incorrect.<sup>30</sup> They have also inferred that substituents may alter the value of  $B_2^{\text{C}}$ . Thus, the results for 1-4 may be influenced adversely. However, the observed relationship can also be accommodated by the view that the geometry of the alkyl group alters during rotation through angle  $\theta$ . This suggestion is based on the fact that the values of  $\langle \theta \rangle$  derived from  $a_{\beta}^{H}$ for 1-4 do not, in general, correspond to conformations at potential energy minima. At the higher energy, steric interactions may increase the  $C_p C_{\alpha} C_{\beta}$  bond angle, lengthen the  $C_p-C_{\alpha}$  or  $C_{\alpha}-C_{\beta}$  bond, or more likely result in some combination of these deformations to decrease  $a_{\beta}^{C,12}$  With these ideas in mind we reexamined the results shown in Figures 1 and 2. Structural constraints in 5-8 restrict  $C_{\beta}$  to conformations which minimize steric repulsions. The  $a_{\beta}^{c}$  values for 5-8 very nearly conform to linear relationships. The data for 1-4 deviate from these relationships. However, these deviations may be related to structural deformations which are more significant for the cyclopropyl, isopropyl, and *tert*-butyl groups in 2-4 than for the ethyl group in 1. Further study will be necessary to verify these suggestions.

(12) The  $C_p C_{\alpha} C_{\beta}$  angle may decrease when  $\theta$  is small. This decrease may be attributed to steric factors or to electron transfer mechanisms; see, e.g., P. J. Krusic and J. K. Kochi, J. Amer. Chem. Soc., 93, 846 (1971).

(13) Fannie and John Hertz Foundation Fellow at The University of Chicago.

> Leon M. Stock,\* Michael R. Wasielewski<sup>13</sup> Department of Chemistry, University of Chicago Chicago, Illinois 60637 Received July 23, 1973

## **Oxidation of Alkoxides to Carbonyl Compounds** by Singlet Oxygen<sup>1</sup>

Sir:

Singlet oxygen has been shown to react with nucleophilic substrates such as olefins,<sup>2</sup> amines,<sup>3</sup> sulfides,<sup>4</sup> and carbanions,5 to produce products which vary with the nature of the substrate. We have now found that primary and secondary alkoxide ions are readily converted to aldehydes and ketones by dye-sensitized photooxidation.<sup>6,7</sup> The results are summarized in Table I.

$$\begin{array}{c} O^{-} & O \\ RCHR' + O_2 \xrightarrow{h\nu} & RCR' + OOH^{-} \\ RCHR' + O_2 \xrightarrow{h\nu} & RCR' + OOH^{-} \end{array}$$

Table I. Photooxidation of Alkoxide Ionsª h ....

$ \begin{array}{c} & & \\ & & \\ \end{array} \\ \hline \\ CHOH  \\ \end{array} \\ \begin{array}{c} & \\ \\ CHO^{-} \\ \hline \\ \\ \hline \\ \\ \\ Rose \ Bengal \end{array} \\ \begin{array}{c} & \\ \\ \end{array} \\ \hline \\ C=O \\ \hline \\ \\ \end{array} \\ \hline \\ C=O \\ \hline \\ \end{array} \\ \hline \\ \end{array} $			
Product	Base	Temp, °C	Yield, %
Acetone 2-Butanone Cyclohexanone Benzophenone Formaldehyde Acetaldehyde Butyraldehyde Benzaldehyde	Na t-BuOK t-BuOK KOH <sup>4</sup> NaOH NaH NaH NaH	6-8 10 25-27 25-26 2-5 2-5 2-5 2-5 2-4	100 <sup>b</sup> 100 <sup>b</sup> 97 <sup>c</sup> 91 <sup>e</sup> 61 <sup>c</sup> 84 <sup>c</sup> 61 <sup>c</sup> 99 <sup>c</sup>

A 1.

