syn-anti-Zwitterion Equilibration in the Ozonolysis of Di-isopropylethylene

By BRYNMOR MILE* and GARETH M. MORRIS

(*Department of Chemistry and Biochemistry, Liverpool Polytechnic, Byrom St., Liverpool* L3 3AF)

Summary Studies of the effects of temperature on the ozonolysis of *cis*- and *trans*-di-isopropylethylene show that *syn*- and *anti*-zwitterions are in equilibrium but have very different reactivities.

Now that the Criegee mechanism[1] for the ozonolysis of alkenes, extended to include the occurrence of *syn*- and *anti*-zwitterions,[2] is generally accepted, and the aldehyde-interchange mechanism largely abandoned,[3] attention is focussed on the zwitterion intermediates themselves. Here we give a preliminary account of carefully controlled experiments on the ozonolysis of *cis*- and *trans*-di-isopropylethylene (DIPE) which indicate that the two zwitterions can interchange rapidly but have marked differences in reactivity.

Molar solutions of the alkene in pentane were ozonized at selected temperatures in a conventional bubbler reactor, except that samples could be withdrawn from, or added to, the solution during and after ozonolysis without warming the bulk of the solution. This control of sampling and temperature is crucial. Analysis was by temperature-programmed g.l.c. using a di-nonyl phthalate stationary phase, flame ionisation detection, and electronic peak integration.

At −78 °C the two isomers behave quite differently. *cis*-DIPE gave a final ozonide *cis*/*trans* ratio of 1·35 independent of the time of sampling either during or after ozonolysis. For *trans*-DIPE the *cis*/*trans* ratio depended on the length of time the sample had been kept at −78 °C before warm up and analysis. The sample taken immediately at the end of ozonolysis gave a ratio of 0·57 in agreement with the widely reported steric influence of the initial alkene on the ratio.[2] (This stereospecificity has been rationalised by Bauld, Bailey *et al.*[2] into three rules which predict that *cis*-alkenes give predominantly *syn*-zwitterions which in turn combine with aldehyde to give mainly *cis*-final ozonide and *vice versa* for the *trans*-alkene and the *anti*-zwitterions.) However, when the ozonised solution was kept at −78 °C before sampling, although the total ozonide yield remained constant, the ratio increased with time to reach an asymptotic value of 1·25 (Figure). Murray and Hagen[4] found some indications of this effect in their fast and slow warm up experiments.

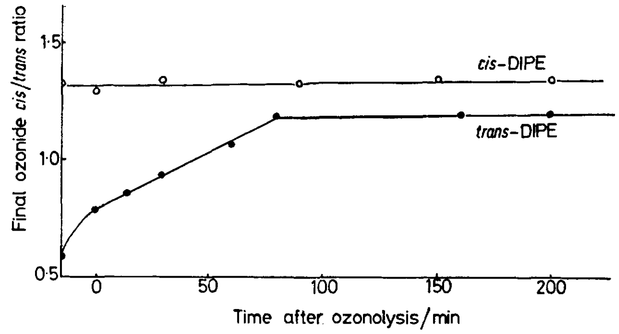
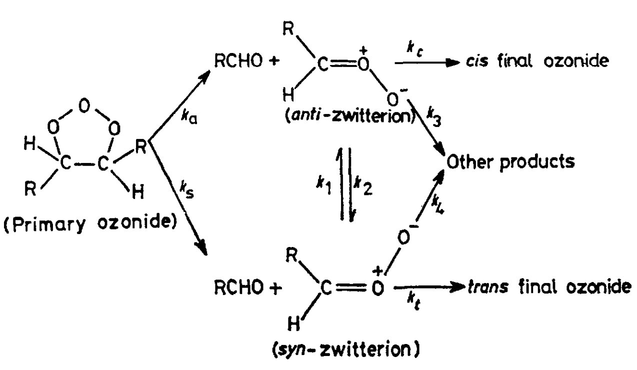


Figure. Change in final ozonide *cis/trans* ratio with delayed warm up time.

The difference in behaviour of the two isomers arises because of the different lifetimes of their primary ozonides at −78 °C, that of the *cis*-isomer being a few seconds and that of the *trans*-isomer being about an hour.[5] Thus only the ratio from samples of the ozonized *trans*-alkene left for several hours at −78 °C (delayed warm up) can really be used for comparison with the *cis*-alkene ratio since at shorter times a large proportion of the reactions leading to the final ozonide occurs not at −78 °C, as in the *cis*-alkene, but between −78 °C and room temperature. The *cis/trans* ratios from the two alkenes, when the reactions of both occur at −78 °C, are remarkably close (*cis* 1·35; *trans* 1·25), and the apparent relationship between the stereochemistry of the final ozonide and that of the parent alkene observed when both ozonised alkenes are sampled immediately after ozonolysis (*cis* 1·35; *trans* 0·57)[2] is largely lost.

We believe that these results are best explained by the occurrence of an equilibration between *syn*- and *anti*-zwitterions which, at −78 °C, is much faster than the coupling reactions with aldehyde to form the final ozonide. The *cis/trans* ratio is then independent of the rates of formation of the individual zwitterions but is dependent only on the relative rates of the two coupling reactions and the equilibrium population.[6] At higher temperatures (*i.e.* the immediate warm up experiments) the coupling reaction disturbs the equilibrium and the *cis/trans* ratio begins to approach the ratio k_a/k_s which would obtain if no equilibration occurred (Scheme).



Scheme

The residual small differences between *cis* and *trans*-DIPE probably arise because the rapid decomposition of the *cis*-primary ozonide results in a high local concentration of the zwitterion and aldehyde species in a narrow sheath around the ozone–oxygen bubble which disturbs the equilibrium even at −78 °C. Murray and Highley[3] have already speculated about the possibility of such equilibration.

It is unlikely that the effects of delayed warm up are due simply to the decomposition route to *anti*-zwitterions (which form the *cis*-final ozonide) having a lower activation energy than that to the *syn*-zwitterion for the following reasons. (i) The arguments of Lattimer *et al.*[7] indicate that the route to *syn*-zwitterion should have the lower activation energy. (ii) A delayed warm experiment (*i.e.* reactions occurring at −78 °C) in which propionic acid (a zwitterion scavenger) was present (10^{-2}M) resulted in a 50% reduction in the total final ozonide yield but still gave a *cis/trans* ratio of 1·25, an effect readily explained by rapid equilibration processes which maintain a constant ratio of *syn*- to *anti*-zwitterions. (iii) The possibility that this result could be due to a similar selectivity ratio for the two zwitterions (*i.e.* $k_c/k_3 = k_t/k_4$) can be discounted by the observation that immediate warm up of the propionic acid solutions caused the *trans* yield to drop by 75% but left that of the *cis*-isomer unchanged. This and other results lead us to think that there is marked differences in reactivity of the two zwitterions, the *anti*-zwitterions coupling much more rapidly than the *syn*.

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