Nucleophilic and Electron Transfer Oxidations of Troponoid Compounds by Superoxide Ion

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Summary Tropone reacts with superoxide ion in Me_2SO to give salicylaldehyde, but not with peroxide ion, while the tropylium ion reacts with both superoxide ion and peroxide ion to give benzene, benzaldehyde, cycloheptatriene, and carbon monoxide.

IT has been demonstrated that the superoxide ion, $O_2^{-\bullet}$, is an important active species in biology[1] and can act both as a nucleophile and as an electron donor,[2] but no systematic investigation of its dual nature has been reported. In order to clarify the dual reactivity of $O_2^{-\bullet}$, its reactions with troponoid compounds such as tropone (**7**) and the tropylium ion (**1**), which have different electronic structures but the same basic framework,[3] were studied. The results were compared with those of reactions with the peroxide ion, O_2^{2-}.

In a typical experiment, a dry Me_2SO solution (5 ml) of (**7**) (1 mmol) was added to a vigorously stirred mixture of powdered KO_2 (2mmol) and 18-crown-6-ether (1 mmol) in dry Me_2SO (20 ml) at room temperature. After the appropriate time, the mixture was poured into water and the products were extracted with ether. Salicylaldehyde (**11**) was obtained in 42% yield together with large amounts of polymeric materials. Salicylic acid, a product of further oxidation, was not formed under these conditions.

TABLE 1. Reaction of (7) with superoxide ion[a]

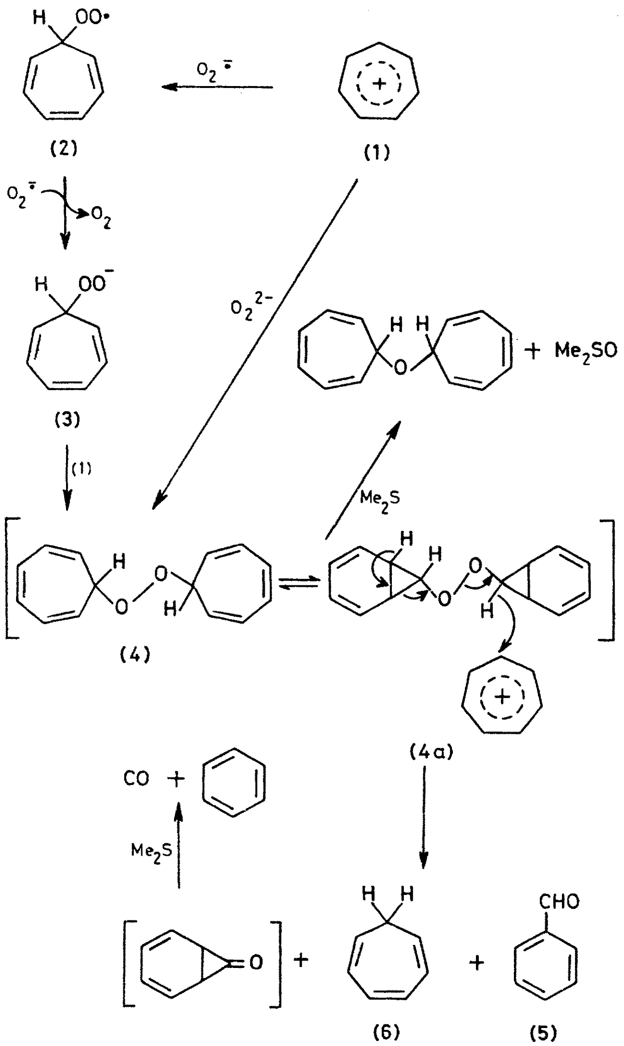
Reagent	Solvent	% Yield of (11)	% Recovery of (7)
KO_2	Me_2SO	42	0
„	„[b]	46	0
„	DMF	0	0
„	C_6H_6	0	0
„	MeCN	0	0
Na_2O_2	Me_2SO[c]	0	70

[a] A mixture of tropone (1 mmol), KO_2 (2 mmol), and 18-crown-6-ether (1 mmol) was stirred for 90 min at room temperature. [b] Under nitrogen. [c] A mixture of tropone (1 mmol), Na_2O_2 (1 mmol), and 15-crown-5-ether (1 mmol) was stirred for 90 min at room temperature.

Of particular interest in this reaction is the role of the solvent. Salicylaldehyde was formed in Me_2SO, but not in dimethylformamide (DMF), benzene, or acetonitrile. The polarity of the solvents has no influence on the formation of (**11**), since DMF has a similar polarity to Me_2SO.[4] A study of the effect of Me_2SO in a mixed solvent indicated that the yield of (**11**) increased in proportion to the mole ratio of Me_2SO to benzene. Tropone reacted more slowly with O_2^{2-}, but (**11**) was not produced under the reaction conditions.

