servable, the unsubstituted bridge carbon is essentially sp^3 hybridized, maximizing in this way the overlap between its electron pair and the proton of the opposite bridge.

Although there appears to exist no previous proof for the existence of an intramolecular hydrogen bond between carbon atoms only, we believe that the data presented here find their most attractive interpretation in a three-center, four-electron C–H–C hydrogen bond.

Acknowledgment. Support of this work through a NATO Postdoctoral Fellowship, administered by the DAAD, to W.P. is gratefully acknowledged. U.M.-W wishes to thank Professor Manfred Schlosser (University of Lausanne) for many very helpful discussions and for providing us with 360- and 90-MHz NMR spectra of various ferrocenophanes. Further 360-MHz proton and 50-MHz ^{13}C spectra were obtained at the NMR facility of the University of California at Davis. We thank Dr. Gerry Matson and Dr. Jerry Dallas at UC Davis for their cooperation and help.

Oxygen-Atom-Transfer Reactions from a Carbonyl Oxide (Produced from a 1,2,3-Trioxolane) to Electron-Deficient Unsaturated Compounds

William A. Pryor* and C. K. Govindan

Deparment of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803

Received August 13, 1981

Many recent studies have focused attention on the transfer of an oxygen atom from carbonyl oxides, a reaction believed to be a model for certain reactions catalyzed by monooxygenase enzymes.[1] Carbonyl oxides are produced in the ozonolysis[2] of alkenes, alkynes, and ketenes and during the photooxidation of diazo compounds.[3–5] Carbonyl oxides transfer oxygen atoms to alkanes,[3] alkenes,[4–6] sulfides,[5,7] and aromatic compounds,[5,8] but until recently very little was known about the characteristics of this reaction. Ogata et al.[5] have recently shown that carbonyl oxides are nucleophilic oxygen-atom-transfer agents.

Oxygen-atom-transfer reactions are relevant to the mechanism of ozonolysis of certain olefins as well. For example the ozonolysis of haloolefins leads to high yields of epoxides,[9] and the ozonation of certain olefins in the presence of tetracyanoethylene (TCNE) produces the epoxide of TCNE.[10a] It is generally not possible to identify the actual oxygen-atom-transfer agent in olefin ozonation reactions; ozone, 1,2,3-trioxolane, and the carbonyl oxide are all potential oxygen-atom-transfer agents, and all three coexist under normal ozonolysis conditions. Furthermore, the competing reaction of the carbonyl oxide with aldehydes to form stable ozonides makes it difficult to study the oxygen-transfer reaction of carbonyl oxides under ozonolysis conditions.

We therefore have examined the decomposition of ozone-free samples of the trioxolane of *trans*-di-*tert*-butylethylene (**1**) in the presence of various electron-deficient oxygen acceptors. Compound **1** is an unusually stable trioxolane,[11] stable to −60 °C, and its decomposition in a polar solvent does not yield stable ozonides.[12] Using ESR, product isolation, and carbonyl oxide trapping experiments we show that the carbonyl oxide **2** and not trioxolane **1** is the actual oxygen-atom-transfer agent in our systems (see eq 1, Scheme I).

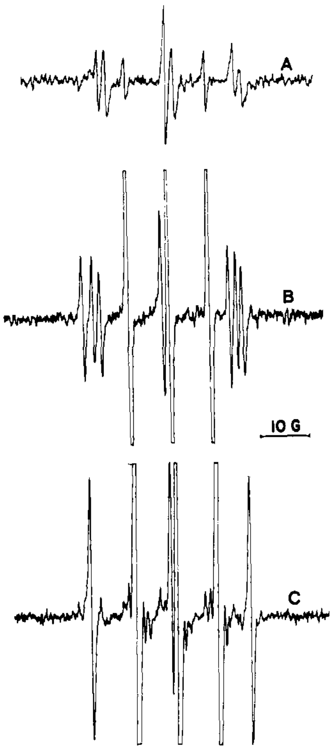


Figure 1. ESR spectra recorded during the decomposition of trioxolane **1** in the presence of PBN. (A) Spectrum recorded at −60 °C; (B) at −30 °C; (C) spectrum recorded on a sample that has been warmed at 20 °C for 5 min.

