Direct Observation of the Molozonide–Ozonide Conversion

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EVIDENCE which indicates that the molozonide is a stable alkene–ozone reaction product has been published.[1] The molozonide is insoluble in n-C_5H_{12}, and on warming one may see the decomposition of the molozonide,[1b] but the decomposition products were not established. More recently, Bailey et al.[2] published evidence which supported a 1,2,3-trioxolane structure for the molozonide, and they stated that aldehyde and polymer were the decomposition products of the molozonide.

Many experiments in our laboratory with but-2-ene, pent-2-ene, and hex-3-ene have shown[3] that the ozonolysis products in an aprotic solvent are ozonide, aldehyde, and oligomer. The relative amounts of these products depended upon alkene geometry, concentration, solvent, and temperature. We can now report direct evidence that the molozonide is an intermediate in the ozonolysis of alkenes. The n.m.r. spectra (−130°) of solutions which were

prepared by the ozonation of CCl_2F_2 solutions of the trans-isomers of the above-mentioned alkenes at −130° indicated the presence of a molozonide (cf. Table). In the −130° spectra the single quartet for trans-but-2-ene and the single triplet for trans-hex-3-ene supports the 1,2,3-trioxolane structure for the molozonide. The molozonides were stable for a long time at −130°; the spectrum of the trans-hex-3-ene ozonation solution after 7 hr. was identical with that taken soon after the preparation of the solution.

In the spectrum of the hex-3-ene ozonation solution, there was no indication of any material other than molozonide. With pent-2-ene there was a very weak ozonide methine absorption and other very weak absorptions indicative of the presence of aldehydes. In the case of but-2-ene the areas of the methine peaks indicated that the molozonide and ozonide were present in the ratio of

TABLE

N.m.r. spectral data[a]

Alkene	Aldehyde CHO, δ[b]	Ozonide CH, δ	Molozonide CH, δ	Propanal CH_3, δ	Ethanal CH_3, δ	Methylene δ	Methyl δ
−130° Spectra							
trans-But-2-ene	9·52 (d)	5·00 (q), 4·90 (q)[c]	4·12 (q)		1·98 (d)		1·15 (d)
trans-Pent-2-ene	9·62 (s)	4·95 (u)	4·08 (m)	2·38 (u)	2·05 (d)	1·52 (m)	1·27 (d), 0·85 (t)
trans-Hex-3-ene			4·07 (t)			1·60 (m)	0·90 (t)
−70° Spectra							
trans-But-2-ene	9·55 (d)	5·07 (q), 4·98 (q)[d]			1·97 (d)		1·13 (d)
trans-Pent-2-ene	9·57 (s)	4·98 (m)[d]		2·27 (q)	1·95 (d)	1·47 (u)	1·22 (d), 0·82 (t)
trans-Hex-3-ene	9·60 (s)	4·93 (t), 4·87 (t)[d]		2·27 (q)		1·48 (m)	0·80 (t)

[a] Authentic ozonides of but-2-ene and hex-3-ene, authentic hex-3-ene ozonation oligomer and aldehydes were used for peak assignments.

[b] All δ values related to internal Me_4Si, 0·00. $CHCl_2F$ used as internal standard.

[c] Oligomer evidenced by weak absorption on low-field side of ozonide CH peak.

[d] Marked absorption, which disappeared on re-cooling the solution to −130°, on low-field side of peak indicated a considerable amount of oligomer.

(d), doublet; (m), multiplet; (q), quartet; (s), singlet; (t), triplet; (u), unresolved

3·1 : 1·0, oligomer was indicated by weak absorption on the low-field side of the ozonide methine peak, and acetaldehyde was clearly present. These facts would suggest that with a certain portion of the smaller alkene molecules the energy liberated during the formation of the molozonide could not be dissipated sufficiently rapidly in the small molecule and to its environment, with the result that these species continued to react to give ozonolysis products. It is conceivable that this phenomenon could occur with higher alkenes under appropriate experimental conditions.

That the molozonide is an intermediate in ozonolysis was confirmed by observing the molozonide methine peak and the ozonide region on an oscilloscope. As each ozonation solution was warmed to −100° the ozonide methine peak began to appear downfield from the molozonide methine peak. The ozonide peak could be observed to increase as the molozonide peak diminished, and when a temperature of −90° was reached the molozonide peak had disappeared completely. The solutions were warmed to −70°, and their n.m.r. spectra verified the usual ozonolysis products of ozonide, aldehyde, and oligomer (cf. Table).

For the ozonations, the theoretical amount of 2 vol. % ozone–oxygen was bubbled into an n.m.r. tube which was cooled to −130° and which contained 0·30 ml. of liquid CCl_2F_2, 0·24 mmole of alkene and a small amount of $CHCl_2F$ as an internal standard. After the ozonation helium was bubbled through the solution (−130°) for 10 min., and the n.m.r. tube then transferred to an n.m.r. probe which was pre-cooled to −130°. The spectra were recorded (Varian HR-60 instrument) at −130°, the solutions were warmed to observe the molozonide-ozonide conversion, and, finally, the spectra were recorded at −70°.

[1] (a) R. Criegee and G. Schröder, Chem. Ber., 1960, 93, 689; F. L. Greenwood, J. Org. Chem., 1964, 20, 1321; (b) F. L. Greenwood, J. Org. Chem., 1965, 30, 3108.

[2] P. S. Bailey, J. A. Thompson, and B. A. Shoulders, J. Amer. Chem. Soc., 1966, 88, 4098.

[3] F. L. Greenwood and H. Rubinstein, J. Org. Chem., in the press.