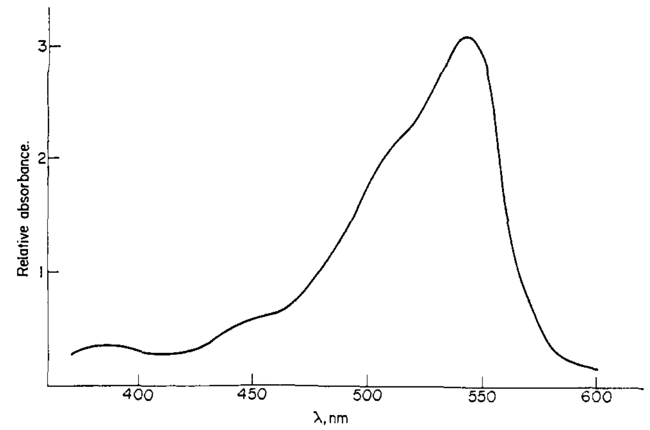
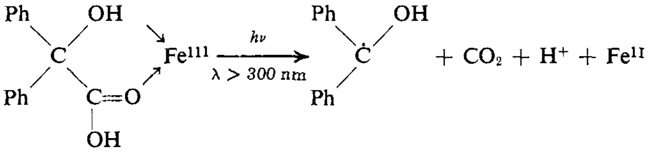


Figure 2. Flash photolysis spectrum obtained from a solution in ethanol of uranyl perchlorate (2 × 10^{-3} M) and benzilic acid (2 × 10^{-3} M).

To ascertain the time scale of production of $Ph_2\dot{C}OH$ we have also flash photolyzed with light of $\lambda > 300$ nm solutions of benzilic acid and various perchlorates, including those of Fe^{III}, U^{VI}, V^{V}, and Cu^{II} (all at 2 × 10^{-3} M concentration). The optical spectrum obtained spectrographically with U^{VI} 1 μsec after the flash (1.1 kJ, ~25 μsec) shown in Figure 2 (λ_{max} 542 ± 3 nm) is identical with that given by Porter and Wilkinson.[10] The other metal ions behaved similarly. Benzilic acid alone gave no transient absorption when flashed with light of $\lambda > 300$ nm and addition of 10^{-2} M naphthalene, which would have quenched any process of abstraction by benzophenone impurity[10] in the benzilic acid, was without effect on any of these systems.

In both the esr and flash photolysis experiments the substrate is subjected to oxidative decarboxylation by the complexed oxidant, *e.g.*



$$Ph_2C(OH)C(=O)OH \rightarrow Fe^{III} \xrightarrow[\lambda > 300\ nm]{h\nu} Ph_2\dot{C}OH + CO_2 + H^+ + Fe^{II}$$

---

(10) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961).

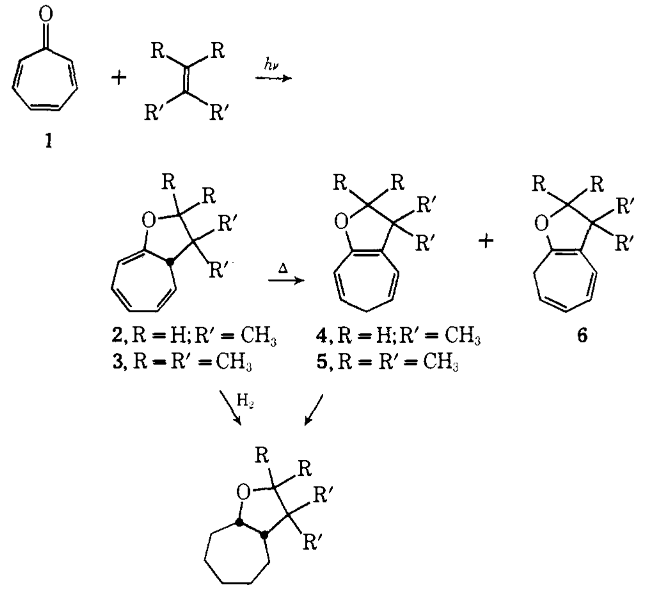
H. D. Burrows, D. Greatorex, T. J. Kemp*
School of Molecular Sciences, University of Warwick
Coventry CV4 7AL, United Kingdom

