

Karl R. Kopecky

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

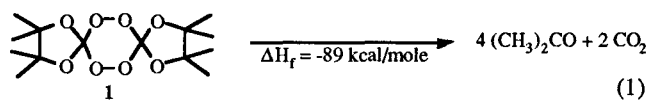
Recent work on formation of luminescent molecules in ozonolysis of electron rich alkenes is reviewed. Ozonolysis of tetramethoxyethene results in formation of ~30% of tetramethoxy-1,2-dioxetane, ~40% of methyl trimethoxyacetate, and ~20% of dimethyl carbonate. None of the sought for carbonyl oxide dimer was formed. This reaction served as a model for the possible preparation of the potentially luminescent molecule octamethyl-1,4,6,7,9,12,13,14-octaoxadispiro[4.2.4.2]tetradecane. This molecule is calculated to release 89 kcal/mole of energy on decomposition to four molecules of acetone and two of carbon dioxide. Ozonolysis of *E*- and *Z*-1,2-dimethoxy-1,2-diphenylethene also yields dioxetanes in 3 and 12%, respectively. Large amounts of oxiranes are formed, mainly by oxygenation of the alkene by (methoxy)phenyldioxirane. The dioxirane is formed by cyclization of the carbonyl oxide and can be prepared in solution in good yield by addition of the alkene to excess ozone. This is the first dioxirane demonstrated to be formed in a solution ozonolysis reaction. It is a strong epoxidizing agent. Ozonolysis of 2-[(methoxy)phenylmethylene]-1,3-dioxolane also results in formation of oxirane and dioxetane together with some 1,4,6,7,9,12,13,14-octaoxadispiro[4.2.4.2]tetradecane. Indanetriene is an efficient carbonyl oxide trap and the resulting ozonides are stable below 0°C. At 20°C they quickly decompose to phthalonic anhydride and a carbonyl compound corresponding to the carbonyl oxide. Acyl ozonides are potentially luminescent. Decomposition of 3,3-diacetyl-5,5-dimethyl-1,2,4-trioxolane to acetone and acetic pyruvic anhydride is calculated to be exothermic by 56 kcal/mole.

Keywords: luminescence; 1,2-dioxetanes; ozonolysis; acyl ozonides; 1,4,6,7,9,12,13,14-octaoxadispiro [4.2.4.2]tetradecanes.

INTRODUCTION

A number of years ago it was reported that 1,2-dioxetanes could be prepared simply and in good yield by carrying out the ozonolysis of alkenes in pinacolone or cyclohexanone as solvent¹. It was soon shown that 1,2-dioxetanes were not present in the reaction mixtures². The notion that 1,2-dioxetanes could not be prepared by ozonolysis of alkenes appeared to be generally accepted, although there are reports that ozonolysis of electron rich alkenes provides 1,2-dioxetanes³.

The present paper is a review of work at Alberta which shows that 1,2-dioxetanes are formed upon ozonolysis of a number of electron rich alkenes and that ozonolysis reactions can lead to two new classes of potentially luminescent molecules. This work grew out of a search for potentially luminous molecules that are not 1,2-dioxetanes. Among several structures that were considered was the tetroxane **1** which might undergo decomposition to four molecules of acetone and two of carbon dioxide (eq. 1). The reaction is calculated⁴ to be exothermic by 89 kcal/mole. Since **1** would quite

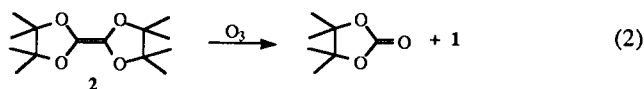


likely be kinetically stable and may require an energy of activation for decomposition of upwards of 30 kcal/mole⁵ the difference in the heats of formation of the transition state for decomposition of **1** and the products should be 120 kcal/mole or more. This is more than enough to form an electronically excited acetone molecule and is greater than that, 90 kcal/mole, available in the thermolysis of tetramethyl-1,2-dioxetane⁶.

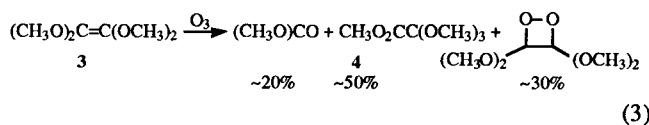
¹ Supported by the University of Alberta and by the Natural Sciences and Engineering Research Council of Canada.

