

THERMAL DECOMPOSITION OF OZONIDES

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In a recent report on the photochemistry of ozonides we found the major products to consist of hydrocarbons which were, in part, formed by way of radical cage recombinations. (1) The present study is concerned with the thermal decomposition of the same ozonides and has yielded mechanistic information pertinent to both studies.

Although the thermal decomposition of several ozonides has been reported, no systematic study has been made; and, indeed, most such investigations suffer from a lack of quantitative data, incomplete product analysis, and, particularly, uncertainty about the purity and nature of the ozonide(s) being decomposed. In one of the most interesting and informative studies (2) of ozone decomposition, Criegee decomposed 1-methyl-1-*tert.*-butylozonide and obtained formaldehyde, *t*-butyl acetate, and methyl *t*-butyl ketone peroxide, suggesting the intermediacy of the Criegee zwitterion. (3) Other investigations include those of Greiner and Mueller (4), Bailey, *et al.* (5), Briner (6), Pasero (7), and Bernatek (8). Criegee (9) and Bailey (10) have investigated the thermal rearrangement of various indenones to anhydrides; more recently, Ullman and Henderson (11) demonstrated that the same rearrangement occurred photolytically. Rieche has investigated the effect of metals and metal salts on ozonide decomposition. (12)

We have again focused our attention on di-isopropyl ozonide ( 1 ) [*cis/trans* mixture] and cyclopentene ozonide ( 2 ) as two relatively simple ozonides, but ones possessing significantly contrasting structural features. In a typical experiment, a 1% solution of ozonide ( 1 ) in heptane was heated at 100° in a sealed tube fitted with a breakseal connection to a second chamber to which access was obtained through a rubber septum. The disappearance of ozonide was monitored by gpc. Products were characterized by means of their gpc retention times and by the infrared and nmr spectra of collected samples. Yields were determined by gpc and are corrected for differences in detector response; standard solutions were used to standardize the gpc prior to each run.

Tables 1 and 2 list the products of thermal decomposition for di-isopropyl ozonide ( 1 ) and cyclopentene ozonide ( 2 ), respectively, at 100° and 180°; the results of photolysis of



of the same ozonides are provided for comparison.

TABLE 1.  
Thermal and Photochemical Decomposition  
of Di-isopropyl Ozonide (1).

Product	Yield, mole %		
	100°, 12 hr.	180°, 5 min.	hν
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	24*	25*	35*
(CH <sub>3</sub> ) <sub>2</sub> CHCH(CH <sub>3</sub> ) <sub>2</sub>	3	3	33
(CH <sub>3</sub> ) <sub>2</sub> CHCHO	77	80	14
(CH <sub>3</sub> ) <sub>2</sub> CHCOOH	62	51	7
CO <sub>2</sub>	0	5	14
CO	5	8	41
HCOOH	22	25	43

\*Assuming two moles propane/mole of ozonide.

TABLE 2.  
Thermal and Photochemical Decomposition  
of Cyclopentene Ozonide (2).

Product	Yield, mole %		
	100°, 50 hr.	180°, 15 min.	hν
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	3	--	--
	25	37	35
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO	17	9	10
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	23	14	14
	1	3	18
CO <sub>2</sub>	0	0	0
CO	38	43	50
HCOOH	47	44	36

In contrast to Criegee's result with the terminal olefin, no ketone peroxide was produced; most simple ketone peroxides are stable at 100° for extended periods and could be expected to survive under these conditions. (13) It seems unlikely, therefore, that the Criegee zwitterion is an important intermediate.

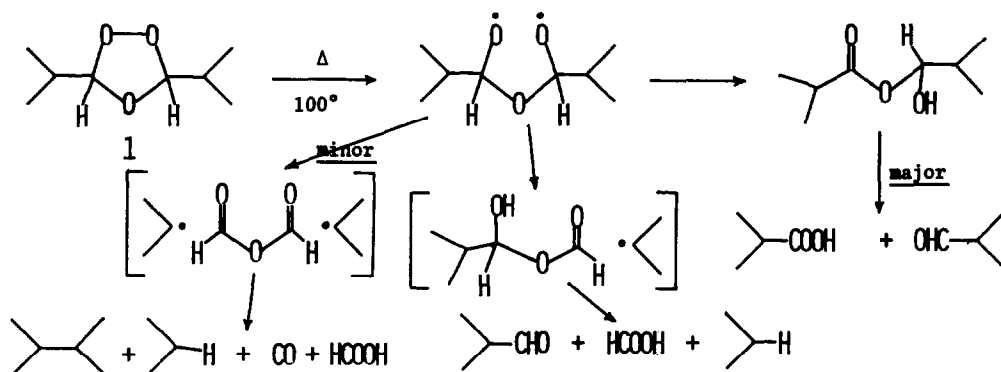
From the results of the photochemical reaction it was evident that the single most important reaction path consisted of oxygen-oxygen bond homolysis followed by a double β-scission to produce alkyl radicals and formic anhydride. The same reaction path is evident in the thermal reactions (*eq. 1*), being most important in cyclopentene ozonide thermolysis at 180° and least important in the case of di-isopropyl ozonide at 100°. It will be noted that cyclopentene ozonide thermolysis at 180° very closely parallels the photolytic decomposition.