<sup>a</sup> Except where noted, excess of corresponding alcohol used as a solvent, and moles  $O_2$  used = moles base. <sup>b</sup> Nmr analysis. <sup>c</sup> Isolation as 2,4-dinitrophenylhydrazone; some loss of yield owing to solubility in aqueous methanol medium used. <sup>4</sup> Mole ratio, 2.0 KOH:1.0 benzhydrol:0.50 O<sub>2</sub>, t-BuOH solvent. <sup>6</sup> Direct isolation.

In a typical reaction, a solution of 15.0 mmol of sodium isopropoxide in 115 ml of isopropyl alcohol containing 6 mg of Rose Bengal was irradiated internally by a 650-W DWY lamp operated at 100 V; 15.40 mmol of oxygen was absorbed within 55 min at 6-8°. Nmr analysis, using toluene as an internal standard, showed the presence of 15.0 mmol of acetone (2,4-DNP, mp 127-128°). The mixture was filtered under dry nitrogen, and the unstable, hygroscopic white residue was washed with isopropyl alcohol and dried in vacuo for 1 hr: Calcd for NaOOH: oxidation equivalent, 28.0; neutralization equivalent, 56.0. Found: oxidation equivalent, 31.9; neutralization equivalent, 59.4.

First-order dependence of the oxidation rate on isopropoxide ion was shown by a linear plot of log [(initia! moles of  $RO^{-}$ ) – (moles of  $O_2$  consumed)] vs. time for a constant temperature run at 9°. The intermediacy of singlet oxygen was indicated by the fact that the initial rate of oxygen uptake by a  $1.5 \times 10^{-2} M$  isoproposide solution containing either of the specific singlet oxygen quenchers  $\beta$ -carotene<sup>8</sup> (3  $\times$  10<sup>-4</sup> M) or 1,4-diazabicyclo-[2.2.2] octane<sup>8,9</sup> (5  $\times$  10<sup>-2</sup> M) was 30-40% of the rate observed in the absence of added quenchers. Under our conditions, oxidations of alcohols were never observed in the absence of either base, light, or sensitizer.

While secondary alcohol solutions became neutral after absorption of 1 equiv of oxygen and uptake of oxygen diminished to a negligible rate, primary alcohol solutions remained basic and continued to be oxidized at a moderate rate. This behavior may be related to a higher solubility of the basic sodium hydroperoxide in the more acidic <sup>10</sup> primary alcohols.

Photooxidation of primary alkoxides was complicated by the second-stage chemical oxidation of the initially formed aldehydes in the peroxidic reaction mixture. High conversion to carboxylate salts was observed after reaction mixtures from methoxide and ethoxide were allowed to stand for a few hours. The yields of aldehydes reported in Table I were achieved by photooxidation at low temperatures, followed by quenching with acidic dinitrophenylhydrazine solution.

Considering the electrophilic nature of singlet oxygen,

<sup>(1)</sup> Work done on sabbatical leave at Yale University, 1972.

<sup>(2)</sup> C. S. Foote, S. Wexler, W. Ando, and R. Higgins, J. Amer. Chem. Soc., 90, 975 (1968).

<sup>(3)</sup> W. F. Smith, Jr., J. Amer. Chem. Soc., 94, 186 (1972); M. H. Fisch, J. Gramain, and J. A. Oleson, *Chem. Commun.*, 663 (917); G. O. Schenck, *Angew. Chem.*, 69, 579 (1957).
(4) C. S. Foote and J. W. Peters, *J. Amer. Chem. Soc.*, 93, 3795

<sup>(1971).</sup> 

<sup>(5)</sup> R. H. Young and H. Hart, Chem. Commun., 827 (1967); R. H. Young, ibid., 704 (1970); D. Bethell and R. G. Wilkinson, ibid., 1178 (1970)

<sup>(6)</sup> The oxidations are generally accompanied by the formation of a white precipitate of alkali metal hydroperoxide except in methanol in which the alkali metal hydroperoxides are soluble.

