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CHEMISTRY OF SUPEROXIDE ION. REACTION OF SUPEROXIDE ION WITH SUBSTRATES HAVING LABILE HYDROGENS

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The reactions between superoxide ion with substrates having labile hydrogens were examined by using KO_2-18-crown-6-DMSO system. Superoxide ion abstracts hydrogen from the substrate, only when formed radical can be highly stabilized by conjugating π-electrons.

There has recently been increasing interest concerning superoxide ion chemistry, especially its role in biochemical oxidations.1) Superoxide ion has been also observed in the adsorption or coordination of oxygen on a number of heterogeneous or homogeneous catalysts. However, little work has yet appeared on the chemical reactions which superoxide can undergo with simple organic substrate.2-14) The autoxidation initiated by superoxide ion is one of the current topics of the superoxide chemistry, where superoxide ion has been supposed to act as a hydrogen abstracting agent.11) We wish to report here the investigation of the stoichiometric reactions between superoxide ion with substrates having labile hydrogens.

Superoxide ion was prepared by using potassium superoxide complexed with the equivalent amount 18-crown-6 in dry DMSO.9,10) Three mmoles of substrate dissolved in 10 ml of DMSO was added dropwise to 6 mmol of KO_2 complexed with 18-crown-6 in 20 ml DMSO. The reaction mixture was stirred under a stream of dry high purity nitrogen and the reaction was terminated by pouring the mixture into water. The products were extracted with ether first from basic, then from acidic solution and isolated by silica gel chromatography.

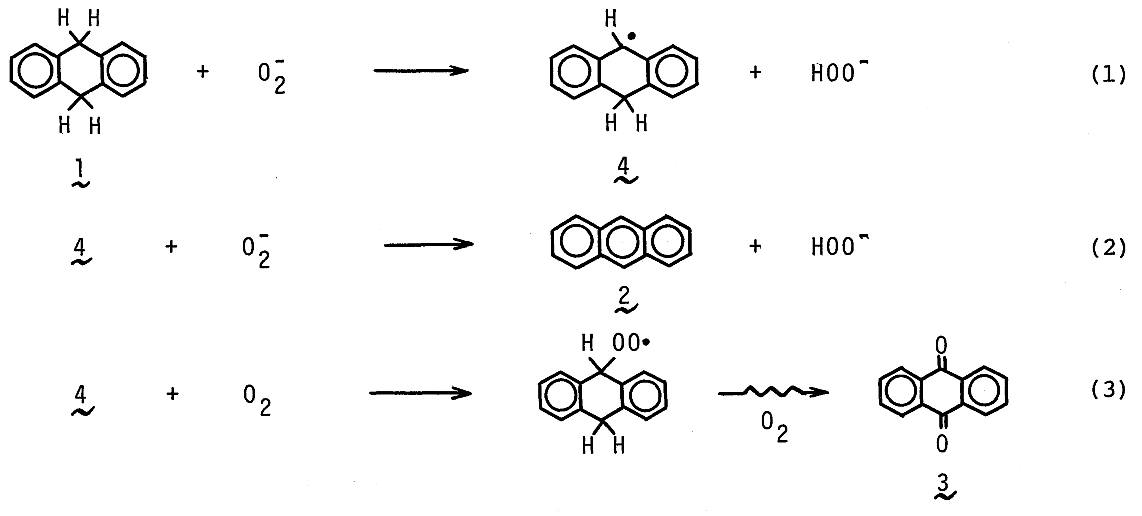
9,10-Dihydroanthracene (**1**) reacted instantly with superoxide ion and gave mainly the dehydrogenated product, anthracene (**2**). The yield of anthraquinone (**3**) was quite low under a nitrogen stream but it was fairly increased in the run under

Table 1. Oxidation of substrates having labile hydrogens by superoxide ion[a]

