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OBSERVATION OF SECONDARY 2-BUTENE OZONIDE IN THE OZONATION OF TRANS-2-BUTENE IN THE GAS PHASE

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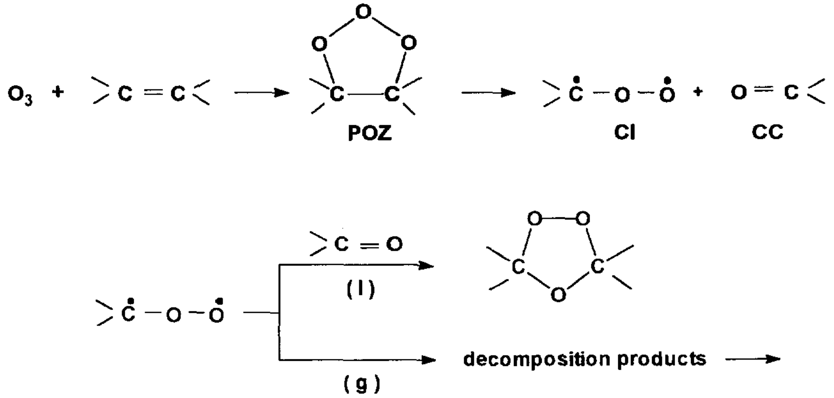
Abstract: GC/MS detection of secondary 2-butene ozonide in the gas-phase ozonation of trans-2-butene provides the first conclusive evidence on the feasibility of the combination of Criegee intermediate with parent carbonyl compound, which is not facilitated by solvent. Copyright © 1996 Elsevier Science Ltd

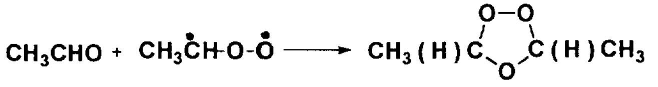
Gas-phase ozone-olefin reactions present interpretative difficulties and are therefore of continuing interest[1]. They are considered[2] to be initiated by formation of primary ozonide (POZ) and its unimolecular dissociation into a carbonyl compound (CC) and a biradical Criegee intermediate (CI), analogous to the corresponding solution-phase reaction[3]. Considerable uncertainties persist, however, regarding the reactions of the CI biradicals. The lack of solvent stabilization of energy rich POZ, CO and their transition states as well as the absence of solvent cage effect (holding CC and CI in close proximity) is believed[3] to result in suppressing the formation of secondary ozonides (SOZ) and favouring various decomposition modes of CI and other subsequent reactions (Scheme 1).



Scheme 1

Different fates of CI, manifesting themselves by different final products, were inferred also for the gas-phase ozonation of 2-butenes. The ozonation in the presence of oxygen at low pressures studied by photoionization mass spectrometry[4] affords e.g. CH_3CHO, H_2CO, CO_2, CH_4, CH_3OH and also more complex oxygenated products, and it is believed[4c] to occur via three, namely the ester, O-atom- and hydroperoxide channels of CI decomposition. A very minor signal at m/e 104 tentatively assigned to secondary

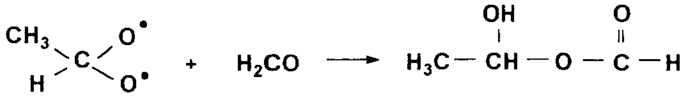
2-butene ozonide (SBOZ) and observed to increase upon addition of CH_3CHO to O_3 + 2-butene was judged to reflect a "titration" of CI (CH_3HCOO) with CH_3CHO (eq. 1),



(1)

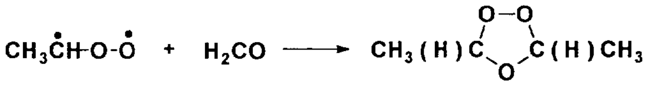
but this view will have to be reconsidered in view of the possible occurrence of SBOZ isomers originating from SBOZ decomposition[5] and/or of another mode of the association reaction between both species as noted below.

