way with Zn, Co(II), Mn(II), or Mo(II), instead of Fe(II); however, these latter compounds may have physical, chemical, and catalytic properties significantly different from the aluminum–iron complex.

Oxygen binding by this iron oxo alkoxide in heptane solution at 298°K occurs rapidly until a O_2/Fe ratio of about 0.25; then a slower absorption is observed until a final O_2/Fe (0.5) ratio is reached.

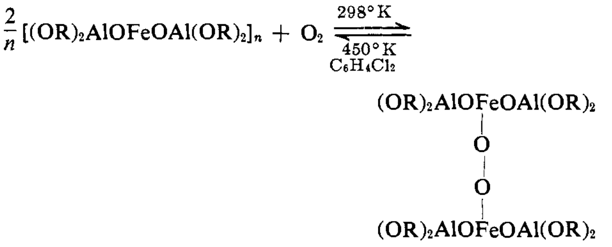
The kinetics of molecular oxygen absorption do not correspond to any simple reaction order process, most probably as the degree of association of the oxo alkoxide molecules in solution changes from $n = 8$ (initial complex) down to $n = 2$ (completely oxidized complex) in the course of the oxygen absorption process (cryoscopic measurements).

The oxidized compound behaves as a strong peroxidic oxidation agent toward KI in 10 *N* hydrochloric acid, immediate and quantitative oxidation of iodide to I_2 occurring under argon at 373°K (two molecules of I_2 per molecule of complex I).

Oxygen may also be swept off quantitatively by refluxing the complex in *o*-dichlorobenzene. Upon oxidation, the solution which is initially green (in heptane or other solvents) turns red; refluxing in $C_6H_4Cl_2$ yields back the initial green coloration and the process may be repeated several times.

By redox titration, Fe(II) is found to be the dominant species in the unoxidized complex, while, after O_2 absorption, Fe(III) is the only valence state as observed by a specific EDTA complexometric titration. This valency change of Fe is supported by uv–visible spectra which show a band at 950 nm in the unoxidized complex; this band, characteristic of the high-spin Fe(II) complexes and assigned to the $^5T_{2g} \rightarrow {}^5E_g$ transition,[2] disappears upon oxidation.

Supported by the former data, a reversible oxygen transport mechanism (eq 2) may be postulated.



$$\frac{2}{n}[(OR)_2AlOFeOAl(OR)_2]_n + O_2 \underset{\substack{450°K \\ C_6H_4Cl_2}}{\overset{298°K}{\rightleftharpoons}} \begin{array}{c} (OR)_2AlOFeOAl(OR)_2 \\ | \\ O \\ | \\ O \\ | \\ (OR)_2AlOFeOAl(OR)_2 \end{array} \qquad (2)$$

I

The reversibility of a mechanism such as eq 2 (with respect to Fe) has been ascertained over four complete redox cycles from epr data. No signal is detected for the unoxidized material at 298°K; hence, this species probably contains Fe(II) which is not detected by epr at this temperature. Upon oxidation, a broad resonance line (peak-to-peak line width = 1500 Oe) centered near $g = 2.3$ appears gradually. Internal calibration with respect to a known standard (Varian Strong Pitch) was used to evaluate the relative spectral intensities and to show that the epr signal was of the order of magnitude expected for the oxidized compound in solution at the used concentration level, hence ruling out impurity effects; this signal is assigned to Fe(III) species.

The epr signal of the oxidized solid compound has an intensity which is nearly independent of temperature in the range 77–320°K. The behavior of this signal compares itself quantitatively to that reported for Fe(III) in zeolites;[3] accordingly, we propose that the solid compound shows ferromagnetic behavior.

From a catalytic standpoint, this reversible oxidation of the ferrous ions, associated with oxygen transport, seems quite interesting and rather unusual; to our knowledge, very few similar examples have been reported: one in the case of heterogeneous catalysts[4] and another one for a soluble complex.[5]

Acknowledgment. The authors are indebted to the Institut Français du Pétrole for financial support.

---

[2] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1966, p 857.

[3] L. S. Singer and D. N. Stamires, *J. Chem. Phys.*, **42**, 3299 (1965).

[4] R. L. Garten, W. N. Delgass, and M. Boudart, *J. Catal.*, **18**, 90 (1970).

[5] L. Vaska, Abstracts of the American Chemical Society Summer Symposium on Coordination and Activation of Small Molecules by Transition Metals, Buffalo, N. Y., June 1972.

