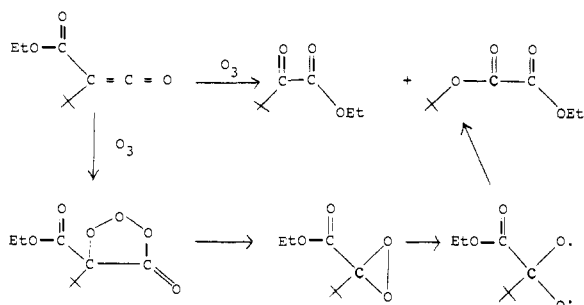
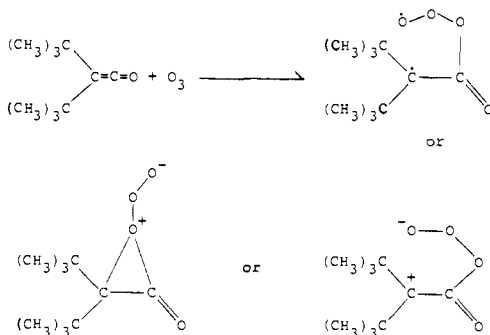


Scheme IV



Scheme V



Oxygen transfer from $(\text{C}_6\text{H}_5)_2\text{CO}_2$ to diphenylketene can be readily diverted by TCNE or propionaldehyde.

Finally returning to the case of di-*tert*-butylketene (entry VIII) the question remains as to why a mechanism different from that observed in the ozonations of diphenylketene and diethylketene occurs. It may be that the initial ozonide is an open diradicaloid or zwitterionic intermediate due to the stabilizing influence of two *tert*-butyl groups. Singlet diradical and zwitterionic character represent a continuum which is affected by substituents.²⁷ Rearrangement of these species to α -lactones via a peroxy oxide may be favored.² Also the di-*tert*-butyl groups may hinder trioxalane formation.²⁸ (See Scheme V.)

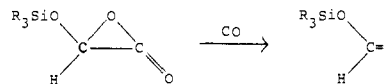
Acknowledgments. The authors thank Professor N. J. Turro, Columbia University, for stimulating discussions of this work, for sharing results, and agreeing to publish his study simultaneously with ours. We also thank the National Science Foundation for support of this work under Grant CHE-77-06617.

References and Notes

- R. Wheland and P. D. Bartlett, *J. Am. Chem. Soc.*, **92**, 6057 (1970).
- N. J. Turro, M.-F. Chow, and Y. Ito, *J. Am. Chem. Soc.*, preceding paper in this issue.
- J. K. Crandall, S. A. Sojka, and J. B. Komin, *J. Org. Chem.*, **39**, 2172 (1974).
- W. T. Brady and K. Saidi, *Tetrahedron Lett.*, 721 (1978).
- G. A. Cook, A. D. Kiffer, C. V. Klumpp, A. H. Malik, and L. A. Spence, *Adv. Chem. Ser.*, No. 21, 44 (1959).
- P. S. Bailey and A. M. Reader, *Chem. Ind. (London)*, 1063 (1961).
- P. S. Bailey and A. G. Lane, *J. Am. Chem. Soc.*, **89**, 4473 (1967).
- P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958), and references therein.
- P. D. Bartlett and M. Stiles, *J. Am. Chem. Soc.*, **77**, 2806 (1955).
- R. C. Fuson, M. D. Armstrong, W. E. Wallace, and J. W. Kneisley, *J. Am. Chem. Soc.*, **66**, 1274 (1944).
- R. Criegee, *Rec. Chem. Prog.*, **18**, 11 (1957).
- L. A. Hull, I. C. Hisatsune, and J. Hecklen, *J. Am. Chem. Soc.*, **94**, 4856 (1972), and references cited therein.
- R. W. Murray and A. Suzui, *J. Am. Chem. Soc.*, **95**, 3343 (1973).
- Alternatively the primary ozonide could cleave to yield R_2CO and CO_3 . We prefer R_2CO_2 to CO_3 as the oxygen atom donor because of variations in the overall reaction as a function of differences in the nature of R (Table I). Were CO_3 the common oxidizing agent, a greater uniformity in the yield of ketone would be expected.
- W. R. Wadt and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 3004 (1975).
- R. Huisgen, *J. Org. Chem.*, **41**, 403 (1976), and the discussion therein.
- N. J. Turro, Y. Ito, M.-F. Chow, W. Adam, O. Rodriguez, and F. Yany, *J. Am. Chem. Soc.*, **99**, 5836 (1977).
- This experiment was suggested by the classical work of Günther and

Criegee¹⁸ on the deoxygenation of intermediates in the ozonation of olefins.

