

Epoxidation of Olefins by Sodium Chlorate and Osmium Tetroxide

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K. A. HOFFMANN¹ found that the oxidation of inorganic and organic compounds by chlorates is catalyzed by OsO₄. He reported that aqueous solutions of sodium chlorate, in the presence of low concentrations ($5 \times 10^{-4}\text{M}$) of OsO₄ were able to hydroxylate ethylenic double bonds to diols. He suggested that an OsO₄-ClO₃⁻ addition complex was the oxidizing species, with the oxygen of the OsO₄ being transferred to the substrate. More recently it was proposed that this reaction occurred by addition of OsO₄ to the ethylenic double bond to form the cyclic osmium(VI) ester, which then is decomposed oxidatively to the *cis*-diol.^{2,3} It has now been found that the combination of NaClO₃ and OsO₄ is able to oxidize a short-chain olefin to epoxide in 50% aqueous acetic acid. We find that the epoxide oxygen is derived solely from the chlorate and that the epoxidation is nonstereospecific: no epoxide was found by decomposing the osmium(VI) ester with chlorate under our reaction conditions.

In a typical experiment, 2.5 ml. of aqueous 2M-NaClO₃ was mixed with 2.5 ml. of 0.1M-OsO₄

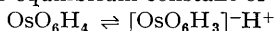
in glacial acetic acid in a capped pressure tube; the mixture was stirred and propene was introduced to give a pressure at 2 atm. at 0°. After 30 min. the reaction mixture was analyzed by v.p.c.; it was 0.2M in both propene oxide and 1-chloropropan-2-ol; smaller amounts of 2-chloropropan-1-ol and a trace of a high-boiling product were also found. Within one hour the concentration of propene oxide had increased to 0.5M and the concentration of 1-chloropropan-2-ol to 0.7M. The peak area of the high-boiling product had increased considerably and was identified as 1-acetoxypropan-2-ol. To show that the epoxide was not formed in the inlet of the gas chromatograph (250°), the reaction mixture was subjected to distillation under reduced pressure at room temperature; propene oxide was identified in the distillate. The rate of propylene uptake was dependent on both the OsO₄ and ClO₃⁻ concentrations. In an experiment performed as described above a solution of 0.2M-OsO₄ in glacial acetic acid was mixed with an equimolar aqueous solution of ¹⁸O enriched NaClO₃. Within 20 min. the reaction

mixture was 0.07M in propene oxide. Mass spectral analysis showed the $^{18}\text{O} : ^{16}\text{O}$ ratio in the epoxide to be almost exactly that of the ^{18}O tagged NaClO_3 itself; therefore, chlorate is the only source of the epoxide oxygen.

In similar experiments with *cis*- and *trans*-but-2-ene a 2:2:1 ratio of *trans*- to *cis*-butene oxide was found in both cases, indicating the formation of a common intermediate. On the other hand, we found that CrO_3 in acetic anhydride formed only *cis*-butene oxide with *cis*-but-2-ene and only *trans*-butene oxide in 20% yield with *trans*-but-2-ene. This stereospecificity agrees with a suggested⁴ cyclic intermediate.

When the osmate ester of propene was prepared in glacial acetic acid and 1M aqueous NaClO_3 solution was added, large amounts of CO_2 were formed; no propene oxide was detected.

The tetrahedral OsO_4 is able to increase in co-ordination number to six by taking up, for example, two pyridine³ or two water⁵ molecules. For the last example Bavay, *et al.*, determined the value for the equilibrium constant of the reaction:



to be 6.3×10^{-8} at 1M ionic strength and at 20°. In water-dioxan or methanol only traces of epoxides were formed. Probably only the weak acid $\text{OsO}_4 \cdot 2\text{H}_2\text{O}$ is able to exchange one of its co-ordinated water molecules with ClO_3^- . As we

were not able to detect any change in the u.v. spectrum after addition of an excess of NaClO_3 , the concentration of the addition complex must be very low or the interaction between the two molecules must be very weak.

According to Halperin and Taube,⁶ the rate of oxygen exchange between chlorate and water under acidic conditions is slow. After the oxygen transfer, HClO_2 ($\text{p}K$ 2.31) is formed and its decomposition is quite rapid.⁷ The e.s.r. spectrum showed the presence of ClO_2 : it does not form epoxides in our reaction medium and reacts slowly with propene. The large amount of 1-chloropropan-2-ol arises mainly from the addition of HOCl to the double bond.⁸ About 1% acetone, based on the epoxide, was found. It probably originated from acid hydrolysis of 1-chloropropan-2-ol. Using LiBrO_3 instead of NaClO_3 gave a small yield of propene oxide and acetone in the ratio of about 1:1.

Ethylene reacts slower under our reaction conditions than propene and only traces of ethylene oxide were detected. This observation is in agreement with a postulated electrophilic attack on the ethylenic double bond, which is accelerated by the electron-donating methyl group.

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