AN UNSUCCESSFUL MODEL REACTION

An obvious reaction that might lead to **1** is the dimerization of a suitable carbonyl oxide. This is the dominant reaction of many carbonyl oxides that are formed from ozonolysis of some relatively hindered alkenes⁷. Thus, a likely substrate for the preparation of **1** would be the alkene **2** (eq. 2). Since it was not obvious how **2** could be prepared the ozonolysis of

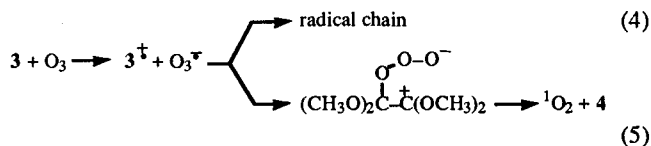


the readily available⁸ model compound tetramethoxyethene **3** was reexamined⁹ to determine whether any carbonyl oxide did indeed result from ozonolysis of ethenes with four alkoxy ligands. The ozonolysis was first carried out a number of years ago¹⁰. It was reported that equal amounts of cleavage and noncleavage products dimethyl carbonate and methyl trimethoxyacetate **4**, respectively were produced. The reexamination revealed that a complex reaction occurs in which only a small amount of cleavage product is formed. The major products are the acetate and tetramethoxy-1,2-dioxetane (eq. 3). No



evidence could be obtained for the formation of any intermediate carbonyl oxide in the reaction. The dioxetane was shown to be formed by the reaction between **3** and singlet oxygen. The same products were produced when the ozonolysis was carried out in methanol. The yields of the products depended upon the solvent, temperature and the initial concentration of

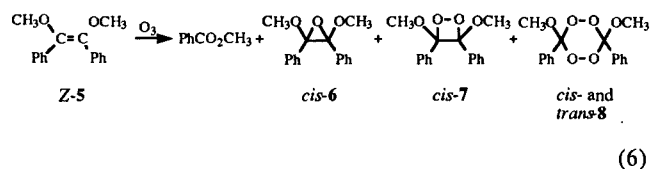
3. Up to 2.5 moles of **3** are consumed for each mole of ozone introduced which indicates that a radical chain oxidation of **3** by triplet oxygen contributes to the reaction. It was proposed that an electron transfer reaction between **3** and ozone leads to both the radical chain reaction and a route to singlet oxygen (eq. 4 and 5).



DIOXETANES, OXIRANES AND DIOXIRANES FROM OTHER ELECTRON RICH ALKENES

It could logically be concluded from the above results that **1** cannot be produced by an ozonolysis reaction and attention was turned to a study of the reaction between ozone and other electron rich alkenes. The ozonolyses of 1,1-dimethoxyethene, 1,1-dimethoxypropene and 1,1-dimethoxy-2-methylpropene result in the formation of quantitative yields of cleavage products: dimethyl carbonate and compounds derived from the carbonyl oxides of formaldehyde, acetaldehyde and acetone, respectively¹¹. No luminescence could be observed from any of these reaction mixtures upon heating to temperatures at which any 1,2-dioxetane would be expected to luminesce brightly. Thus the ozonolyses of these alkenes proceed according to the normal Criegee pathway as do the ozonolyses of 1,2-dimethoxy-1,2-dimethylethene¹² and a number of vinyl ethers¹³.

However, the observation of bright luminescence from reaction mixtures from ozonolysis of either *E*- or *Z*-1,2-dimethoxy-1,2-diphenylethene *E*- and *Z*-**5** was clear evidence that at least some anomalous reaction was occurring. A detailed investigation of these reactions has revealed a rich chemistry in these systems¹⁴. Both cleavage and noncleavage products are formed as illustrated for *Z*-**5** (eq. 6). As with the ozonolysis of **3** the product yields vary with solvent, initial



concentration, and, more dramatically, with temperature and whether alkene or ozone is always in excess during the reaction, Table 1. Both oxirane **6** and dioxetane **7** are formed stereospecifically. Only the *cis* isomers are formed from *Z*-**5** and only the *trans* isomers from *E*-**5**. In contrast to the ozonolysis of **3** moderate quantities of the carbonyl oxide dimers, equal amounts of *cis*- and *trans*-**8**, are formed here at low temperature, especially from *E*-**5**. Up to 20% of dioxetane is formed from *Z*-**5**, but much less from *E*-**5**. These are formed from singlet oxygen which was shown to be produced during the reaction. As much as 65% of the noncleavage products are formed from *Z*-**5**.