When a degassed sample of trioxolane **1** in dichloromethane at −90 °C is allowed to warm up in the ESR cavity, free radical signals are not observed, confirming the result of Murray and Ramachandran.[12] However, when **1** is allowed to warm in the presence of α-phenyl-*tert*-butyl nitrone (PBN), a well-known spin trap,[13] ESR signals begin to appear at about −60 °C. The spectrum obtained at −60 °C shows (Figure 1A) a triplet of doublets ($a^N = 13.40$ and $a^H = 1.25$ G) and a triplet ($a^N = 7.85$ G); these two signals can be ascribed to the peroxyl radical spin adduct of PBN[14] and an acyl radical spin adduct of 2-methyl-2-nitrosopropane (NtB).[15] As the temperature is raised above −60 °C, these signals grow and a second triplet ($a^N = 15.84$ G) due to di-*tert*-butyl nitroxide appears (Figure 1B). As the reaction mixture is warmed to room temperature, the triplet of doublets slowly disappears, as would be expected of a peroxyl radical spin adduct,[14] but the other signals remain (Figure 1C).

The formation of di-*tert*-butyl nitroxide indicates that NtB and *tert*-butyl radicals are produced in this system. The appearance of a blue color in the reaction mixture, characteristic of nitroso compounds, also indicates the formation of NtB. The decomposition of **1** in the presence of NtB in the dark gives an acyl-*tert*-butyl nitroxide and di-*tert*-butyl nitroxide but not a peroxyl radical spin adduct. This result indicates that the acyl nitroxide produced in the presence of PBN probably is not benzoyl-*tert*-butyl nitroxide (PBNOx);[15] rather, it seems likely that the acyl nitroxide

---

(1) (a) Hamilton, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 3391. (b) Hamilton, G. A. In "Molecular Mechanisms of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press: New York, 1974; p 405.

(2) (a) For a comprehensive review on the ozonolysis of carbon–carbon double bonds, see: Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. 1. (b) Bailey, P. S. *Chem. Rev.* **1958**, *58*, 925.

(3) Hamilton, G. A.; Giacin, J. R. *J. Am. Chem. Soc.* **1966**, *88*, 1584.

(4) Murray, R. W.; Ramachandran, V.; Hinirichs, T. A. *J. Am. Chem. Soc.* **1979**, *101*, 1282.

(5) Ogata, Y.; Kato, H.; Sawaki, Y. *J. Am. Chem. Soc.* **1981**, *103*, 3832.

(6) Hamilton, G. A.; Keay, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 6876.

(7) Ando, W.; Kohmoto, S.; Nishizawa, K. *J. Chem. Soc., Chem. Commun.* **1978**, 894.

(8) (a) Murray, R. W.; Hoyt, R. A.; Chaudhary, S. K. *Tetrahedron Lett.* **1976**, 4235. (b) Jerina, J. W.; Jerina, D. M.; Witkop, B. *Experimentia* **1972**, *28*, 1129.

(9) See ref 2a, Chapter X.

(10) (a) For a discussion, see ref 2a, p 135. (b) Reference 2a, pp 83–88.

(11) (a) Criegee, R.; Schroder, G. *Chem. Ber.* **1960**, *93*, 689. (b) Bailey, P. S.; Thompson, J. A.; Shouders, B. A. *J. Am. Chem. Soc.* **1966**, *88*, 4098.

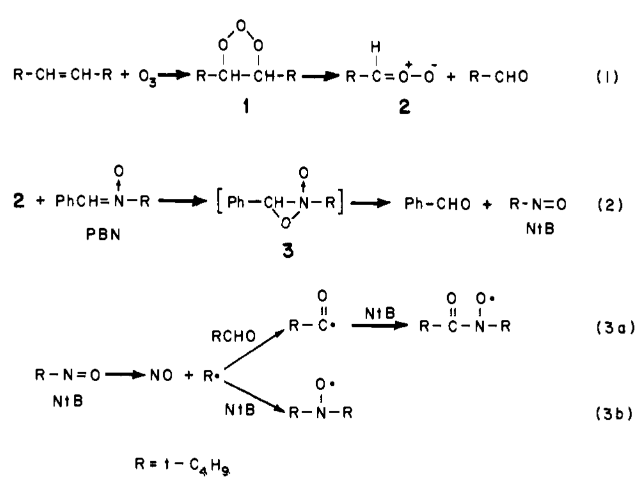
(12) Murray, R. W.; Ramachandran, V. *J. Am. Chem. Soc.* **1978**, *100*, 2197.