- R. Criegee and P. Günther, *Chem. Ber.*, **96**, 1564 (1963).
- F. J. Lovas and R. D. Suenram, *Chem. Phys. Lett.*, **51**, 453 (1977).
- P. E. Eaton and G. H. Temme III, *J. Am. Chem. Soc.*, **95**, 7508 (1973).
- P. R. Story, J. A. Alford, J. R. Burgess, and W. C. Ray, *J. Am. Chem. Soc.*, **93**, 3042 (1971).
- Reference 4. These workers propose a basically different mechanism which involves a key step loss of carbon monoxide from an α -lactone. The gas-



eous product CO vs. CO_2 was not reported. In a footnote they recognize that $\text{R}_3\text{Si}^+\text{CH}-\text{O}-\text{O}^-$ could also yield the silylformate.

- P. Sundararaman, E. C. Walker, and C. Djerassi, *Tetrahedron Lett.*, 1627 (1978).
- Reference 3. These workers mention the dioxirane as a possible intermediate.
- W. J. Linn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, **87**, 3651 (1965).
- L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).
- We thank a reviewer for this suggestion.

R. M. Moriarty,* Kenneth B. White, A. Chin

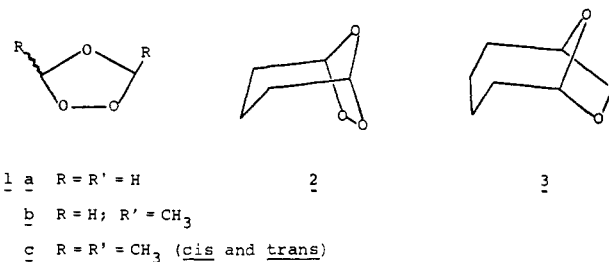
Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680

Received May 20, 1978

Photoelectron Spectra of the Ozonides of Ethylene, Cyclopentene, and Cyclohexene. Experimental Evidence for the Magnitude of the "Pure" Inductive Effect of an Ether Oxygen on Ionization Energy

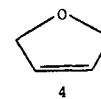
Sir:

While ozonides have been used as valuable synthetic intermediates for some time, relatively little structural information is available about them except in the case of ethylene ozonide (**1a**),^{1a} propylene ozonide (**1b**),^{1b} and *trans*-2-butene ozonide (**1c**).^{1b}



As part of our continuing effort² to determine the effects of remote substituents on ionization energies (IP), we have prepared and determined the photoelectron spectra (PES) of the ozonides of ethylene (**1a**),³ cyclopentene (**2**),⁴ and cyclohexene (**3**).⁵ From microwave data **1** exists in the gas phase in a half-chair conformation having C_2 symmetry.¹ Importantly, however, the symmetry characteristics of the component oxygen orbitals of **1a** offer a unique opportunity to assess the inductive effects of the peroxide and ether oxygens on each other in the absence of interfering conjugative effects.

From an analysis of the PES of tetrahydrofuran ($n_o = 9.47$ eV),⁶ cyclopentene ($\pi = 9.18$ eV),⁷ and 2,5-dihydrofuran (**4**)



