# Pre-zwitterion Intermediates in the Liquid-phase Ozonolysis of Alkenes

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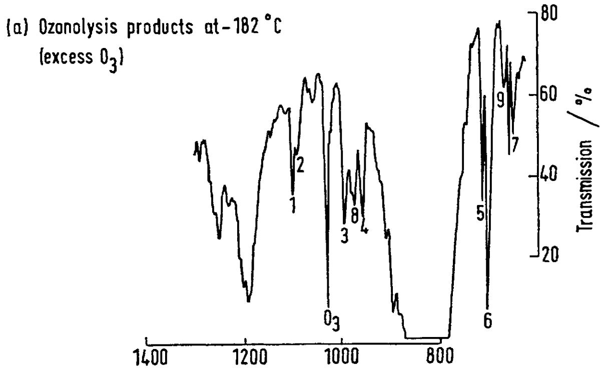
*Summary* Ozonolysis of 2,4,4-trimethylpent-1-ene at −180 °C gives a coloured π-complex between ozone and the alkene that rearranges at −165 °C to form the primary ozonide.

There is still considerable uncertainty about the nature of the pre-zwitterion intermediates in the liquid-phase ozonolysis of alkenes[1] and about the part played by such intermediates in the overall mechanism.[2] Bailey and co-workers[1,3,4] have reported the formation at −155 °C of coloured complexes of ozone with aryl-substituted alkanes and alkenes. The seat of complexation is generally at the aromatic π-system, though in one case it is possibly at a conjugated styrene π-system. However, these workers did not observe such complexes when aliphatic alkenes were used,[4] so that the occurrence of ozone complexes for this important class of reactants remains speculative.

We have recently reported[5] our observation of the primary ozonide in the ozonolysis of an internal alkene at −105 °C. We now report studies on a terminal alkene (2,4,4-trimethylpent-1-ene) at much lower temperatures using solvents such as liquid ethane. Below −180 °C we have observed the i.r. spectrum of the primary ozonide and a red-coloured compound which we believe to be the postulated π-complex between ozone and aliphatic alkenes.

At these temperatures a flocculant precipitate forms as the ozone–nitrogen gas mixture passes through a modified Beckman VLT-2 cell, containing the alkene solution, and the cell develops a distinct red-brown colour. The red-brown colouration is not associated with the precipitate, but is either in solution or possibly associated with alkene frozen on the silver chloride windows of the inner cell. Figure (a) shows the i.r. spectrum recorded *in situ* at −182 °C. Only seven of the absorptions, observed at −182 °C (1 to 7) occur if the ozonolysis is carried out at higher temperatures (−165 °C), and at this higher temperature no red-brown colouration is observed.

We attribute these seven absorptions to the primary ozonide (probably a 1,2,3-trioxolan) since they are similar to the bands of a primary ozonide of an internal alkene[5] and disappear on warming to −120 °C to be replaced by those


(a) Ozonolysis products at −182 °C (excess $O_3$)

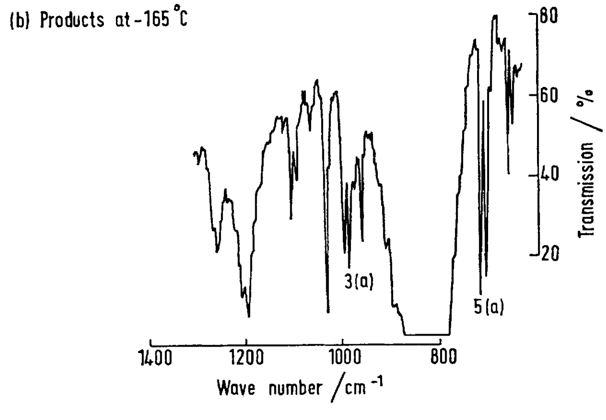

(b) Products at −165 °C

Figure. I.r. spectra during ozonolysis of 2,4,4-trimethylpent-1-ene in liquid ethane.

of the stable ozonide of 2,4,4-trimethylpent-1-ene. Thus we confirm that the primary ozonides of terminal alkenes are stable at much lower temperatures than those of internal alkenes (−105 °C).

It is only at the lowest temperatures used (<−180 °C) that ozonolysis simultaneously produces the red-brown colour and two additional bands at 978 cm$^{-1}$ and 669 cm$^{-1}$ (bands 8 and 9). On warming to −165 °C both the red colour and absorptions 8 and 9 disappear simultaneously [Figure (b)] and we therefore attribute both features to the same compound, a $\pi$-complex of ozone with the alkene. The colour formation is reminiscent of the conjugated ozone $\pi$-complex observed by Bailey[1] and co-workers at −155 °C. It is interesting to note the rapid disappearance of the aliphatic alkene–ozone complex at temperatures above −165 °C, just 10 degrees lower than the lowest temperature used previously.

The i.r. spectrum of a $\pi$-complex is commonly a composite of the spectrum of the components with minor differences associated with the weak bonding. In this particular case, we might expect to see only a shift in the $\nu_3$ and $\nu_2$ bands of ozone. In liquid ethane we have recorded $\nu_3$ and $\nu_2$ at 1032 cm$^{-1}$ and 698 cm$^{-1}$ respectively, and we therefore associate the bands at 978 cm$^{-1}$ and 669 cm$^{-1}$ with the $\nu_3$ and $\nu_2$ bands of ozone in a weak $\pi$-complex. Heicklen[6] *et al.* have recorded a band at 1030 cm$^{-1}$, which in one explanation, they attribute to a $\pi$-complex, our own observations would however favour their alternative explanation that this band should be attributed to uncomplexed ozone.

One puzzling feature remains to be explained. At a temperature of −165 °C, the loss of the $\pi$-complex bands does not result solely in the formation of trioxolan bands but new absorptions also appear at 987 cm$^{-1}$ and 713 cm$^{-1}$ (enhanced contribution) [bands 3(a) and 5(a) Figure (b)]. These bands which are close to two strong trioxolan bands also behave in a similar fashion to the trioxolan bands disappearing at −120 °C to be replaced by stable ozonide bands. We, therefore, attribute these absorptions to the same trioxolan intermediate possibly associated with alkene frozen on the cell windows, the band displacement being due to a 'matrix' shift.

We consider that we have observed consecutive intermediate stages in the ozonolysis of a terminal alkene, the $\pi$-complex (<−182 °C), the primary ozonide (<−165 °C) and the stable ozonide. We are currently investigating these intermediates for other alkenes by i.r. and u.v.–visible spectroscopy using unusual low-temperature solvents.

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