(13) (a) Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31. (b) Janzen, E. G. In "Free Radicals in Biology"; Pryor, W. A., Ed.; Academic Press: New York, 1980: Vol. IV, Chapter 4.

(14) (a) Merrit, M. V.; Johnson, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 3713. (b) Howard, J. A., Tait, J. C. *Can. J. Chem.* **1978**, *56*, 176.

(15) Janzen, E. G.; Blackburn, B. J. *J. Am. Chem. Soc.* **1969**, *91*, 4481 and references therein.

Scheme I



is derived from spin trapping the acyl radical produced by hydrogen abstraction from trimethylacetaldehyde, a product of ozonolysis of *trans*-1,2-di-*tert*-butylethylene.

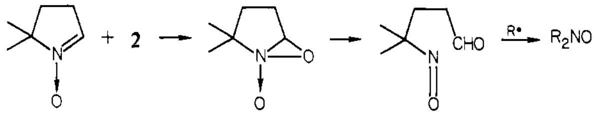
Benzaldehyde also is produced during the decomposition of **1** in the presence of PBN. The yield of benzaldehyde (by GLPC), based on the amount of olefin, is 30% for a 1:1 mole ratio of the olefin to PBN and 40% for a 1:2 mole ratio of olefin to PBN. Generally PBN is stable, and its decomposition to NtB and benzaldehyde is unusual under spin-trapping conditions at low temperatures. Previous work of ours has shown that warming ozone–olefin reaction mixtures from −78 to 20 °C does not produce NtB from PBN.[16] Therefore, we propose the mechanism shown in Scheme I to explain the production of NtB (and the radicals derived from it) from PBN in the present system. We suggest that the carbonyl oxide **2** reacts with the nitrone double bond to produce intermediate **3** by an oxygen-atom transfer.[17] Intermediate **3** is similar to the intermediate proposed in the oxidation of oxaziranes by peracids[18] and is known to decompose to a carbonyl compound and nitrosoalkanes. The oxidation of oxaziranes is a well-known synthetic procedure for the preparation of nitrosoalkanes. The formation of di-*tert*-butyl nitroxide and the acyl radical spin adduct of NtB can then be rationalized by the reactions shown in Scheme I (reaction 3a,b).

The fact that all the ESR signals shown in Figure 1 originate from the reactions of carbonyl oxide **2** is shown by the following observations: (a) The addition of methanol before the addition of PBN to **1** inhibits the formation of all the spin adducts. Methanol scavenges carbonyl oxides to produce methoxy hydroperoxides preventing their reaction with PBN. (b) When **1** is allowed to warm up to −40 °C until its decomposition is complete and then treated with PBN, no free radical signals are produced.

It has been reported that the 1,2,3-trioxolanes produced during the ozonation of alkynes are oxygen-atom-transfer agents.[6] However, since no free radical signals are produced when **1** is incubated at −80 °C with PBN for periods up to 2 h, we conclude that the trioxolane itself is not the oxygen-atom-transfer agent in our system. Moreover, addition of methanol should not have any effect on the reactions of the trioxolane itself.[6]

The mechanism of the formation of the peroxyl radical spin adduct (Figure 1A,B) is not clear. The reaction of *tert*-butyl radicals with residual exogenous oxygen cannot be the source of the peroxyl radicals, since the samples were first deoxygenated with N_2 and then degassed by repeated freeze–pump–thaw cycles. The decomposition of the polyperoxides or ozonide oligomers induced by PBN also is not the source of the peroxyl radicals, since samples that have been warmed to −40 °C and then treated with PBN do not yield any free radical products. However, the decomposition of the peroxide oligomers induced by *tert*-butyl radicals cannot be ruled out, especially since the structure of the oligomers and polymers from the ozonolysis of olefins are not well understood.[10b]