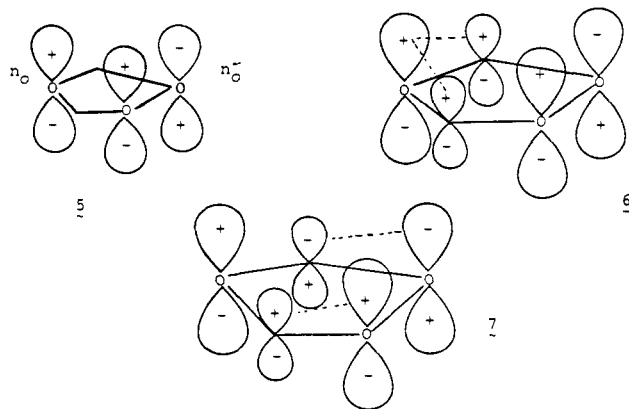
($n_o = 10.59$ eV, $\pi = 9.14$ eV),⁶ Bain et al.⁶ concluded that, in the latter compound, the inductive stabilization of the π bond by the electronegative allylic oxygen (assumed to be 0.8 eV)

Table I. Vertical Ionization Energies (IP) and Assignments for Ozonides **1**, **2**, and **3**

compd	ionization energy, eV ^a	assignment
Ethylene ozonide (1) ^b	10.67 ($\nu^+ \approx 0.12$ eV)	n_o^- (peroxide)
	10.96	n_o (ether)
	12.40, 13.38, 14.5, 15, 16.15, 17, 18	
	9.63	n_o^- (peroxide)
Cyclopentene ozonide (2)	10.35	n_o (ether)
Cyclohexene ozonide (3)	9.61	n_o^- (peroxide)
	10.26	n_o (ether)

^a Values have a precision of ± 0.03 eV and are calibrated against argon. ^b Introduced into the spectrometer from a -95° bath through a glass-Teflon inlet system.

was exactly compensated by a conjugative destabilization between n_o and π , of a symmetry-allowed through-space or through-bond⁸ nature. In the case of **1**, PES shows that the two highest occupied orbitals are the peroxide n_o^- (10.67 eV)⁹ and ether oxygen n_o (10.96 eV) (Figure 1). Under the C_2 point group, the peroxide n_o^- and ether n_o orbitals in **1** transform as a and b, respectively, and therefore cannot interact directly by a through-space mechanism (**5**). Similarly the pseudo-p orbitals located on the methylene units must also transform pairwise as a and b and cannot act as intervening orbitals in a through-bond fashion (**6** and **7**). Hence, when compared with



the peroxide n_o^- orbital in 1,2-dioxacyclopentane¹⁰ (Figure 1) at 9.86 eV, the 0.8-eV stabilization¹¹ of that orbital in **1** must be a result of the inductive effect of the ether oxygen.¹² Additionally one notices that, when compared with tetrahydrofuran ($n_o = 9.57$ eV),⁶ the ether oxygen of **1** (Table I) is stabilized by ~ 1.4 eV, owing to the inductive effect of the two peroxide oxygens.

The ozonides from cyclopentene and cyclohexene (**2** and **3**) both show similar values for the n_o and n_o^- IP's. In the absence of the ether bridge, we might reasonably assume that the peroxide n_o^- orbital would have an IP of roughly 8.9 eV.¹³ In both **2** and **3**, the presence of the ether bridge stabilizes the peroxide n_o^- orbital by roughly 0.7 eV, although the bicyclic framework causes the trioxacyclopentane portion to assume an envelope shape and reduces the overall symmetry. While a through-space interaction between the ether n_o and n_o^- is symmetry forbidden, a potential hyperconjugative interaction between the appropriate combination of ether C-O bonds or bridge C-C bonds and n_o^- is allowed which might serve to destabilize the latter. This must be small, however, since the peroxide stabilization similar to that in ozonide **1** is observed. On the other hand, the ether oxygen at ~ 10.3 eV in both **2** and **3** when compared with that of model ethers such as tetrahy-

