

SOLVOLYSIS OF OZONIDES

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Decomposition of ozonides or ozonisation mixtures has been attained with a great variety of reagents and over a wide range of reaction conditions. The methods can be divided into three main categories; viz. oxidative, reductive and solvolytic decompositions.

While the oxidative methods have been investigated and used to a fair degree, a special importance is attached to the reductive methods, since the desired products from ozonolyses are often sensitive aldehydes. Experimental details have been reviewed by Long¹ and Bailey². Solvolytic decompositions, on the other hand, do not seem to have been subjected to systematic investigations, the only example known so far being hydrolysis.

Solvolysis of an ozonide can be defined as a reaction where the active oxygen of the ozonide is transferred to the solvent and retained by it as such. In the case of hydrolysis the overall reaction may be represented as follows:

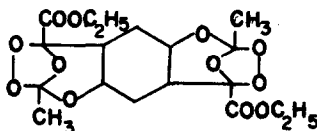
¹Long, L. Jr. Chem.Revs. 27 (1940) 437.

²Bailey, P.S. Chem.Revs. 58 (1958) 925.

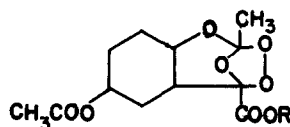


The active oxygen is transferred to water and retained in its active state in hydrogen peroxide.

In principle there is no reason why this type of reaction should not be extended to other solvents capable of incorporating active oxygen. It is a commonplace that a number of organic acids can take up an additional oxygen atom in the carboxyl group, thereby forming peracids. We considered it possible that carboxylic acids could also acquire an active oxygen from ozonides under suitable circumstances. Experiments were therefore carried out on the acidolysis of the stable ozonides I - IV.³⁻⁵



I

II: R=CH₃; III: R = C₂H₅; IV: R = C₃H₇

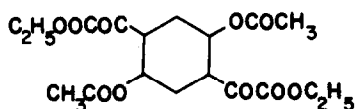
When dissolved in formic acid (98-100%) at room temperature, I and II smoothly formed performic acid which could be distilled

³Bernatek, E. and Thoresen, F. Acta Chem.Scand. 9 (1955) 743.

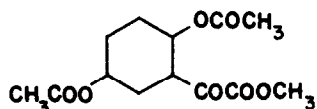
⁴Bernatek, E. and Bø, I. Acta Chem.Scand. 13 (1959) 337.

⁵Bernatek, E. and Hvatum, M. Acta Chem.Scand. 14 (1960) 836.

off in vacuo and amounted to 62 and 45% of theoretical respectively. The somewhat low yield is partly attributed to decomposition of peracid in the vapour phase. The distillation residues contained no active oxygen and from I the expected reduction product V was isolated in good yield.



V



VI

In glacial acetic acid the solvolysis proceeded tardily at room temperature, but the addition of catalytic amounts of perchloric acid accelerated the reaction. Distillation in vacuo afforded peracetic acid in 78, 60 and 60 % yield from the ozonides I, II and IV respectively. Again the content of active oxygen in the residues was nil and from I and II the reduction products V and VI were isolated in good yield.

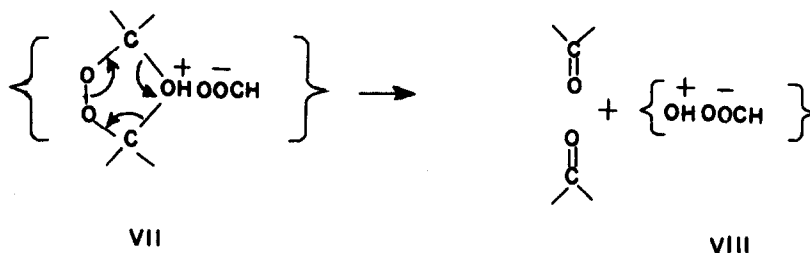
Peracids could also be determined directly in the reaction mixture by diluting aliquots with large volumes of ice-water, adding potassium iodide and titrate rapidly with sodium thiosulphate⁶. It was found in this way that ozonides II and

⁶Hatcher, W.H. and Holden, G.W. Trans.Roy.Soc. Canada 21 (1928) 238.

III in formic acid gave 87 and 93 % of performic acid. In acetic acid containing perchloric acid the ozonides I and III gave 86 and 97 % of peracetic acid.

Qualitative experiments were performed with propionic and dichloroacetic acids. Propionic acid needed perchloric acid as a catalyst and gave then with I and II ample amounts of perpropionic acid. Dichloroacetic acid, on the other hand, reacted smoothly without a catalyst forming peracid. Some side-reaction also occurred in this case imparting a dark colour to the reaction mixture.

The acidolysis of ozonides is probably a specific proton-catalysed reaction. From considerations of the basicity of the atoms in the ozonide ring the proton attack is most likely to take place at the ether oxygen. The protonated ozonide and e.g. a formate ion can form an ion-pair VII which by a concerted



collapse as indicated by the arrows forms two carbonyl groups and a new ion-pair VIII. The latter will of course immediately combine to performic acid.

Acidolysis, especially formolysis, may turn out to be a valuable method in decomposing ozonides which are only slowly attacked by water or are slightly soluble in aqueous solutions. Preliminary experiments indicate that no other organic peroxy compounds undergo the acidolysis reaction with the formation of peracids and work is in progress concerning the exploitation of the reaction as a diagnostic test for ozonides.