The formation of the tetroxane **7** is strong evidence that carbonyl oxide **9** is an intermediate during the reaction. It was initially felt that the oxirane **6** might be formed by transfer of an oxygen atom from **9** to alkene **5** which is always in excess and that if ozone were always in excess this transfer would be greatly suppressed. More tetroxane should result. The yield of oxirane did drop markedly when alkene was added slowly to excess ozone but there was no corresponding increase in the yield of dimer. Instead the now yellow solution contained large

Table 1. Product distribution from ozonolysis of *E*- and *Z*-**5** in CD₂Cl₂.

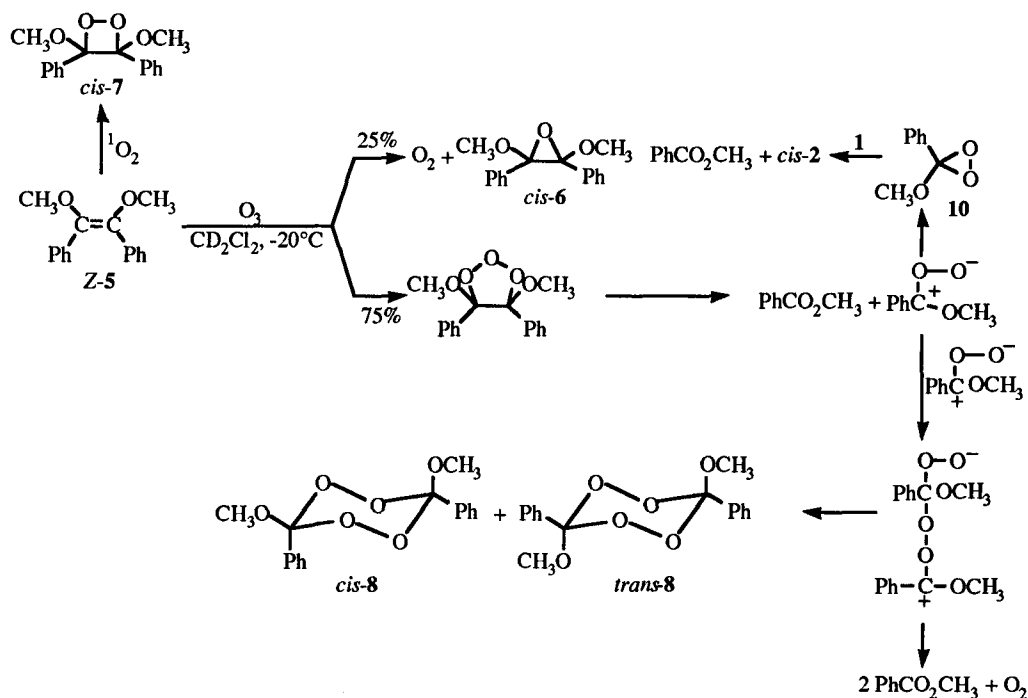
Alkene	Temp., °C	Products, moles per mole of 5				
		PhCO ₂ CH ₃	6 ^a	7 ^a	8 ^b	10
<i>E</i> - 5	-20 ^c	0.92	0.48	0.01	0.03	0
	-70 ^c	1.00	0.28	0.02	0.20	0
	-20 ^d	0.86	0.20	0.03	0	0.68
	-70 ^d	1.02	0.12	0.02	0.19	0.25
<i>Z</i> - 5	-20 ^c	0.66	0.53	0.12 ^e	0.03	0
	-70 ^c	0.50	0.47	0.20	0.07	0
	-20 ^d	0.50	0.37	0.18	0	0.46
	-70 ^d	0.46	0.32	0.23	0.06	0.28

- Only *trans* from *E*-**5** and only *cis* from *Z*-**5**.
- Equal amounts of *cis* and *trans*.
- Normal addition of ozone to ~0.1 M solutions of alkene.
- Slow addition of ~0.01 M solutions of alkene to solutions of excess ozone.
- None in the presence of 2,5-dimethylfuran.