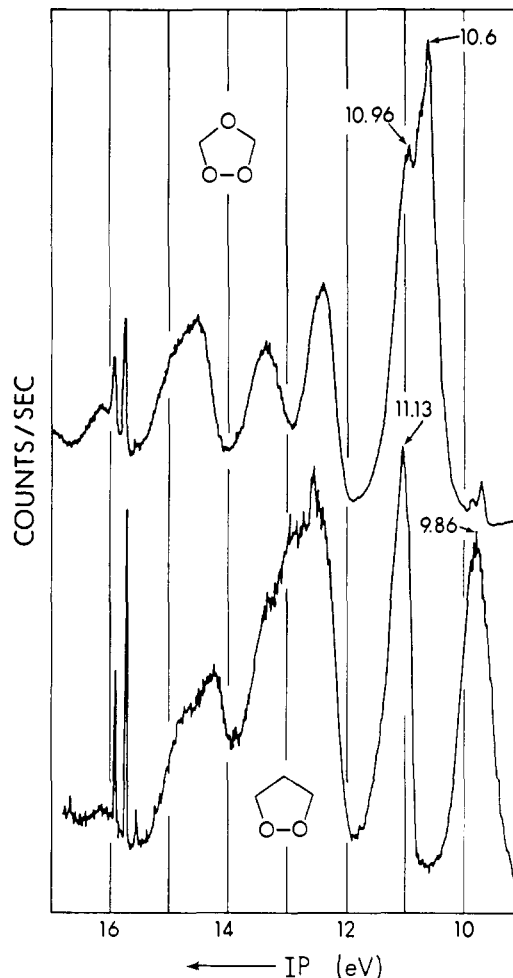


Figure 1. The PES of ethylene ozonide (**1**) and 1,2-dioxacyclopentane using Ar as an internal calibrant. For the latter, the first two ionizations are assigned as the peroxide n_o^- orbital⁹ and an antisymmetric combination of bonding C-O σ bonds.⁹ In the case of **1** the first two bands are assigned as n_o^- and the ether n_o orbital.

dropyran (9.50 eV),^{14a} 7-oxanorbornane (9.57 eV),⁶ and diisopropyl ether (9.35 eV),^{14b} appears to be stabilized in the presence of the peroxide unit by some 0.8–1.0 eV, somewhat less than in the case of **1**. The reasons for this attenuation of the “inductive” effect of the peroxide on the ether could be related to substitution effects and/or interaction of the ether orbital with lower lying σ levels within the six- and seven-membered rings.¹⁵

The PES of ozonide **1** with its unique symmetry characteristics allows experimental corroboration of the assumed 0.8-eV inductive stabilization⁶ of an allylic oxygen.

Acknowledgment. The authors gratefully acknowledge the University of Alberta and NRC of Canada for support of this work.

References and Notes

- (1) (a) C. W. Gilles and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **94**, 6336 (1962); (b) R. P. Lattimer, C. W. Gillies, and R. L. Kuczkowski, *ibid.*, **95**, 1348 (1973).
- (2) (a) R. S. Brown and R. W. Marcinko, *Can. J. Chem.*, submitted for publication; (b) R. S. Brown and R. W. Marcinko, *J. Am. Chem. Soc.*, in press; (c) R. S. Brown, *Can. J. Chem.*, **54**, 805, 1521 (1976).
- (3) Prepared according to the procedure in ref 1a: ¹H NMR (acetone-*d*₆, -90°C) δ 5.20 (s).
- (4) Prepared in 2.1% overall yield according to the procedure of R. Criege, *Justus Liebigs Ann. Chem.*, **583**, 2 (1953); IR (CCl₄) 2965, 2934, 1458, 1435, 1341, 1316, 1114, 1093, 1061, 1044, 1011, and 914 cm⁻¹; ¹H NMR (CDCl₃) δ 5.75 (m, 2 H, bridgehead); exact mass calcd for C₅H₈O₃ 116.0473, found 116.0474.
- (5) Prepared as in ref 3: IR (CCl₄) 2954, 2932, 1262, 1124, and 979 cm⁻¹; ¹H

NMR (CDCl_3) δ 5.60 (m, 2 H, bridgehead); exact mass calcd for $\text{C}_6\text{H}_{10}\text{O}_3$ 130.0630, found 130.0627.