T. Ouhadi, A. J. Hubert, Ph. Teyssie*
Laboratoire de Chimie Macromoléculaire
et de Catalyse Organique

E. G. Derouane
Laboratoire de Résonance Magnétique et de Catalyse
Université de Liège au Sart Tilman
4000 Liège, Belgium

Received February 24, 1973

A General Method for the Determination of Steric Effects during Collisional Energy Transfer. Partial Photoresolution of Penta-2,3-diene

Sir:

Since an electronically excited sensitizer (P*) and a quencher (A) must be very close during collisional energy transfer, bulky groups close to the chromophores of P and A should be important in determining the efficiency of transfer. Demonstration of such effects has proved difficult[1] and only in a few cases have they been reported.[2,3] The main problem has been to separate a group's electronic pertubation on a chromophore (auxochromic effect) from its steric influence on the ease of approach of another molecule. We have devised a general method for the study of steric influences on collisional energy transfer which excludes auxochromic effects.[4] We report here its first application: the partial photoresolution of penta-2,3-diene (**1**).

Since the energy levels of any pair of enantiomeric allenes are the same, the rate constants for energy transfer from a nonchiral P to (*R*)- and (*S*)-**1** must be identical (*i.e.*, $k_r = k_s$). When P is optically active, k_r and k_s need not be equal. The collision complexes, $[P\cdots(S)\text{-}\mathbf{1}]^*$ and $[P\cdots(R)\text{-}\mathbf{1}]^*$ are diastereomeric and, in principal, chemically distinguishable. We have mea-

---

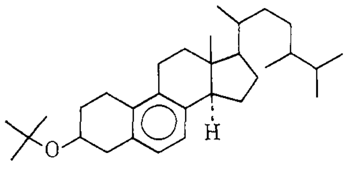
[1] See, for example, P. J. Wagner, J. M. Mc Grath, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 6883 (1972).

[2] (a) G. S. Hammond and R. S. Cole, *ibid.*, **87**, 3256 (1965); (b) W. G. Herkstoeter, L. B. Jones, and G. S. Hammond, *ibid.*, **88**, 4777 (1966).

[3] K. Janda and T. S. Wattack, *ibid.*, **94**, 305 (1972).

[4] The work of Hammond and Cole, ref 2a, originally led us to consider this problem. Their system, except for the existence of a meso form of their quencher, would have allowed exactly the same treatment as applied here. We thank Professor Hammond for helpful discussions. For a pertinent, theoretical discussion of asymmetric inductions, see L. Salem, *J. Amer. Chem. Soc.*, **95**, 94 (1973).

sured k_r/k_s with the *tert*-butyl ether of 21,22-dihydroneoergosterol (**2**) as a sensitizer.[5]



2

Scheme I, although simplified, represents the probable, important steps in the sensitized isomerization of **1** by **2**. At the photostationary state for **1**, eq 5 is

Scheme I

$$\mathbf{2} \xrightarrow{h\nu} \mathbf{2}^* \qquad (1)$$

$$\mathbf{2}^* + (R)\text{-}\mathbf{1} \xrightarrow{k_r} \mathbf{2} + \mathrm{X}^* \qquad (2)$$

$$\mathbf{2}^* + (S)\text{-}\mathbf{1} \xrightarrow{k_s} \mathbf{2} + \mathrm{X}^* \qquad (3)$$

$$\mathrm{X}^* \xrightarrow{k_x} \beta[(R)\text{-}\mathbf{1}] + (1 - \beta)[(S)\text{-}\mathbf{1}] \qquad (4)$$

$$k_s/k_r = ([(R)\text{-}\mathbf{1}]/[(S)\text{-}\mathbf{1}])_{\mathrm{PSS}}[(1 - \beta)/\beta] \qquad (5)$$

valid. The ratio of $[(R)\text{-}\mathbf{1}]/[(S)\text{-}\mathbf{1}]$ can be determined from the specific rotation of **1**, measured after prolonged sensitization by **2**, and from the absolute rotation of optically pure **1**, calculated by Brewster[6] to be $[\alpha]_{589}$ 174°. Subject to the provisions that X* is achiral and that it does not begin to decay to **1** until it separates from **2**, the decay ratio, $(1 - \beta)/\beta$, *must be* unity (*vide infra*).