Received December 12, 1970

Photochemical 8 + 2 Cycloadditions of Tropone

Sir:

The thermal cycloaddition of tropone to various unsaturated molecules gives, depending on the nature of the addend and on reaction conditions, products resulting from 6 + 4, 4 + 2, and 8 + 2 addition processes,[1] all of which are predicted to be symmetry allowed by the now well-known orbital symmetry selection rules.[2] Tropone has been reported to undergo photochemical dimerization to afford, in acetonitrile, a mixture of 6 + 4, 6 + 2, and 4 + 2 dimers,[3] and in aqueous sulfuric acid, a low yield of the anti 6 + 6 dimer.[4] The 6 + 4 dimer, at least, seems to be the result of a nonconcerted, multistep process and the Woodward–Hoffmann rules of course do not apply to this and other two-step processes. We report here the *photochemical* 8 + 2 addition of tropone to simple olefins, which leads to products of the 8-oxabicyclo[5.3.0]decane type.



1

2, R = H; R' = CH_3
3, R = R' = CH_3

4, R = H; R' = CH_3
5, R = R' = CH_3

6

7, R = H; R' = CH_3

Irradiation of tropone (**1**, 0.02 mol, Pyrex filter, acetonitrile solvent) for 3 hr in the presence of a tenfold excess of isobutene gave 35–40% of a 1:1 adduct, **2**, bp 44–45° (0.2 mm). Compound **2** exhibits infrared bands at 1634 (m) and 1070 (s) cm^{-1}, indicative of a vinyl ether linkage; the nmr spectrum (CCl_4) includes signals at τ 3.72 (2 H, m, H-4, H-5), 4.26 (2 H, m, H-3, H-6), 4.77 (1 H, 2 d, J = 10.1, J' = 3.0 Hz, H-2), 5.88 (1 H, 2 d, J = 3.0, J' = 2.2 Hz, H-7), 6.36 (2 H, s, $-OCH_2$), and 8.74 and 8.88 (3 H each, s, $-CCH_3$). The chemical-shift assignments and couplings were verified by double resonance experiments and by comparison with the spectrum of the thermal adduct of tropone and diphenylketene, whose structure is analgous to that of **2**.[5] Adduct **2** exhibits $\lambda_{max}^{CH_3OH}$ 279 nm (ϵ 3400), in agreement with expectation for a fused cycloheptatriene chromophore, and a mass spectral parent ion at m/e 162 (relative intensity 40) as well as major fragment ions at 147 (100), 119 (62), 107 (48), 91 (95), and 77 (82). Heating **2** to 180° under nitrogen, or simply gas chromatography on a column at 200°, caused isomerization *via* 1,5-sigmatropic shifts of hydrogen to the air- and heat-sensitive isomers **4** and **6** (3:1 ratio). Compound **4** showed ir_{max}^{film} 1640 and 1029 cm^{-1}; nmr (CCl_4) τ 4.08 and 4.12 (2 H, 2 d,

---

(1) (a) R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Commun.*, 15 (1966); (b) K. N. Houk and R. B. Woodward, *J. Amer. Chem. Soc.*, **92**, 4143, 4145 (1970), and references cited therein; (c) M. Oda, M. Funamizu, and Y. Kitaharu, *Chem. Commun.*, 737 (1969).

(2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969.

(3) (a) A. S. Kende, *J. Amer. Chem. Soc.*, **88**, 5026 (1966); (b) A. S. Kende and J. E. Lancaster, *ibid.*, **89**, 5283 (1967).

(4) T. Mukai, T. Tezuka, and Y. Akasaki, *ibid.*, **88**, 5025 (1966).

(5) (a) Nmr data at 100 MHz are given for the tropone–diphenylketene adduct by C. Jutz, J. Rommel, I. Lengyel, and J. Feeney, *Tetrahedron*, **22**, 1809 (1966). However, the structure assigned by these authors was later shown to be incorrect; see (b) R. Gompper, A. Studemeer, and W. Elser, *Tetrahedron Lett.*, 1019 (1968). Furthermore, the spectrum we obtain for this adduct exhibits couplings significantly different from those published by Jutz, *et al.*, and closely resembles the spectra of **2** and **3**.