# Epoxidation of Olefins by Sodium Chlorate and Osmium Tetroxide

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K. A. HOFFMANN[1] found that the oxidation of inorganic and organic compounds by chlorates is catalyzed by $OsO_4$. He reported that aqueous solutions of sodium chlorate, in the presence of low concentrations ($5 \times 10^{-4}$M) of $OsO_4$ were able to hydroxylate ethylenic double bonds to diols. He suggested that an $OsO_4$–$ClO_3^-$ addition complex was the oxidizing species, with the oxygen of the $OsO_4$ being transferred to the substrate. More recently it was proposed that this reaction occurred by addition of $OsO_4$ 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 $NaClO_3$ and $OsO_4$ 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-$NaClO_3$ was mixed with 2·5 ml. of 0·1M-$OsO_4$ 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 $OsO_4$ and $ClO_3^-$ concentrations. In an experiment performed as described above a solution of 0·2M-$OsO_4$ in glacial acetic acid was mixed with an equimolar aqueous solution of $^{18}O$ enriched $NaClO_3$. Within 20 min. the reaction mixture was 0·07M in propene oxide. Mass spectral analysis showed the $^{18}O$ : $^{16}O$ 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 suggested[4] 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 pyridine[2] or two water[5] molecules. For the last example Bavay, *et al.*, determined the value for the equilibrium constant of the reaction:

$$OsO_6H_4 \rightleftharpoons [OsO_6H_3]^-H^+$$

to be $6 \cdot 3 \times 10^{-8}$ at 1M ionic strength and at 20°. In water–dioxan or methanol only traces of epoxides were formed. Probably only the weak acid $OsO_4,2H_2O$ 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, $HClO_2$ (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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