The sequence for the $R \rightleftharpoons S$ isomerization of chiral allenes is thought to proceed from an antiplanar gound state and pass through one or both of two possible planar (achiral) excited states, *cis*-X* and *trans*-X*, which decay to regenerate the ground state.[7] Even if (*R*)- and (*S*)-**1** produce different ratios of *cis*-X*/*trans*-X* after excitation by **2**, eq 5 remains valid since *each* excited state must decay with equal probability to (*R*)- and (*S*)-**1**.[8]

In a typical experiment,[5] a 6-ml portion of a deoxygenated, argon-saturated isooctane solution of racemic **1** (4.3×10^{-2} *M*; $[\alpha]_{250}$ 0 ± 0.5°[11] (isooctane)) and **2** (5.3×10^{-2} *M*) was irradiated at 0° for 3 hr with four 125-W low-pressure mercury lamps. Glpc analysis demonstrated that 100 ± 5% of the starting **1** remained after irradiation. The allene **1** and part of the solvent were distilled directly from the irradiation vessel and their ORD spectrum was recorded. A graph of $[\alpha]$ *vs.* λ was constructed for it and for a solution of independently synthesized *S*-enriched **1** ($[\alpha]_{589}$ 1.7 ± 0.3°).[12]

From a comparison of the two curves and from Brewster's[6] calculated rotation for optically pure **1**, the per cent of resolution of irradiated **1** was calculated. Since both the ORD curves of (*S*)-**1** and of irradiated **1** were negative in the ultraviolet region, sensitization by **2** produces an excess, *ca.* 3.4%, of (*S*)-**1** (k_r/k_s = 51.7/48.3). Irradiations for periods up to 9 hr did not change the enantiomeric compositions or absolute quantities of **1**. The ORD curve of **2** is positive throughout the uv region.

Molecular models (Fisher–Taylor–Hirschfelder) indicate a slight steric preference for transfer from excited **2** to (*R*)-**1**. They also predict that good π overlap between **2** and either enantiometer of **1** will be difficult.

By the PPP method, Borden[7a] calculated E_s = 147 kcal/mol and E_t = 99 kcal/mol for the first excited singlet and triplet of antiplanar allene. This makes "vertical" energy transfer from a tetraalkyl-substituted phenyl chromophore (E_s = 105 kcal/mol,[13] E_t = 80 kcal/mol[14]) to **1** improbable. A reversible, stepwise addition of **1** to the phenyl chromophore of **2** is unlikely, also, since irradiation of benzene–allene solutions produces stable adducts.[15] Calculated energies for the planar excited states of allene[7a] (E_s = 94 kcal/mol, E_t = 62 kcal/mol) indicate that a "thermally activated" transfer[16] could occur. In fact, it is possible that an *electronically* excited state of **1** is not obtained during isomerization. Elucidation of the nature of the energy transfer step[17] and experiments with other allenes and optically active sensitizers are in progress and will be presented in a full paper.

While we have not mentioned the possible synthetic importance of this work it should be noted that with better selectivity, this method would offer a simple, one-step alternative to existing methods[10, 12, 18] for the resolution of allenes.

Acknowledgments. We wish to thank the Conselho Nacional de Pesquisas of Brazil, the National Academy of Sciences, the National Science Foundation, the Agency for International Development, and Atlantic Richfield of Brazil for generous financial support.

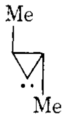
---

(5) Experimental details will be included in a full paper.

(6) J. H. Brewster, *Top. Stereochem.*, 2, 35 (1967).

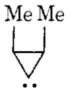
(7) (a) W. T. Borden, *J. Chem. Phys.*, **45**, 2512 (1966); (b) H. R. Ward and E. Karafiath, *J. Amer. Chem. Soc.*, **91**, 7475 (1969). For other discussions of this problem, see: R. J. Buenker, *J. Chem. Phys.*, **48**, 1368 (1968); J. M. Andre, M. C. Andre, and G. Leroy, *Chem. Phys. Lett.*, 3, 695 (1969); L. J. Schaad, *Tetrahedron*, **26**, 4115 (1970); L. J. Weimann and R. E. Christoffersen, *J. Amer. Chem. Soc.*, **95**, 2074 (1973). In each of these, the calculated barrier to rotation is lower than was calculated in ref 7a.

(8) It is possible,[9a] but improbable,[7b,9b] in this case that the ultimate precursors to the regeneration of **1** after its excitation are cyclopropylidenes, i–iii. Since i and ii are chiral, they could "decay" *via* a conrotatory opening to give an excess of (*R*)- or (*S*)-1.[10] However, if any point along the reaction, **1** → X* → 1, includes a planar configuration, eq 5 is still valid. The work of Ward and Karafiath[7b] indicates that a planar configuration is obtained.



i

ii



iii

(9) (a) W. T. Borden, private communication in ref 7b; (b) W. T. Borden, *Tetrahedron Lett.*, 447 (1967).