- (6) A. D. Bain, J. C. Bünzli, D. C. Frost, and L. Weiler, *J. Am. Chem. Soc.*, **95**, 291 (1973).
- (7) P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1677 (1970).
- (8) R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971).
- (9) Identified as such by the vibrational spacing in the ion state, $\nu^+ = 0.12$ eV. The peroxide unit should exhibit both a bonding and antibonding combination of the oxygen lone pairs (n_o^+ and n_o^-), but only the latter is easily identifiable in all known cases: R. S. Brown, *Can. J. Chem.*, **53**, 3439 (1975).
- (10) Kindly supplied by Professor R. G. Salomon of Case Western Reserve University.
- (11) In this case within the framework of Koopmans' theorem (T. Koopmans, *Physica*, **1**, 104 (1934)), an increase in IP constitutes a stabilization of the orbital giving rise to that ionization.
- (12) We assume that replacement of the methylene unit by an oxygen in changing from 1,2-dioxacyclopentane to **1** does not cause major distortions in the ring which would alter the n_o^- IP. Implicit in this argument is also the idea that changes in interaction of n_o and n_o^- with low lying σ orbitals in passing from tetrahydrofuran, and 1,2-dioxacyclopentane, to **1** are negligible (see ref 6).
- (13) Based on experimental IP's for 2,3-dioxabicyclo[2.2.1]heptane (8.99 eV), 2,3-dioxabicyclo[2.2.2]nonane (8.82 eV), 6,7-dioxabicyclo[3.2.2]nonane (8.97 eV), and 7,8-dioxabicyclo[4.2.2]decane (9.05 eV): D. J. Coughlin, R. S. Brown, and R. G. Salomon, unpublished work.
- (14) (a) D. A. Sweigart and D. W. Turner, *J. Am. Chem. Soc.*, **94**, 5599 (1972); (b) quoted value in R. Hoffmann, P. D. Mollère, and E. Heilbronner, *ibid.*, **95**, 4860 (1973).
- (15) Molecular models of **2** and **3** suggest that the ether n_o orbital is appropriately aligned to interact with a like symmetry "ribbon orbital" 14b which could lead to the observed effect.

R. S. Brown,* R. W. Marcinko

Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada T6G 2G2

Received June 7, 1978

An Exceedingly Short Quadruple Bond Involving Tungsten and the Enigma of Heteronuclear Metal-Metal Bonds with Multiple Bond Character

Sir:

In recent years there has been considerable interest in developing and understanding the chemistry of compounds with metal-metal bonds of multiple bond character. Especially compounds of Mo¹ and W,² having metal-metal triple bonds, and of Cr,³ Mo,^{4,5} Tc,^{4,6} and Re,^{4,7} having metal-metal quadruple bonds, have been intensely investigated. An important question raised by recent results concerns the ability of tungsten to participate in quadruple bonds, even though it is now well established that, like molybdenum, the tungsten atom can easily form stable triply bonded compounds.² Whereas a plethora of quadruply bonded molybdenum compounds have now been prepared and structurally characterized,^{4,5} only one compound providing unequivocal structural evidence of the W-W quadruple bond has been reported. In this case, $\text{Li}_4\text{W}_2(\text{CH}_3)_{8-x}\text{Cl}_x \cdot 4\text{THF}$,⁸ the W-W bond distance, 2.261 (2) Å, proved to be quite long compared with the bond distance of the closely related $\text{Mo}_2(\text{CH}_3)_8^{4-}$, for which $d(\text{Mo}-\text{Mo}) = 2.147$ (2) Å.⁹ This comparison implies that the W-W quadruple bond should be much weaker than the corresponding Mo-Mo bond.

By contrast, our previous report¹⁰ of the Mo-W bond distance in $\{\text{MoW}[\text{O}_2\text{CC}(\text{CH}_3)_3]_4\} \text{I} \cdot \text{CH}_3\text{CN}$, 2.194 (2) Å, with formal bond order 3.5, suggested that tungsten may enter into such bonds as strongly as molybdenum. This result, however, is somewhat indecisive since the bond order differs from 4.0 and the comparatively tight binding of the axial ligands, I and CH_3CN , exert an undetermined influence on the metal-metal bonding. We have now completed the structure determination of $\text{MoW}[\text{O}_2\text{CC}(\text{CH}_3)_3]_4$ in order to gain more definitive information.