Studies at atmospheric pressure provide different and conflicting results. SBOZ was claimed to be detected by matrix isolation FTIR and microwave spectroscopy in cis-2-butene ozonation carried out in argon[6]. This SBOZ detection, possibly sufferring from the concommitant occurrence of many other products like esters, epoxides, hydroxyketones and oligomers containing C-O-C and C-O-O-C linkages, was however not confirmed in a similar matrix isolation FTIR spectral study of trans-2-butene ozonation in argon containing oxygen[7]. The latter examination[7] revealed, apart from other compounds, hydroxymethyl formate as a major product and explained its formation by eq. 2.



(2)

However, this type of association product, although observed in the gas-phase ozonation of ethene[8], was not been found in the FTIR spectral study of the ozonation of cis-2-butene in air in the presence of formaldehyde when propene ozonide was observed instead[9]. This observation was explained by eq. 3.



(3)

These data thus show that despite special attention continuously paid to the formation of SBOZ in the gas-phase ozonation of butenes under various conditions, there is no conclusive evidence on a bimolecular reaction of the CI (CH_3CHO_2) with the parent CO (CH_3CHO) yielding SBOZ.

In our note we report the first convincing evidence on the formation of SBOZ in the gas-phase ozonation of trans-2-butene, carried out in nitrogen at low and ambient temperatures, by detecting this species using GC/MS technique. The findings allows us to infer for the first time that under the conditions used the bimolecular coupling of CI with CC can compete with CI decomposition and that the complete Criegee mechanism (until now valid only for the liquid phase) can also operate in the gas phase.

The ozonation of trans-2-butene was carried out[10] by mixing gaseous mixtures of ozone and alkene (both 0.09 % in N_2) at ambient or lower (at most -40 °C) temperatures. The depletion of ozone was complete, whereas that of trans-2-butene corresponded to only 60 % and was not affected by the reaction temperature. The ozonation products separated[11] by GC and identified by GC/MS are CH_3CHO, $CH_3C(O)OH$, and secondary butene-2-ozonides. Amounts of these products (in molar %) determined by gas-chromatography do not vary within the temperature range -40 - 20 °C and are, in the given order, 43-54, 0-2, and 6-7. Some other GC/MS peaks are very insignificant and belong to very minor products. Typical GC/MS trace showing the separartion of cis- and trans- ozonides is given in Fig. 1

Both peaks show identical mass (70 ev) spectrum: (m/e (rel intensity) 104 (M, 4), 89 (M-CH_3, 15), 72 (8), 61 (7), 60 (10), 45 (30), 44 (32), 43 (100), 31 (9), 29 (30) corresponding to the common fragmentation scheme[12].The assignment of the cis and trans structures is based on the generally known longer GC retention time for the former isomers on polar columns[3c]. The trans-2-butene ozonide/cis-2-butene ozonide ratio[13] ranges between 2.3 - 2.5. The comparison of this ratio with those observed in the liquid ozonation of trans-2-butene in different solvents is of interest. The ratio for the ozonation in hydrocarbons (1.6 - 1.9) is lower, but that for ozonation in a polar dimethyl ether (2.3) is comparable[3c]. In view of the accepted stereoselectivity in

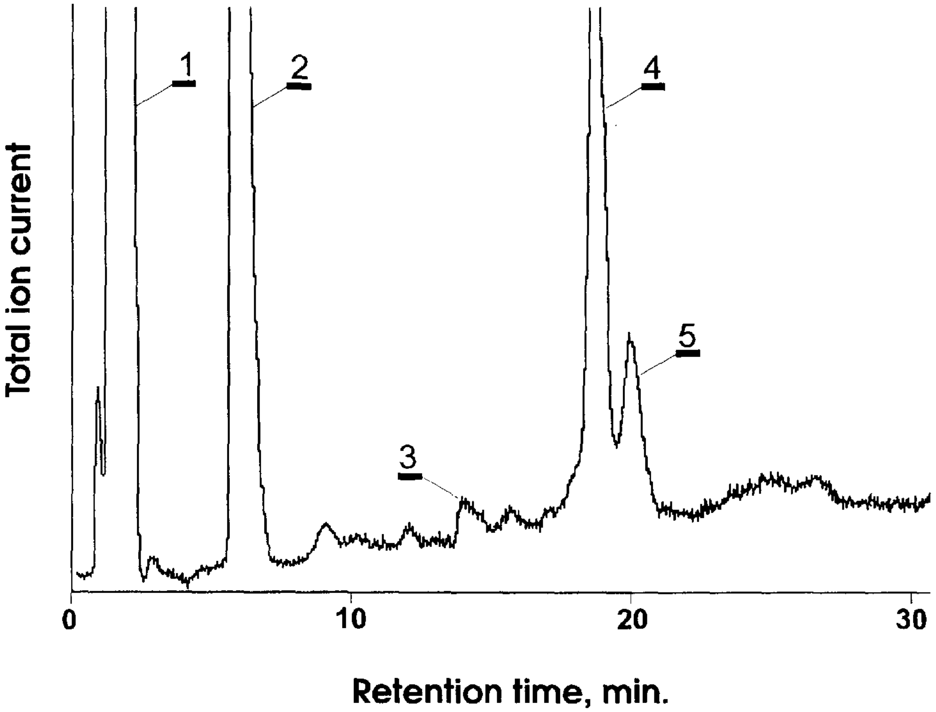
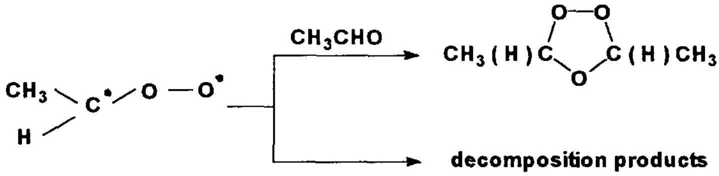


Fig. 1. GC/MS trace of ozonation products of trans-2-butene.
1 trans-2-butene, 2 acetaldehyde, 3 methanol, 4 trans-SBZO, 5 cis-SBZO

the POZ cycloreversion and/or CI and CO combination (e.g.[3a]), this finding is, however, uneasy to explain at present. Relative amounts of CH_3CHO, $CH_3C(O)OH$ and SBOZ as well as no observation of other ozonation products imply that major portion of CH_3CHOO biradical gets lost by decomposition (and other consecutive) reactions into apparently a number of very small quantity products, (as typically observed in other gas-phase studies, e.g. refs.[4c,7,9]), and that only a minor portion of CH_3CHOO is utilised in the combination with CH_3CHO to afford SBOZ (Scheme 2).



Scheme 2

It is thus apparent that the low temperatures and the absence of oxygen in our system are still not sufficient conditions for making the CI and CC combination dominant. It appears that the failures to observe secondary butene ozonide in other studies carried out at atmospheric pressure[7,9] is associated with the intervention of reactions with molecular oxygen.

Further study of gas-phase ozonation of other alkenes using GC/MS analysis is under way.

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10. 4.5 x 10^{-2} kPa of trans-2-butene and 13.5 x 10^{-2} kPa of O_3 in 150 kPa of N_2, each contained in a 2 l Pyrex flask, were equilibrated by opening the interposed PTFE stopcock. Both flasks were accommodated in a 15 l box and immersed in dry ice-ethanol.

11. Gaseous samples were withdrawn by a gas-tight syringe through a septum and analysed by gas chromatography (FID) and gas-chromatography-mass spectrometry on 3.3 m long columns packed with 5 % SE-30 on Chromosorb W and 5% 2,2'-oxydipropionitrile on Chromosorb 6-HP. Responce FID factors were determined: acetaldehyde 0.30, acetic acid 0.24, trans-2-butene 1.00, 2-butene-ozonide 0.12.

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13. Determined as the ratio of the areas for total ion current peaks.

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