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Acidolysis of Some Stable Ozonides

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Eight stable ozonides have been subjected to acidolysis in formic and acetic acid. The amounts of peracids formed were determined in the reaction mixture and after distillation. The highest yields were obtained with ketozonides.

Solvolysis of ozonides as a more general reaction was established some years ago by two of the present authors.[1,2] Especially the reaction with formic acid was investigated. Here the acid took up active oxygen from the ozonide, giving performic acid. It could also be demonstrated that performic acid was produced by ozonisation of various compounds in concentrated formic acid.

This paper reports the solvolysis of some stable ozonides described in the literature. The work was undertaken with the aim of ascertaining whether ozonides from rather different unsaturated molecules would participate in the solvolysis reaction, and to which degree peracid was formed and could be isolated. As solvent and reagent was used concentrated formic acid as well as glacial acetic acid to which 0.2 % perchloric acid had been added as a catalyst. Ozonides of the following compounds were investigated: 1-Hexene, 2-hexene, styrene, stilbene, 1,1-diphenylethylene, 2-phenylskatole, and methyl *p*-methoxycinnamate. In addition, the ozonide from ethyl 2,6-dimethylbenzo[1,2-b, 4,5-b′]difuran-3,7-dicarboxylate was reinvestigated for the sake of comparison. It was found that the amount of peracid increased with time until a maximum was reached and thereafter a slow decrease was observed. In Table 1 are given the maximum values for performic and peracetic acids determined directly in the reaction mixture as well as after distillation *in vacuo*.

The fact that the ozonides did not give 100 % active oxygen on analysis (with sodium iodide in glacial acetic acid) does not necessarily mean that they are impure. The low results are probably caused by a rearrangement of the ozonides competing with the reduction in the acidic solution as observed by Criegee.[3]

The form of the curve obtained when the content of peracid (by direct titration) was plotted against the time elapsed since the start of the reaction was, in the case of ethyl dimethylbenzodifurandicarboxylate, as found previ-

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Table 1. Formation of peracids.

Ozonide of	Content of active oxygen in %	Performic acid in % of theoretical		Peracetic acid in % of theoretical	
		In reaction mixture	Distilled *in vacuo*	In reaction mixture	Distilled *in vacuo*
1-Hexene	94	58	27	30	30
2-Hexene	82	72	31	53	48
Styrene	70	68	30	39	25
Stilbene	71	63	26	36	28
1,1-Diphenylethylene	69	57	23	34	27
2-Phenylskatole	98	98	51	95	85
Methyl *p*-methoxycinnamate	64	32	17	20	14
Ethyl dimethylbenzodifuran-dicarboxylate	97	94	53	97	90

ously.[1] The same type of curve (see Fig. 1), (*i.e.* a relatively high initial titration value decreasing rapidly to a minimum for again to rise to a maximum value with an ensuing slow decrease), was also found in the formolysis and acetolysis of 2-phenyl-skatole ozonide and in the formolysis of methyl *p*-methoxycinnamate ozonide.

In the other cases a low value was obtained in the initial titration followed by a gradual rise to the maximum value and then the characteristic slow decline. We suppose that in the cases with a minimum on the curve there exists initially a very reactive peroxidic species other than peracid, for instance a protonated ozonide.[1] This entity is not directly converted to peracid, but as the curve suggests, goes through an intermediate of less reactivity as a perester or a hydrogen-bonded hydroperoxide. The last leg of the curve is entirely due to peracid, which could be confirmed by titration in the presence of ether and carbon tetrachloride. Ether as the stronger base removes the proton from the ozonide and a reasonable curve (dotted on Fig. 1) for peracid formation is obtained. That our curves in the majority of cases did not show any minimum value, is most likely explained by differences in reaction rates as the ozonides in question are the more reactive ones and run so rapidly through the protonated stage that it cannot be detected with our standard procedure.

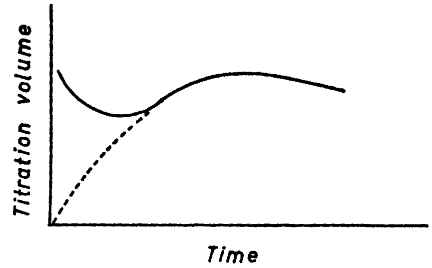

Fig. 1. Typical form of curve obtained when plotting titration volume *vs.* time.

When considering the amounts of peracid formed from the various ozonides, there is one conspicuous feature, *viz.* that the two stable ketozonides (from phenylskatole and ethyl dimethylbenzodifurandicarboxylate) give far higher yields than the aldozonides. Among the latter, however, there seems not to be any systematic differences whether there are 2 or 3 hydrogen atoms at the ozonide ring. This situation must in part hinge on the reaction rates and in part on the reactivity of the reduction products (ketone, ester, amide, or aldehyde) towards the peracid.

The average ratio of directly titrated to distilled peracid varies from performic to peracetic as 2.1 to 1.2, which is in accordance with the greater reactivity and lesser stability of performic compared to peracetic acid.

EXPERIMENTAL

Ozonides were prepared according to the literature; ethyl 2,6-dimethylbenzo[1,2-b, 4,5-b′]difuran-3,7-dicarboxylate diozonide as described by Bernatek,[1] 2-phenylskatole ozonide as described by Witkop and Patrick,[4] hexene-1 ozonide, hexene-2 ozonide, styrene ozonide, and stilbene ozonide as described by Criegee *et al.*,[3] methyl *p*-methoxycinnamate ozonide according to Kolsaker.[5] 1,1-Diphenylethylene ozonide was not described in the literature and was prepared as follows: The olefin (5 g) was dissolved in hexane-methylene chloride (100 ml, 1:2) and ozonised with one mole of ozone at −70°C. The solvent was removed *in vacuo* and the residue consisted of a colourless oil with a small amount of a solid substance which was removed by filtration. The oil (4.5 g) could not be purified by distillation because of its explosive character and was therefore used in the crude form.

Acidolyses were performed at 20°C in the appropriate acid (50 ml). The amounts of ozonides in each run ranged between 0.1 and 0.4 g. Samples (2 ml) were withdrawn at regular intervals and analysed according to Bernatek.[1]

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