Substrate, Condition	Product	Yield (%)	Recovered substrate (%)
9,10-dihydroanthracene	anthracene anthraquinone	92.7 6.7	0
9,10-dihydroanthracene, under O_2	anthracene anthraquinone	56.1 32.3	0
2,5-di-tert-butylhydroquinone[b]	2,5-di-tert-butylbenzoquinone	65.0	0
1,4-hexadiene	benzene	79.5	19.2
1,4-hexadiene, O_2^-/subst = 4/1	benzene	89.2	9.4
1,3-hexadiene	benzene	64.7	35.0
1,3-hexadiene, React time, 1 hr	benzene	32.3	67.7
anthrone	anthraquinone	68.7	31.0
fluorene[b]	fluorenone	33.0	41.7
xanthene	xanthone	23.0	76.7
diphenylmethane	benzophenone	6.7	87.3

a) Reaction conditions other than noted: React. time, 3 hr; Temp, 25°C; O_2^- : crown ether : substrate = 2 : 2 : 1. Solvent, dry DMSO 30 ml.

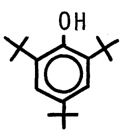
b) Polymerized product other than described was obtained.



atmospheric oxygen. The reaction seems to follow the mechanism suggested by Tezuka et al.,11) where superoxide ion acts mainly as a hydrogen abstracting agent. Although both superoxide ion and molecular oxygen have the unpaired electron, molecular oxygen seems to be more active than superoxide ion for the radical recombination. Superoxide ion abstracted hydrogens both from 1,3- and 1,4-hexadiene to yield benzene as the sole product. The reactions were not completed within 3 hr and the yield of benzene increased with the increase of the reaction time or the ratio of O_2^-/substrate. Anthrone, fluorene, xanthene and diphenylmethane were also oxidized by superoxide ion, however the reactivity decreased in this order. Every product was in accordance with expectation based on the mechanism that superoxide ion first abstracts hydrogen to form a radical intermediate.

9,10-Dihydrophenanthrene, acenaphthene, cyclohexene, 2,3-dimethyl-2-butene, tetraline and cummene were further tested but all these substrates were not oxidized by superoxide ion. More than 97% of each substrate was recovered after the reaction. Since 2,3-dimethyl-2-butene has been known as the most excellent acceptor for singlet oxygen O_2 ($^1\Delta_g$), the fact shows that KO_2-18-crown-6-DMSO system is quite free from singlet oxygen. According to Tezuka et al., the autoxidations of cummene and cyclohexane are initiated by electrogenerated superoxide ion.[11] However, even under atmospheric oxygen, no reactions were observed for these substrates. Thus, it is evident that superoxide ion abstracts hydrogen from the substrate, only when formed radical can be highly stabilized by conjugating π-electrons.[15] It is not clear why the nature of superoxide ion differs depending on its origin. We think that platinum electrode may play some important role as a catalyst in the oxidation by electrogenerated superoxide ion.

It is noteworthy that 2,5-di-tert-butylhydroquinone is rapidly oxidized to the corresponding quinone by superoxide ion. Several oxidations of phenolic substrates such as 2,4,6-tri-tert-butylphenol (**5**),[14] 3,5-di-tert-butylcatechol (**6**),[13] epinephrine (**7**)[4] and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (**8**)[16] have been reported involving superoxide ion as the models for the biological oxidations. All these reactions are easily understood assuming that superoxide ion initiates the oxidations by hydrogen abstraction to form semiquinone radicals. Further detailed studies of hydrogen abstraction by superoxide ion in biochemical oxidation are now in progress.



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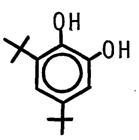

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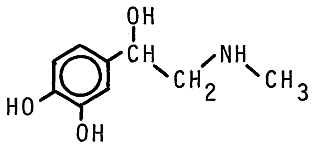

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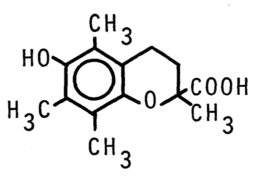

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