The major products from the photochemical reactions are hydrocarbons which, as indicated earlier, most reasonably are formed by β-scission following homolytic cleavage of the oxygen-oxygen bond. The photochemical data, however, did not lend itself for a proper assessment of the reaction(s) involved in formation of aldehydes and acids. The combination of photochemical and thermal data from both systems now permits such an assessment.

The major products from the thermal decomposition of 1 at both temperatures are aldehyde and acid. It will be noted, however, that at 100° no carbon dioxide and very little carbon monoxide is obtained. Consequently, the propane that is obtained in 24% yield results largely

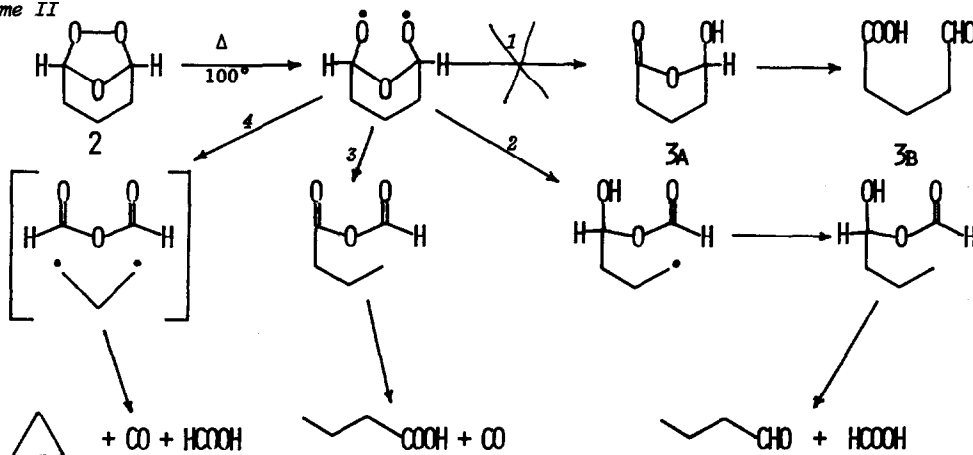
from some process other than a double  $\beta$ -scission to isopropyl radicals and formic anhydride; yet, a relatively large yield of formic acid is obtained. We offer the following rationale:

Scheme I



The concept of intramolecular hydrogen abstraction by alkoxy radical illustrated above is further strengthened by the data from cyclopentene decomposition. *Cyclopentene ozonide does not yield a product (3) which corresponds to the isobutyraldehyde and isobutyric acid obtained from 1.* We attribute this to the inability of the intermediate alkoxy radical to intramolecularly abstract a hydrogen. All, or almost all, cyclopentene ozonide molecules, then, undergo either single  $\beta$ -scission or a double  $\beta$ -scission. Butyraldehyde and butyric acid result from single  $\beta$ -scission. The absence of an intramolecular hydrogen abstraction process in cyclopentene ozonide decomposition probably accounts for the observation that its thermal decomposition much more nearly approximates the photochemical reaction.

Scheme II



We conclude that both the photochemical and thermal decomposition of aliphatic ozonides of this general type proceeds through homolysis of the oxygen-oxygen bond initially. Product distribution, then, is determined by a number of competing reaction paths open to the di-alkoxy radical. In the case of the photochemical reactions, the major reaction involves a simultaneous or near simultaneous double  $\beta$ -scission. For the thermal reactions of **1** at both temperatures, double  $\beta$ -scission is a minor contributor, the most important reaction pathway being intramolecular hydrogen abstraction to yield an acid-aldehyde. For cyclopentene ozonide, intramolecular hydrogen abstraction (*path 1, Scheme II*) is sterically less favorable and, therefore, even at 100° double  $\beta$ -scission (*path 4*) is relatively important. It is noteworthy that cyclopentene ozonide is appreciably more stable than the monocyclic ozonide, where intramolecular hydrogen abstraction appears feasible; in addition, hydrogen abstraction from solvent (*path 2*) appears to make a significant contribution. The formation of butyric acid (*path 3*) very possibly involves a  $\beta$ -scission followed by intramolecular hydrogen abstraction to yield the mixed formic anhydride as shown. The mixed anhydride would be expected to thermally decompose to butyric acid and carbon monoxide.

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