Detection of Unstable Intermediates During the Liquid-phase Ozonolysis of *trans*-Di-isopropylethylene

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Summary *In situ* i.r. studies and the effects of the delayed addition of propionaldehyde after ozonolysis show conclusively the existence and persistence of unstable intermediates in the ozonolysis of *trans*-di-isopropylethylene in the liquid phase at −105° to −78 °C.

THE generally accepted mechanism for the ozonolysis of alkenes is that proposed by Criegee[1] in which an unstable primary ozonide cleaves rapidly to form a zwitterion, $\mathrm{R^1R^2\overset{+}{C}OO^-}$, and a carbonyl moiety which can then either couple together to form a stable ozonide or diffuse apart to produce carbonyl compounds, peroxides, and acids in the bulk solution. Direct spectroscopic observation of the unstable primary ozonide or other intermediates is limited to the observation of the n.m.r. spectra of ozonized alkene solutions, the spectra indicating a 1,2,3-trioxolane structure.[2,3] Hull, Hisatsune, and Heicklen[4] have recently reported the observation of new i.r. absorptions during the reaction of ozone with olefins co-condensed as solid films.

If the unstable intermediates cleave only slowly at −78 °C, the effect of the addition of a foreign aldehyde will depend crucially on the time of addition. Immediately after ozonolysis, the intermediate will be present in excess and thus addition at this stage will suppress the formation of the normal ozonide and result in the production of a mixed ozonide. If the ozonized solution is left for a few

TABLE

Time after ozonolysis/ min	Normal ozonide/ $M \times 10^{-2}$	Mixed ozonide/ $M \times 10^{-2}$
0	7·06	5·68
30	8·08	2·68
120	13·36	0·50
No addition	15·12	—

hours, then most of the intermediate will have been converted into zwitterions and then stable ozonide and thus the addition of the aldehyde will have little effect. The results shown in the table for the ozonolysis of *trans*-di-isopropylethylene (DIPE) indicate that propionaldehyde can intercept zwitterion intermediates even two hours after ozonolysis and demonstrate that even at −78 °C the precursor has a half life of about an hour.

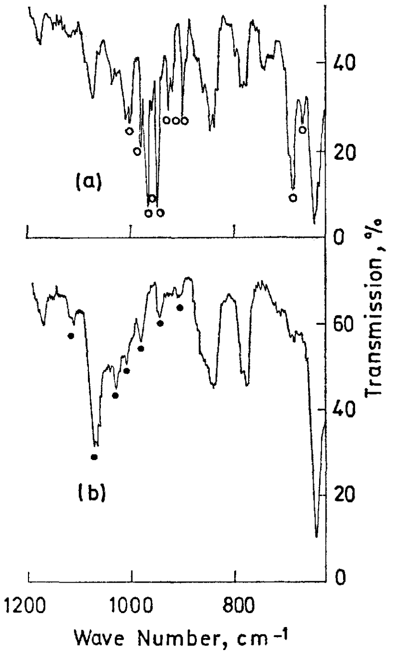
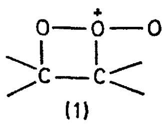
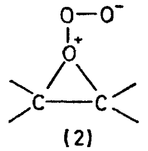


FIGURE. *In situ i.r. studies of the ozonolysis of* trans-*di-isopropylethylene* (0·04M) *in* CS_2 *at* −105 °C. ○ *Absorptions assigned to low-temperature intermediates.* ● *Stable products of* DIPE *ozonolysis.*

A Beckman VLT-2 variable-temperature i.r. cell was modified to allow *in-situ* ozonolysis to be carried out at temperatures down to −180 °C. The cell, of path length 3 mm, was maintained at −105 °C during ozonolysis. Figure (a) shows the spectrum of a solution (0·04 M DIPE in CS_2) during ozonolysis and Figure (b) that after a warming–recooling cycle. Several new bands (673, 692, 949, 959, 981, 1001 cm^{-1}) not ascribable to the starting materials or to the stable ozonide can be seen. During warm-up these bands disappear and are replaced by those of the stable ozonide, the rate of disappearance of the bands again indicating a half life of about an hour.

Provisionally we attribute the transient spectra to a 1,2,3-trioxolane molecule but structures such as the Staudinger molozonide (**1**) and the peroxy epoxide (**2**), cannot be entirely excluded though a π-complex is ruled out. We


(1)


(2)

associate the bands between 900 and 1001 cm^{-1} with asymmetric C–O modes in a ring structure; the bands are shifted to lower frequencies compared with those in the stable ozonide as might be expected because of the weaker bonding in the intermediate. The very strong band at 692 cm^{-1} is assigned to an asymmetric O–O stretching mode because (i) the ν_3 mode in ozone is its most intense i.r. absorption,[5] and (ii) since the frequency of the O–O mode drops in going from O_2 with a bond order of 2(ν_3 = 1556 cm^{-1})[6] to H_2O_2, with a bond order of 1(ν_1 = 877 cm^{-1})[7], a similar reduction might be expected between ozone (ν_3 = 1033 cm^{-1})[5] and the trioxolane (ν_3 = 692 cm^{-1}). In contrast to the matrix spectra[4] we find no evidence for unstable intermediate bands above 1001 cm^{-1} and we attribute absorptions in this region to the stable ozonide which is slowly formed even at these low temperatures. There is broad agreement on the position of the other new bands though our assignments are different largely because of the absence of bands above 1001 cm^{-1}.

We believe these are the first observations of the i.r. spectra of intermediates prior to the zwitterion stage recorded during the ozonolysis of alkenes in the liquid phase.

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