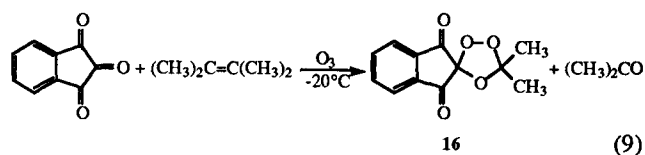
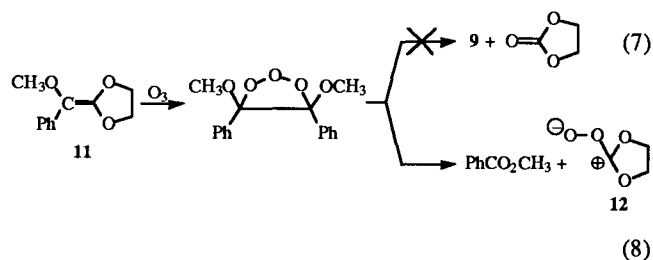
amounts of (methoxy)phenyldioxirane **10**. This dioxirane is a strong oxygen atom donor, as are other dioxiranes¹⁵. Even at -70°C a rapid, stereospecific, reaction occurs between **10** and *E*- or *Z*-**5** to form oxirane and methyl benzoate with a discharge of the yellow color. The reactions which are believed to occur during normal ozonolysis of these alkenes are illustrated for *Z*-**5** in Scheme 1. The initial reaction between ozone and the alkene produces the mole ozonide which cleaves normally to methyl benzoate and carbonyl oxide **9**. The latter may either cyclize to dioxirane **10** or dimerize to tetroxane **8**. There must be an energy barrier to the cyclization to dioxirane¹⁶ as much more dimer is formed at low temperature. The dioxirane then transfers an oxygen atom to the excess alkene. Consideration of the mass balance indicates that there must be an additional route to oxirane: a reaction between alkene and ozone which produces oxirane and singlet oxygen¹⁷. It was estimated that the initial reaction between ozone and alkene at -20°C produces 97% mole ozonide and 3% oxirane and oxygen from *E*-**5**. The corresponding ratio from *Z*-**5** is 75:25. About 1.4 moles of alkene are consumed for each mole of ozone introduced and there is no evidence for a radical chain oxidation.

Ozonolyses of the bis-4-methoxy- and bis-4-nitro derivatives of **5** results in the same types of products, except that no dioxetane is formed from the latter compound because it is not reactive enough toward singlet oxygen¹⁸.

A search is being made for alkenes that on ozonolysis yield dioxiranes in good yield and have fewer side products than are formed on ozonolysis of **5**. One of the alkenes being studied has yielded another surprising result. The mole ozonide of 2-[(methoxy)phenyl]methylene-1,3-dioxolane **11** was expected to cleave to form ethylene carbonate and the carbonyl oxide **9** of methyl benzoate (eq. 7). Instead the cleavage proceeds in the other direction (eq. 8) as evidenced by the isolation of the tetroxane **13** from dimerization of ethylene carbonate oxide **12**¹⁸. None of the expected tetroxane **8** could be detected. Experiments to determine if **13** is luminescent have not yet been made as the small amount of pure product isolated to date has all been consumed by characterization experiments. However, formation of **13** in this reaction lends hope to the possibility that the preparation of the tetroxane **1**, which was the initial goal of the research, can after all be achieved by ozonolysis of a suitable precursor. Ozonolysis of **11** also re-

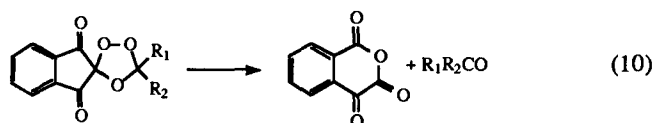


Scheme 1



being passed. Thus the trione is also an efficient trap for the carbonyl oxide 9. However, the carbonyl oxide 9 from ozonolysis of Z-5 was only partially trapped by the trione under identical conditions. The two alkenes thus give rise to different carbonyl oxides¹⁸.

The acetone oxide-trione adduct 16 as well as that resulting from trapping of the carbonyl oxide 9 are stable only up to about 0°C. Above 0°C the adducts decompose readily to form phthalonic anhydride and acetone or methyl benzoate (eq. 10). The instability of these acyl ozonides is in strong

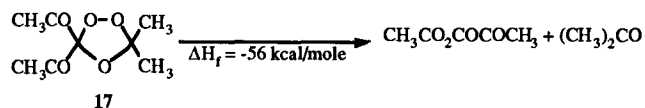


sults in oxirane 14 and dioxetane 15 as well as methyl benzoate and some unidentified products. A radical chain reaction may be involved as well, about 1.9 moles of alkene are consumed per mole of ozone.