<sup>(7)</sup> Earlier related work (e.g., G. O. Schenck and H. D. Becker, Angew. Chem., 70, 504 (1958); G. O. Schenck, H. D. Becker, K. H. Schulte-Elte, and C. H. Krauch, Ber., 509 (1963)) was concerned with photooxidation of alcohols using benzophenone as sensitizer. These studies were carried out in the absence of base and the products were  $\alpha$ -hydroxy hydroperoxides. The mechanism, which seems to be well accepted, appears to involve reaction of oxygen with radicals produced by abstraction of hydrogen by triplet sensitizer.

<sup>(8)</sup> C. S. Foote, R. W. Denny, L. Weaver, Y. C. Chang, and J. Peters, Ann. N. Y. Acad. Sci., 171, 139 (1970).
(9) C. Ouannes and T. Wilson, J. Amer. Chem. Soc., 90, 6527 (1968);
R. H. Young and R. L. Martin, *ibid.*, 94, 5183 (1972).

<sup>(10)</sup> J. Hine and M. Hine, J. Amer. Chem. Soc., 74, 5266 (1952).



the mechanism outlined in Scheme I is a reasonable and attractive one for these reactions. In view of the fact that attempted photooxidations in aprotic solvents (DMF, pyridine, diglyme) proceeded with extreme sluggishness, if at all,<sup>11</sup> we favor the intermolecular process (a) for decomposition of the putative trioxide ion intermediate 1 rather than the intramolecular process (b). On the other hand, our results do not appear to rule out the possibility of mechanisms involving electron transfers.12

The photooxidation of benzhydrol in a solution of KOH in tert-butyl alcohol was unique among these studies in that complete conversion to benzophenone required only 0.5 mol of oxygen per mole of benzhydrol, and the resulting solution was free of peroxides. The possibility that half the benzhydrol was being oxidized by a rapid reaction with inorganic peroxide was ruled out by the fact that treatment of benzhydrol with a slight excess of hydrogen peroxide in a reaction mixture essentially identical with that used in the photooxidation produced at most a 2% yield of benzophenone. The contrast with the results from aliphatic alkoxides suggests that with benzhydrol there may be formed an appreciable concentration of the carbanion 3, which could become hydroxylated<sup>13</sup> by reaction with a peroxidic intermediate such as 2, formed during the photooxidation.

$$\begin{array}{cccc} H & OH \\ & & & \\ Ph_{2}CHOO & O & + & \\ 2 & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & &$$

Acknowledgments. We thank the National Institutes of Health for financial support.

(11) Similar solvent effects have been noted in the oxidation of sulfides, 4 for which an intermediate analogous to 1 has been proposed. (12) The following radical process is one such example



(13) Cf. the reaction of 9-alkylfluorene anion with the corresponding hydroperoxide to give 2 equiv of alkylfluorenol: Y. Sprinzak, J. Amer. Chem. Soc., 80, 5449 (1958).

Harry H. Wasserman\*

Department of Chemistry, Yale University New Haven, Connecticut 06520

James E. Van Verth

Department of Chemistry, Canisius College Buffalo, New York 14208 Received August 25, 1973

## Vinylic Cations from Solvolysis. XVII. An Unusual Solvent Effect and Common Ion Rate Depression in Aqueous Trifluoroethanol<sup>1</sup>

Sir:

2,2,2-Trifluoroethanol (TFE) and aqueous TFE mixtures have become popular solvolytic media.<sup>2</sup> This is due to the low nucleophilicity of TFE<sup>2c, 3</sup> coupled with the relatively high "ionizing power" of the mixtures as judged by "Y" values<sup>4</sup> based on the solvolysis of t-BuCl  $(Y_{\text{TFE}} = 1.045, Y_{40\% \text{ TFE}} = 2.60).^{2a}$  Sunko, Szele, and Tomić found recently<sup>5</sup> that the solvolysis of 7-methyl-7-norbornyl tosylate (MNBOTs) in 100-70% TFE gave an m value of the Winstein-Grunwald equation, 4a  $\log (k/k_0) = mY$ , of 0.062. They noticed that other secondary and tertiary systems gave much lower mvalues in aqueous TFE than in aqueous EtOH. These results prompt us to report the peculiar solvolytic behavior of several vinylic substrates in aqueous TFE.