(10) W. M. Jones and J. M. Walbrick, *ibid.*, 5229 (1968).

(11) We wish to thank Miss Adelaide Faljoni, Mr. Kenji Nishiyama, and Dr. Klaus Zinner for their gracious assistance, cooperation, and advice in obtaining the ORD spectra.

(12) W. L. Waters and M. C. Caserio, *Tetrahedron Lett.*, 5233 (1968); W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, 90, 6741 (1968).

(13) I. B. Berlman, "Handbook for Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965.

(14) W. G. Herkstroeter, A. A. Lamola, G. S. Hammond, and S. L. Murov, unpublished results.

(15) D. Bryce-Smith, B. E. Foulger, and A. Gilbert, *J. Chem. Soc., Chem. Commun.*, 664 (1972).

(16) A. A. Lamola in "Energy Transfer and Organic Photochemistry," A. A. Lamola and N. J. Turro, Ed., Interscience, New York, N. Y., 1969, pp 60–70.

(17) Experiments to determine which excited state of 2 is responsible for isomerization are in progress.

(18) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, pp 386–389.

One of us (C. S. D.) acknowledges a scholarship from the Fundação de Amparo a Pesquisa do Estado de Sao Paulo.

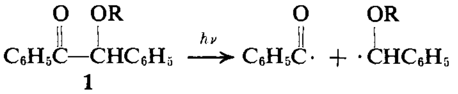
[19] Overseas Fellow of the National Academy of Sciences.

Carmela Satchy Drucker, Vicente G. Toscano, Richard G. Weiss*[19]
Instituto de Química, Universidade de São Paulo
Cidade Universitária, São Paulo, Brazil
Received March 17, 1973

Photochemistry of Benzoin Ethers. Type I Cleavage by Low Energy Sensitization

Sir:

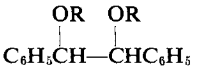
The photochemistry of benzoin ethers (α-alkoxy-α-phenylacetophenone derivatives) is of considerable interest, particularly in view of their extensive commercial usage as "photosensitizers" in "solventless" coatings and printing inks curable by ultraviolet radiation.[1,2] Recent studies on product quenching[3] and the utilization of radical trapping agents[4] have provided evidence for facile type I cleavage in this system (eq 1). The



$$C_6H_5C(=O)-CH(OR)C_6H_5 \xrightarrow{h\nu} C_6H_5\dot{C}(=O) + \cdot CH(OR)C_6H_5 \quad (1)$$

1

a, R = $(CH_3)_2CH-$



$$C_6H_5CH(OR)-CH(OR)C_6H_5$$

2

resulting radicals presumably initiate conventional polymerization of vinyl monomers,[3] although the reported incorporation of more than 12 benzoin methyl ether residues per poly(methyl methacrylate) molecule[5] remains unexplained. Herein, we wish to report the results of a mechanistic study on the photochemistry of benzoin isopropyl ether, which, we believe, provides the first example of low energy sensitization of type I cleavage.

Irradiation of benzoin ethers (**1**) in benzene provides α,α'-dialkoxybibenzyls (**2**) in high yield, together with benzaldehyde and benzil.[3] At low conversions in acetonitrile, benzoin isopropyl ether (**1a**) yields only **2a** and benzil in approximately equal amounts as evidenced by glc analysis, although several products, which were not identified, appeared with time at the expense of benzil. Quantum yields for the formation of **2a** (<10% conversions) were found to be 0.35 and 0.20 at 313 and 366 nm, respectively.[6] The phosphorescence spectrum of **1a**, obtained in an EPA glass at 77°K, exhibited 3 bands with vibrational spacings of 1200–1600 cm^{-1} and a lifetime of 30 msec, characteristic of an n,π^* state.[7] The short wavelength band corresponded to 73.4 kcal/mol.

Based on the lack of quenching of the photocleavage of benzoin ethers by naphthalene (<1 *M*) and 1,3-pentadiene (>1 *M*), Heine has suggested that reaction may occur *via* the excited singlet state of **1**.[3] Our analogous results with 1,3-cyclohexadiene support the intermediacy of a short-lived reactive state. However, we find that the formation of **2a** is sensitized by *m*-methoxyacetophenone (E_t = 72.4 kcal/mol).[9] The efficiency of sensitization exhibits a slight dependency on the concentration of *m*-methoxyacetophenone, increasing from 0.10 to 0.16 as the concentration of sensitizer decreases from 0.48 to 0.10 *M*. The corresponding yield of 0.35 in the direct reaction at 313 nm raises the possibility of a competitive singlet process. However, it appears as likely that the reduced yield may reflect inefficient energy transfer to **1a** (0.078 *M*) as a consequence of the equivalent triplet energies and self-quenching of the sensitizer.[10] The latter interpretation is more in accord with related findings on dibenzyl[11] and cyclic[12] ketones, particularly in view of the faster intersystem crossing rates of aryl ketones.[13]