The compound was prepared according to the previously reported procedure¹⁰ and crystals suitable for X-ray crystallographic examination were obtained after slow recrystalli-

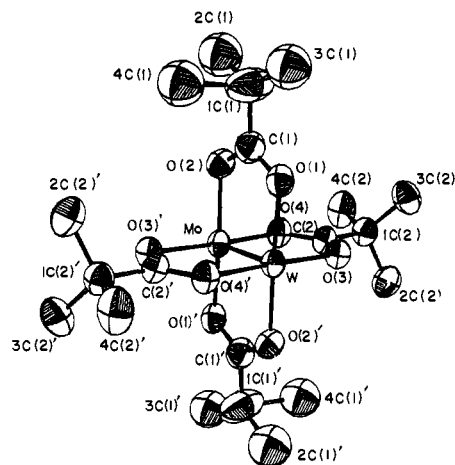


Figure 1. Structure and labeling scheme for the molecule $\text{MoW}[\text{O}_2\text{CC}(\text{CH}_3)_3]_4$. Thermal ellipsoids enclose 50% of the electron density. Metal positions are disordered and occupied with equal probability by either Mo or W.

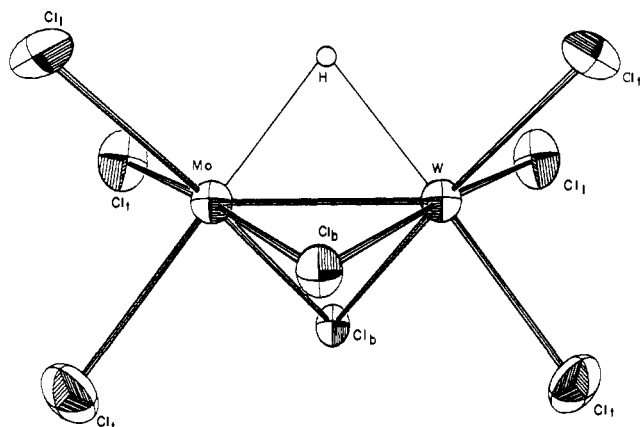


Figure 2. Structure of $\text{MoWCl}_8\text{H}_3^-$ ion. Bridging Cl and H positions are statistically disordered in the real structure. Metal positions are occupied with equal probability by either Mo or W. Thermal ellipsoids enclose 50% of the electron density.

zation from acetonitrile. The crystal used for data collection provided the following unit cell information: triclinic; space group $P\bar{1}$; $Z = 1$; $a = 10.886$ (4), $b = 5.774$ (1), $c = 11.263$ (2) Å; $\alpha = 92.81$ (2), $\beta = 109.63$ (2), $\gamma = 89.61$ (2)°.

The molecular structure of $\text{MoW}[\text{O}_2\text{CC}(\text{CH}_3)_3]_4$ is shown in Figure 1.¹¹ Since the molecule occupies a site with inversion symmetry the metal positions are disordered and occupied with equal probability by either Mo or W. However previous work has shown that each molecule indeed contains one Mo and one W atom;¹⁰ so the disordering involves only statistical orientation of the molecules with respect to the direction of the Mo-W vector. Thus only average M-O distances can be obtained.¹²

The important and surprising result revealed by the structure determination is the remarkably short Mo-W bond distance of 2.080 (1) Å. This is 0.01 Å shorter than the average Mo-Mo distance of 2.092 ± 0.004 Å reported for several $\text{Mo}_2(\text{O}_2\text{CR})_4$ derivatives, including $\text{Mo}_2[\text{O}_2\text{CC}(\text{CH}_3)_3]_4$.¹³ Only the Mo-Mo distance in $\text{Mo}_2(\text{DMP})_4$,¹⁴ 2.064 (1) Å, is shorter. In terms of the "formal shortness" suggested by Cotton, Koch, and Millar,¹⁴ the Mo-W quadruple bond found here has the value 0.800 which is exceeded among metal-metal bonds only by $\text{Mo}_2(\text{DMP})_4$ and $\text{Cr}_2(\text{DMP})_4$ with values of 0.796 and 0.778, respectively. We conclude that tungsten can indeed form strong quadruple bonds and assert that other examples are likely to be found as work in this field continues.

Let one too quickly concludes that it is the heteronuclear