The decomposition of **1** in the presence of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) also yielded a nitroxide (a^N = 15.50 G); this probably arises from a nitroso compound, as shown in reaction 4. However, ESR signals were not produced in this case until the reaction mixture was warmed to room temperature, probably because of the stability of **4** or **5** at lower temperatures. Note that the peroxyl radical spin adduct of DMPO has been reported to be too unstable to be observable.[14]

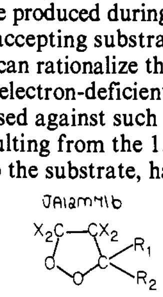


(4)

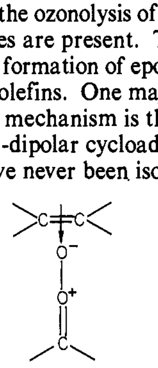
4 5

The decomposition of the trioxolane **1** in the presence of TCNE in ethyl acetate at −60 °C gave TCNE oxide in 60% isolated yield. (TCNE oxide was identified by its melting point and by comparisons of its infrared spectrum with an authentic sample prepared by the method of Criegee and Gunther.[19]) The formation of TCNE oxide provides further support for the proposed oxygen-atom-transfer mechanism for the reaction between **2** and nitrones. The double bonds in PBN and TCNE are both electron deficient. As mentioned, carbonyl oxides are nucleophilic oxygen-atom-transfer agents; thus they would not be expected to react with normal olefins under ozonolysis conditions. Our preliminary results indicate that only a trace, if any, of cyclohexene oxide is formed when **1** is allowed to decompose in neat cyclohexene at −60 °C.[20]

We suggest that oxygen-atom transfer is a general reaction of the carbonyl oxide produced during the ozonolysis of olefins when suitable oxygen-accepting substrates are present. This oxygen-transfer reaction can rationalize the formation of epoxides during the ozonolysis of electron-deficient olefins. One major objection that has been raised against such a mechanism is that 1,2-dioxetanes like **6**, resulting from the 1,3-dipolar cycloaddition of the carbonyl oxide to the substrate, have never been isolated. This is a valid argument if the cycloaddition mechanism is operative. However, ozone and carbonyl oxides are isoelectronic, mainly differing in their reactivity toward various substrates; therefore, the oxygen-atom transfer we observe could involve a complex **7**, similar to the mechanisms proposed for the epoxidation of sterically hindered olefins by ozone.[21] Such a mechanism also is supported by the product studies on the ozonolysis of fluoroolefins by Gilles[22a] and Gilles and Agopovich.[22b]



6



7

Acknowledgment. This work was supported by grants from the National Institute of Health (HL-16029) and the National Science Foundation.

---

[16] Prier, D. G.; Church, D. F.; Pryor, W. A., to be published.

[17] (a) A referee has pointed out that the ring-opened diradical form of trioxolane **1** or the adduct resulting from the nonconcerted addition of **2** to trimethylacetaldehyde[12] could be the oxygen-transfer agent. However, the decomposition of **1** to **2** by a diradical pathway has been shown to be energetically unfavorable by Benson and Nangia[17b] and the addition of methanol would not be expected to have a large effect on the oxygen-transfer reactions of diradicals. Oxygen transfer from the carbonyl oxide–aldehyde adduct has no precedent. (b) Nangia, P. S.; Benson, S. W. *J. Am. Chem. Soc.* **1980**, *102*, 3105.

[18] Emmons, W. D. *J. Am. Chem. Soc.* **1957**, *79*, 6522.

[19] Creigee, R.; Gunther, P. *Chem. Ber.* **1963**, *96*, 1546.

[20] Details of these and related experiments will be published in a forthcoming paper.

[21] Bailey, P. S.; Lane, A. G. *J. Am. Chem. Soc.* **1967**, *89*, 4473. Also see ref 2a, Chapter XI.

[22] (a) Gillies, C. W.; Agopovich, J. W. *J. Am. Chem. Soc.* **1980**, *102*, 7572. (b) Gilles, C. W. *Ibid.* **1977**, *99*, 7239.