However, the reaction of (**1**) with $O_2^{-}\cdot$ gave benzene, benzaldehyde (**5**), cycloheptatriene (**6**), and carbon monoxide. The same results were also obtained in the reaction with O_2^{2-}.[5] This reaction was not dependent on the solvent.

These oxidations by $O_2^{-}\cdot$ may be interpreted as follows. The superoxide ion reacts as a nucleophile in the reaction with (**1**) to give the peroxyl radical (**2**) which can be easily converted into the peroxy anion (**3**) by electron transfer from $O_2^{-}\cdot$. Ditropyl peroxide (**4**) formed from the reaction of (**3**) with (**1**) equilibrates with the norcaradiene isomer (**4a**), which may be oxidized by (**1**) to benzene and (**5**) as shown in Scheme 1. The formation of (**4**) as a possible intermediate is supported by the reaction of (**1**) with O_2^{2-} in the presence of dimethyl sulphide. Equimolar amounts of ditropyl ether and Me_2SO were each formed in 8% yields together with benzene, (**5**), and (**6**) in *ca.* 19% yields, respectively.

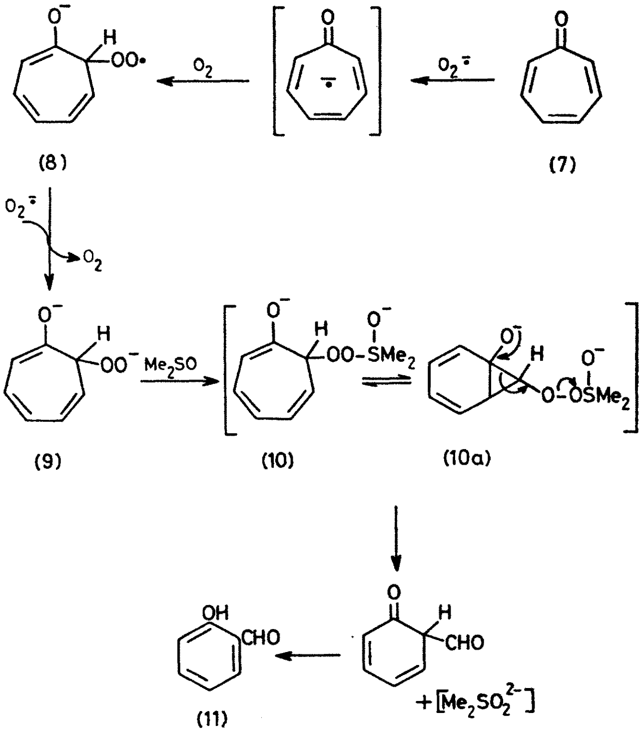


SCHEME 1

TABLE 2. Reaction of (1) with superoxide ion[a]

Reagent	Mole ratio [KO_2 or Na_2O_2/(1)]	% Yield C_6H_6	(5)	(6)	CO
KO_2	1	26	25	22	48[e]
„	1[b]	22	26	25	f
„	1[c]	27	24	24	f
„	2	20	23	25	f
Na_2O_2	0·5	22	26	27	11[d]
„	1	23	25	23	f

[a] The reactions were carried out in $(CD_3)_2SO$ for 30 min, and the product yields were calculated based on (**1**) by means of n.m.r. spectroscopy. [b] Under nitrogen. [c] $[^2H_7]$-DMF was used as solvent. [d] CO was identified by g.l.c., and its yield was estimated from its volume. [e] The gas measured was a mixture of CO and O_2. [f] The yield was not determined.



SCHEME 2

In contrast, $O_2^{-}\cdot$ probably behaves as an electron donor in the reaction with (**7**) to give a tropone radical anion[6] from which a peroxyl radical may arise. Such an electron transfer from $O_2^{-}\cdot$ to $\alpha\beta$-unsaturated ketones has been reported[7] and the fact that O_2^{2-} does not give (**11**) in the reaction with (**7**) supports this electron transfer pathway. The peroxyl radical (**8**) may collapse to give the anion (**9**) by electron transfer from $O_2^{-}\cdot$ which in turn is trapped by Me_2SO to form (**10**). Salicylaldehyde may arise from (**10**) *via* the norcaradiene isomer (**10a**) as shown in Scheme 2. Thus one of the functions of Me_2SO may be to induce monodeoxygenation.

In conclusion, the reactivity of the superoxide ion is altered by substrates which have different electronic structures; its ability to act as a nucleophile becomes the predominant feature in the reaction with tropylium ion, while with tropone it acts as an electron donor.

(*Received*, 23*rd November* 1978; *Com.* 1262.)

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