Thus, the quenching and sensitization results indicate that the triplet-state lifetime of the benzoin ethers is considerably less than 10^{-10} sec, which may be attributed to facile type I cleavage. The absence of products resulting from intramolecular H abstraction, which has been reported to occur with rates on the order of 10^{10} sec^{-1} for α-alkoxyacetophenones,[14] is in accord with this conclusion.

Of considerable significance was the finding that Michler's ketone (4,4′-bis(dimethylamino)benzophenone) (E_t = 61.0 kcal/mol)[15] sensitized the formation of **2a** with ϕ = 0.05 at 366 nm in acetonitrile. This experiment was undertaken as part of an investigation of synergism in radiation curing, as, for example, has been implied for combinations of Michler's ketone and benzophenone.[16] Recently, Hammond has clarified this interaction by providing evidence for an exciplex, derived from the triplet state of Michler's ketone, in

---

[1] For a discussion of the economic and ecological aspects of ultraviolet radiation curing, see S. B. Levinson, *J. Paint. Technol.*, **44**, 28 (1972).

[2] For a review on photopolymerization, see G. Oster and N.-L. Yang, *Chem. Rev.*, **68**, 125 (1968).

[3] (a) H.-G. Heine, H.-J. Rosenkranz, and H. Rudolph, *Angew. Chem., Int. Ed. Engl.*, **11**, 974 (1972); (b) H.-G. Heine, *Tetrahedron Lett.*, 4755 (1972).

[4] A. Ledwith, P. J. Russell, and L. H. Sutcliffe, *J. Chem. Soc., Perkin Trans. 2*, 1925 (1972).

[5] W. E. Mochel, J. L. Crandall, and J. H. Peterson, *J. Amer. Chem. Soc.*, 77, 494 (1955).

[6] Irradiations of degassed solutions of **1a**, 0.078 *M* in acetonitrile, were conducted in a merry-go-round apparatus with a 450-W Hanovia medium-pressure mercury lamp. The 313 and 366 nm lines were isolated by a potassium chromate solution and a Corning 7-83 filter combination, respectively. Quantum yields for the formation of **2a**, monitored by glc analysis, were determined by 0.05 *M* benzophenone–0.20 *M* benzhydrol actinometry, for which ϕ was taken as 0.85. The quantum yield values in the text account for the requirement of 2 photons per molecule of **2a** formed. The wavelength effect on quantum yields probably reflects higher light intensity at 313 nm, rather than incomplete vibrational equilibration in the excited state manifold of **1a**.

[7] Emission and excitation spectra were obtained on a Perkin-Elmer MFP-3 fluorescence spectrophotometer with a phosphorescence attachment. A relatively weak emission ($\phi \approx 0.01$, benzophenone standard)[8] with the same general appearance and band positions of the low-temperature spectrum, although broader, was also observed at room temperature in carbon tetrachloride solution (0.01 *M* **1a**). Based on studies with several benzoin ether derivatives as well as sensitization by *m*-methoxyacetophenone and lack of quenching by 1,3-cyclohexadiene, we suspect that the room temperature emission is predominately short-lived phosphorescence of **1a**. This aspect of our study will be discussed in a full report.

[8] J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle, and M. Wrighton, *J. Amer. Chem. Soc.*, **92**, 410 (1970).

[9] N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *ibid.*, **89**, 5466 (1967).

[10] O. L. Chapman and G. Wampfler, *ibid.*, **91**, 5391 (1969).

[11] (a) P. S. Engel, *ibid.*, **92**, 6074 (1970); (b) W. K. Robbins and R. H. Eastman, *ibid.*, **92**, 6076 (1970).

[12] J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Barltrop, and J. D. Coyle, *ibid.*, **93**, 7213 (1971).

[13] M. A. El-Sayed, *Accounts Chem. Res.*, **1**, 8 (1968). See, also, P. M. Rentzepis and G. E. Busch, *Mol. Photochem.*, **4**, 353 (1972).

[14] F. D. Lewis and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 311 (1970).

[15] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

[16] J. F. Ackerman, J. Weisfield, R. G. Savageau, and G. Beerli, U. S. Patent 3,673,140 (1972); *Chem. Abstr.*, 77, 890223 (1972).