DISCOVERY OF ANOTHER POTENTIALLY LUMINESCENT PEROXIDE

Before it was found that dioxirane 10 could be formed in good yield from ozonolysis of 5 at -20°C there was concern about whether much carbonyl oxide 9 was produced at this temperature. Very little tetroxane 10 was produced and ozonolysis of 5 in methanol did not result in the formation of any new molecule that would result from trapping of 9 by methanol. Accordingly, another type of carbonyl oxide trap was sought. It was felt that the central carbonyl group of indanetrione might be quite reactive toward carbonyl oxides. Indeed, exploratory experiments showed that the trione scavenges acetone carbonyl oxide quantitatively (eq. 9)¹⁹. No dioxirane was formed upon addition of E-5 to acetone solutions saturated with the trione and through which ozone was

contrast to the stability of simple alkyl ozonides which can be purified by gas chromatography at 100°C²⁰. The thermolysis of acyl ozonides is quite exothermic. Thermochemical calculations⁴ show that conversion of 3,3-diacetyl-5,5-dimethyl-1,2,4-trioxolane 17 to acetone and acetic pyruvic anhydride should be exothermic by 56 kcal/mole (eq. 11).



(11)

An energy of activation of about 20 kcal/mole for the decomposition of 17 would place the transition state about 75 kcal/mole above the products of the reaction. Thus, acyl ozonides represent a new class of potentially luminescent molecule. Such compounds should be easy to prepare and we are currently preparing examples of these molecules that will produce products with low excitation energies in order to test this proposal.

REFERENCES

1. (a) Story, P. R.; Whited, E. A. and Alford, J. A.; *J. Am. Chem. Soc.* (1989), **94**, 2143; (b) Yang, N. C. and Carr, R. V.; *Tetrahedron Lett.* (1973), 5143.
2. (a) Kopecky, K. R.; Lockwood, P. A.; Filby, J. E. and Reid, R. W.; *Can. J. Chem.* (1973), **51**, 468; (b) Bailey, P. S.; Carter, T. P.; M. Fischer, Jr., C. and Thompson, J. A.; *Can. J. Chem.* (1973), **51**, 1278; (c) Criegee, R. and Banciu, A.; *Chem. Ztg.* (1974), **98**, 261; (d) Yang, N. C. and Libman, J.; *J. Org. Chem.* (1974), **39**, 1782.
3. (a) Janzen, E. G.; Lopp, L. G. and Happ, J. W.; *Chem. Commun.* (1970), 1140; (b) Fang, T. S. and Mei, W. P.; *Tetrahedron Lett.* (1987), **28**, 329.
4. (a) Benson, S. W.; *Thermochemical Kinetics*. John Wiley and Sons. New York. (1976); (b) Hine, J. and Klueppel, A.W.; *J. Am. Chem. Soc.* (1974), **96**, 2924.
5. Story, P. R.; Denson, D. D.; Bishop, C. E.; Clark, B. C., Jr. and Farine, J. C.; *J. Am. Chem. Soc.* (1968), **90**, 817.
6. O'Neal, H. E. and Richardson, W. H.; *J. Am. Chem. Soc.* (1970), **92**, 6553.
7. Criegee, R. and Lohaus, G.; *Ann.* (1953), **583**, 6.
8. Scheeren, J. W.; Straps, R. J. F. M. and Nivard, R. J. F.; *Recl. Trav. Chim. Pays-Bas.* (1973), **92**, 11.
9. Kopecky, K. R.; Molina, J. and Rico, R.; *Can. J. Chem.* (1988), **66**, 2234.
10. Hoffmann, R. W. and Schneider, J.; *Chem. Ber.* (1967), **100**, 3698.
11. Molina, J.; Unpublished results.
12. Xie, Y.; Unpublished results.
13. Keul, H.; Choi, H. S. and Kuczkowski, R. L.; *J. Org. Chem.* (1985), **50**, 3365.
14. Kopecky, K. R.; Xie, Y. and Molina, J.; *Can. J. Chem.* In Press.
15. Murray, R. W.; *Chem. Rev.* (1989), **89**, 1187.
16. Herron, J. T.; Martinez, R. I. and Huie, R. E. *Int. J. Chem. Kinet.* (1982), **14**, 201.
17. Bailey, P. S.; Hwang, H. H. and Chang, C. Y.; *J. Org. Chem.* (1985), **50**, 231.
18. Xie, Y.; Unpublished results.
19. Gerrard, J.; Unpublished results.
20. Murray, R. W.; Youssefyeh, R. D. and Story, P. R.; *J. Am. Chem. Soc.* (1967), **89**, 2429.

This special issue of *Química Nova* is dedicated to Prof. G. Cilento on the occasion of his 70th birthday and is financed by the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP).