The Mechanism of Ozonolysis Revisited by ^{17}O-NMR Spectroscopy

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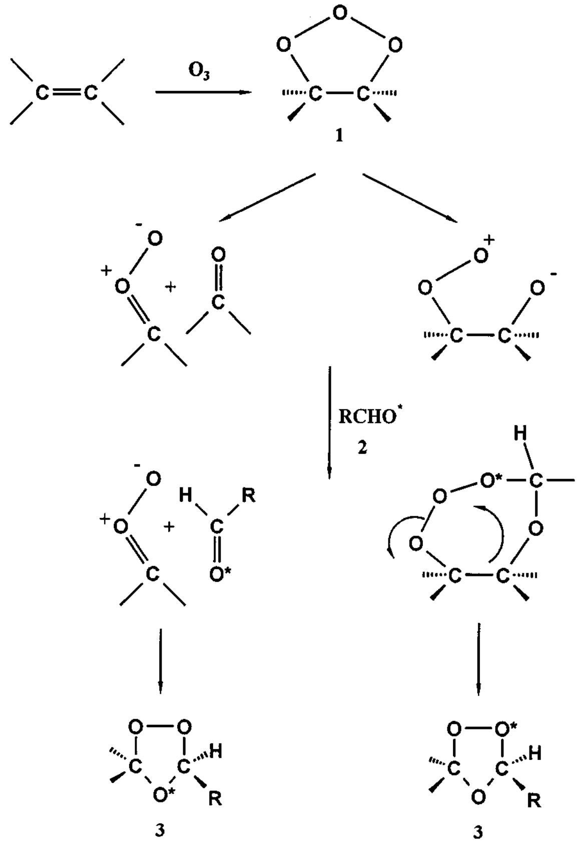
The mechanism of ozonolysis was revisited with the use of ^{17}O-NMR spectroscopy. In a crossover experiment with ^{17}O-labelled benzaldehyde and the ozonides of styrene and ethylidenecyclohexane it was shown that only the ether bridge of the secondary ozonides is carrying the ^{17}O label. This is contrary to results reported earlier and confirms the Criegee mechanism.

Introduction

Ozonolysis is one of the major transformations in organic chemistry and is used very widely in natural product synthesis.[1] The mechanism of this reaction has been amply investigated, mainly by the work of Criegee in the early 1960s.[2] Current research still focuses on the kinetics, the observation of intermediates and the theory of the process.[3][4][5][6][7][8][9] After the Criegee mechanism was established, conflicting evidence was reported by Story and others[10] leading finally to a so-called unified concept,[11] with subtle differences to the Criegee scheme. The major difference between the two mechanisms is the prediction of the positioning of an oxygen label when the primary ozonide **1** is allowed to react with a labelled aldehyde **2** in a crossover experiment (see Scheme 1). The Criegee model requires the positioning of the oxygen label only in the ether linkage of the secondary ozonide **3**, whereas the unified concept predicts the introduction of the label also in the peroxo bridge.

Indeed, by use of ^{18}O labelling and mass-spectrometric techniques it was reported[11][12] that the label has been found in the peroxo bridge, thus supporting the unified concept. However, the reported results from different groups were conflicting.[13] Despite the importance of the question, a decisive investigation has not been reported to the best of our knowledge. The mass-spectrometric analysis relies on the fact that no label scrambling occurs during the mass-spectrometric procedures employed. Therefore, ^{17}O NMR should be a better choice, since with this tool a direct observation of the label in the intact secondary ozonide might be possible. To our surprise a ^{17}O-NMR study of ozonides has not been reported, and only during the course of this work appeared the first study with ^{17}O-chemical shifts of some stable ozonides.[14] Here we report the results of our labelling and crossover experiments.

Scheme 1. Mechanism of ozonolysis



Results and Discussion

We have chosen two olefins, styrene (**4**) and ethylidenecyclohexane (**5**) for this investigation. Styrene was chosen, because the secondary ozonide **6** of styrene is very well documented[15] and can be prepared in high purity. Further-

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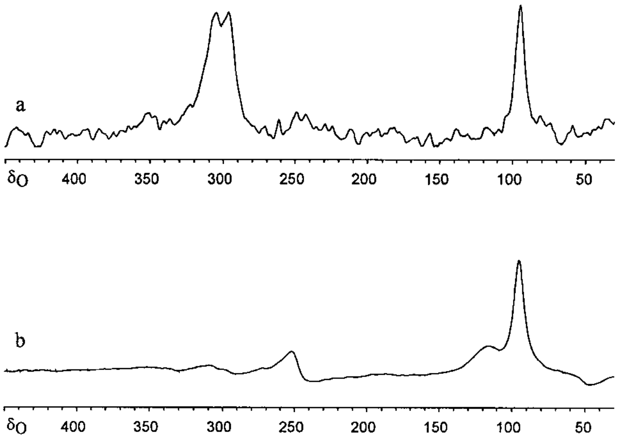
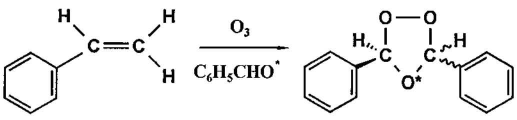
more, it offers no stereochemical complications of *cis* and *trans* isomerism of the ozonide, thus simple and clear ^{17}O-NMR spectra were expected. This was indeed the case and in Figure 1a the ^{17}O-NMR spectrum recorded at room temperature as obtained after the ozonolysis at −78 °C in pentane with ozone in natural abundance is shown. The two distinguishable oxygen atoms of the peroxo bridge resonate at $\delta_{\Omega} = 300$ and the signal of the ether oxygen atom appears at $\delta_{O} = 100$. This is in accordance with the findings of Griesbaum et al.[14] In Figure 1b the same compound is shown, but when ozonylated in the presence of 1.0 equiv. of ^{17}O-labelled benzaldehyde. Clearly only the ether bridge is carrying the label. The small additional broad signals stem probably from oligomers.

Figure 1. (a) Room-temperature ^{17}O-NMR spectrum of the secondary ozonide of styrene obtained after ozonolysis in pentane at −78 °C; (b) room-temperature ^{17}O-NMR spectrum of the secondary ozonide of styrene obtained after ozonolysis in pentane at −78 °C in the presence of 1.0 equiv. of ^{17}O-labelled benzaldehyde





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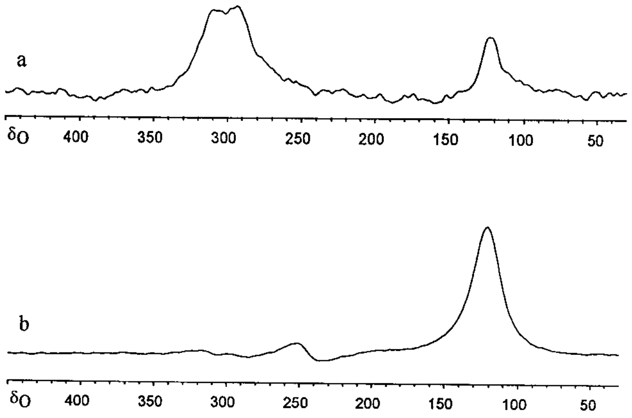
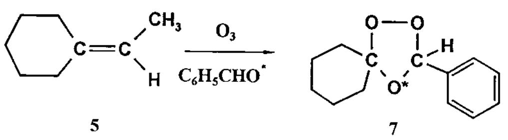
Ethylidenecyclohexane (**5**) was chosen since it was one of the compounds Story and coworkers used to establish the unified ozonolysis scheme.[11] We have tried to follow in our experiments their reported conditions as closely as possible. In Figure 2 the ^{17}O-NMR spectrum of the secondary ozonide **7** is given when ozonylated with ozone at natural abundance in pentane at −78 °C alone (Figure 2a) and in the presence of 1.0 equiv. of labelled benzaldehyde (Figure 2b). Again we do not observe any labelling of the peroxo bridge. This is in contradiction to what was reported earlier for this ozonide based on mass-spectrometric analysis.

Figure 2. (a) Room-temperature ^{17}O-NMR spectrum of the secondary ozonide of ethylidenecyclohexane obtained after ozonolysis in pentane at −78 °C; (b) room-temperature ^{17}O-NMR spectrum of the secondary ozonide of ethylidenecyclohexane obtained after ozonolysis in pentane in the presence of 1.0 equiv. of ^{17}O-labelled benzaldehyde at −78 °C





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Conclusion

By ^{17}O NMR a direct analysis of isotope positioning in secondary ozonides is easily possible. Our results show that crossover experiments with ^{17}O-labelled benzaldehyde lead to an incorporation of the ^{17}O label only into the ether linkage of secondary ozonides. This is not only true for styrene but also for ethylidenecyclohexane, one of the predominant compounds leading to the formulation of the unified scheme of ozonolysis. We therefore conclude, that based on ^{17}O-NMR results the Criegee scheme is still the only one in accordance with the NMR evidence.

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Experimental Section

[^{17}O]Benzaldehyde was prepared by pyridinium chlorochromate (PCC) oxidation of 2.16 g (20 mmol) [^{17}O]benzyl alcohol using 6.46 g (30 mmol) of PCC suspended in 10 ml CH_2Cl_2, and stirring the suspension for 1.5 h at room temp. After addition of SiO_2 suspended in 10 ml of Et_2O, the solution was filtered, the solids were washed with diethyl ether and the combined organic extracts purified on a short column of SiO_2 to yield 1.2 g (56%) of a colorless liquid. Mass-spectrometric analysis showed an isotopic enrichment of 30%.

[^{17}O]Benzyl alcohol was prepared by condensing 350 ml of $^{17}O_2$ (15.6 mmol) into a degassed ether solution of benzylmagnesium bromide (31.25 mmol) After warming to −20 °C, the solution was stirred for 1 h and then hydrolysed with diluted H_2SO_4 and ice. The water phase was rapidly separated and extracted with diethyl ether. After drying of the combined organic phases with $MgSO_4$ and evaporation of the solvent, 2.31 g (67%) of [^{17}O]benzyl alcohol was obtained.

Ozonolysis: The olefins were dissolved in 10 ml of pentane and cooled to −78 °C. By using an ozone generator a stream of O_3/O_2 was passed through the solutions until a slight blue color developed. Surplus O_3 was removed by passing dry nitrogen through the cold solution. The solutions were somewhat concentrated in vacuo, warmed to room temp., and a small amount of THF was added as internal reference for the ^{17}O measurements. For the crossover experiments the procedure was repeated in the presence of 1.0 equiv. of labelled benzaldehyde.

NMR Measurements: ^{17}O-NMR measurements were performed with Bruker AM-400 and DRX-400 spectrometers using a 10-mm multinuclear forward probe head using both conventional data acquisition and ring down suppression techniques. The fids (spectral width 45 kHz) were recorded on 16 k data points for 16 k scans and processed with an exponential window using a line broadening of 200 Hz.

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