Solvolysis of 1-(o-methoxyphenyl)-2-methylpropen-1-yl tosylate (1-OTs) was followed spectrophotometrically from 100% TFE to 2.5% (w/w) aqueous TFE (mole fraction of water  $X_{H_{2}O} = 0-0.995$ ) buffered with Et<sub>3</sub>N. The products were the ether 1-OR and the ketone 3. From the product distribution, the relative rate ratios for capture of the intermediate carbonium ion 2 by water and TFE (in the presence of 2,6-lutidine)  $k_{\rm H_{2}O}/k_{\rm TFE}$  are 0.83-1.20 in 97-80% TFE and they decrease in the more aqueous media. An unusual feature of the plot of log  $k_1$  vs.  $X_{\rm H_2O}$  is the minimum at ca. 70%



(1) Part XVI. Z. Rappoport, A. Pross, and Y. Apeloig, *Tetrahedron* Lett., 2015 (1973). Reported in part at the 42nd Meeting of the Israel Chemical Society, Rehovoth, Dec 1972; Proc. Israel Chem. Soc., 42nd

(2) (a) V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, J. Amer. Chem. Soc., 91, 4838 (1969); (b) V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *ibid*., 91, 7748 (1969); (c) M. D. Bentley and J. A. Lacadie, Tetrahedron Lett., 741 (1971); (d) F. L. Scott, Chem. Ind. (London), 224 (1959); (e) W. S. Trahanovsky and M. P. Doyle, *Tetrahedron Lett.*, 2155 (1968); (f) J. R. Hazen, *ibid.*, 1897 (1969); (g) G. A. Dafforn and A. Streitwieser, Jr., *ibid.*, 3159.(1970); (h) D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, J. Amer. Chem. Soc., 92, 5977 (1970); J. L. Fry, and P. v. R. Schleyer, J. Amer. Chem. Soc., 92, 5977 (1970); (i) V. J. Shiner, Jr., and W. Dowd, *ibid.*, 93, 1029 (1971); (j) W. D. Pfeifer, C. A. Bahn, P. v. R. Schleyer, S. Bocher, C. E. Harding, K. Hummel, M. Hanack, and P. J. Stang, *ibid.*, 93, 1513 (1971); (k) D. S. Noyce, R. L. Castenson, and D. A. Meyers, J. Org. Chem., 37, 4222 (1972); (i) D. S. Noyce and R. L. Castenson, J. Amer. Chem. Soc., 95, 1247 (1973); (m) P. J. Stang and T. E. Dueber, *ibid.*, 95, 2683 (1973). (3) The nucleophilic constants according to the equation log ( $k/k_0$ ) =  $mY + lN^{4b.o}$  are -0.26 (H<sub>2</sub>O) and -3.8 (TFE): T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *ibid.*, 95, 7860 (1973).

K.L. Schadt and P. v. R. Schleyer, *ibid.*, 95, 7860 (1973).
(4) (a) E. Grunwald and S. Winstein, J. Amer. Chem. Soc., 70, 846 (1948);
(b) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, 73, 2700 (1951); (c) S. Winstein, A. H. Fainberg, and E. Grunwald, ibid., 79, 4146 (1957)

(5) D. E. Sunko, I. Szele, and M. Tomić, Tetrahedron Lett., 1827 (1972).

Journal of the American Chemical Society | 96:2 | January 23, 1974