

THE MECHANISM OF AUTOXIDATIONS IN ALKALINE MEDIA

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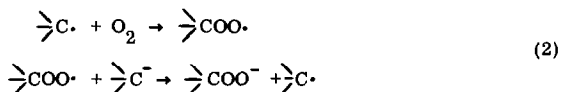
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Autoxidations in alkaline media have come in for much attention in recent years (1). The interest in these reactions has been greatly stimulated by the discovery of efficient basic systems (2) which allow of the rapid oxidation of many weak acids (yielding resonance-stabilized carbanions upon dissociation) at low temperatures. With esters and ketones the isolation of the primary products, the  $\alpha$ -hydroperoxides, has been reported (1a, d).

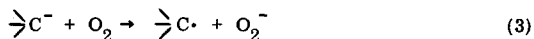
The mechanism of these reactions is still controversial, which is partly due to the fact that kinetic data do not yield decisive information. Reluctance to accept a bimolecular reaction of the carbanion and oxygen (1)



is based mainly on the violation of the spin conservation rule (3). Instead a chain mechanism (2) has been proposed (1e)

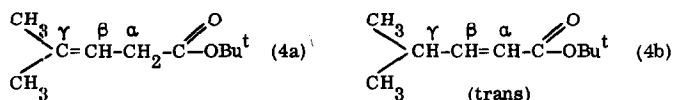


for which initiation could occur by (3)



Compared to a classical free-radical chain oxidation the hydrogen abstraction step is replaced by an electron transfer reaction, which would explain why autoxidations can proceed at a much lower temperature in alkaline than in neutral systems. In principle it should be possible to come to a decision on the mechanism involved by the following reasoning:

In an allylic free radical having a secondary  $\alpha$ -carbon atom and a tertiary  $\gamma$ -carbon atom a certain preference for localization of the unpaired electron in the tertiary position can be expected. Since secondary and tertiary free radicals differ but little in their reactivity towards oxygen, a free-radical type oxidation (the classical reaction as well as mechanism 2) should predominantly yield  $\gamma$ -oxidation products. In contrast, the negative charge in the corresponding allyl carbanion will tend to get localized in the secondary position. On the other hand a tertiary carbanion is more reactive towards oxygen than a secondary one, and accordingly a mixture of  $\alpha$ - and  $\gamma$ -oxidation products is expected to be formed in the direct carbanion oxidation according to mechanism 1. On the basis of these considerations the oxidation of the isomeric esters 4a and 4b was studied:



Free-radical oxidation at 60°C of either ester in benzene solution (initiator: 2,2'-azoisobutyronitrile) gave only  $\gamma$ -oxidation products (at most 2% of  $\alpha$ -product is present). The trans  $\gamma$ -hydroperoxide formed in 90% yield could be isolated. A by-product was probably the  $\gamma$ -alcohol. Alkaline oxidation at -80°C of the esters with potassium tert-butoxide as the base and 1,2-dimethoxyethane as the solvent gave at least 25% of  $\alpha$ -oxidation products. One of these, the  $\alpha$ -keto ester could be identified via its 2,4-dinitrophenylhydrazone. We made sure that the  $\gamma$ -hydroperoxide does not yield  $\alpha$ -oxidation products when dissolved in the alkaline medium at -80°C. The relative amounts of  $\alpha$ - and  $\gamma$ -oxidation products could easily be determined by NMR analysis which is straightforward owing to the small number of different hydrogens.

Our results offer strong support for a direct interaction of the carbanion and oxygen (mechanism 1). Whether this reaction is a one-step process or an electron transfer to oxygen followed by recombination of  $\text{C}^\cdot$  and  $\text{O}_2^-$  (reaction 3) lies beyond the scope of a purely chemical investigation.

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