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Oxidation of Organic Compounds

Medium Effects in Radical Reactions

by

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Preface

This monograph deals with the rôle of solvents and of the composition of phase states in radical-chain processes involved in the oxidation of organic compounds. To begin with, data are gathered and collated, relating to the rôle of the medium in chain-initiation, branching, propagation and termination reactions. Problems are examined relating to the influence of the medium on a series of radical reactions, in which stable and alkyl radicals participate. On the basis of a knowledge of the influence of the medium on elementary reactions (including chain-propagation and termination), the influence of the medium on the rate and course of the oxidation process can be predicted. In this manner the reaction may be regulated, increasing the yield of valuable oxygen-containing compounds and lowering the amount of secondary products formed.

The monograph is intended for scientific research workers specialising in the field of radical reactions and in particular in the oxidation of organic compounds. It will also be of interest to engineers and engineering technologists employed in chemical works and in technical laboratories dealing with problems of oxidation processes.

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TABLE 78 Dependence of $k^{H}_{sec}/k^{H}_{cyclo}$ on the relative concentration of cyclohexane and heptane

T (°C)	Molar ratio of cyclohexane : heptane		
	1.4	1.097	0.0655
85	1.5 ± 0.11	1.4 ± 0.1	1.3 ± 0.1
55	1.3 ± 0.1	1.1 ± 0.1	—

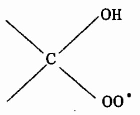
6.7 THE ROLE OF IONIC REACTIONS IN THE ELEMENTARY PROCESSES OF CHAIN-PROPAGATION AND CHAIN-TERMINATION

The influence of both specific solvation and unspecific solvation on the rate constants of the reactions and on the mechanism of the elementary steps of chain-propagation and chain-termination was examined in the preceding sections of this chapter and in Chapter 5. In doing this, however, a problem which was not tackled was the possible occurrence of other processes which may take place in solvents with high dielectric constants. The rôle of ionic reactions in the radical chain processes of the oxidation of organic compounds in the presence of solvents has not been very widely investigated. Until recently, it was assumed (see Chapter 5) that when organic compounds undergo oxidation in aqueous solutions of electrolyte (acids, alkalis, salts) the rôle of ions consisted in changing the rates and mode of decomposition of hydroperoxides: it had been observed as a rule that ions influence the heterolytic decomposition of ROOH and only recently was it shown that they could influence the mode of homolytic decomposition of a hydroperoxide.

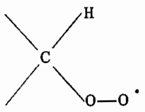
It is now evident that ions can participate in chain-propagation reactions and also inhibit radical chain processes of oxidation of a number of organic compounds. In particular examples exist(67,68) of a negative catalytic effect by the bicarbonate ion on the radical chain process involved in the oxidation of cyclohexanol.

Thus, sodium bicarbonate introduced at 4×10^{-5} mol^{-1} ℓ in the oxidation of cyclohexanol, reduces the rate of oxidation at 75°C by a factor of 3. The rate of inhibition of the reaction remains constant during the experiment (Fig. 102). Measurements of the electrical conductance have shown that the concentration of ions in the solution remains unchanged; hence such a compound can be considered an ideal inhibitor because it is not consumed during inhibition as opposed to, for example, the case of amines or phenols. The constancy of the inhibition rate over a prolonged period implies that inhibition by bicarbonate ions of the oxidation of cyclohexanol is an example of negative homogeneous catalysis in a radical chain-reaction, during which the substance (negative catalyst) which terminates the chain is not itself consumed(*).

Inhibition of oxidation by bicarbonate ions is observed only in the case of hydroxy-peroxyl radicals :



When C_6H_{12} is oxidised, a



radical is formed and no inhibition is observed when bicarbonate ions are introduced (Table 79).

The difference between the α-hydroxyl peroxyl radical and other peroxyl radicals consists in the fact(68) that it can act both as an oxidising agent and a reducing agent and take part in reactions as follows :

 (6.43)

(*) It has been shown that it is the bicarbonate ion which in fact inhibits the reaction, since the inhibitory effect is eliminated if the sodium bicarbonate solution is acidified with perchloric acid (perchloric acid itself does not affect the oxidation reaction).

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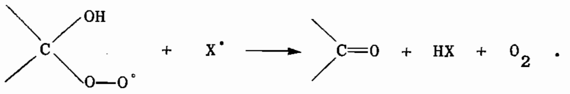


(6.44)

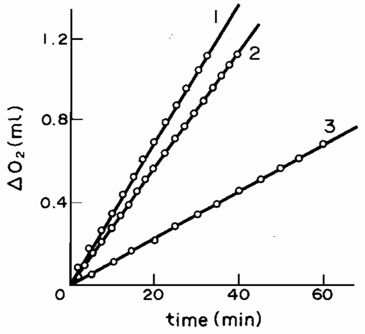


Fig. 102

Kinetic curves relating to the absorption of oxygen in the oxidation of cyclohexanol in the presence of 9 vol % of water.

1. without additive;
2. $[NaHCO_3] = 4 \times 10^{-5}$ mol^{-1} ℓ^{-1}

Temperature 75°C

$W_{inh} = 6.9 \times 10^{-7}$ mol ℓ^{-1} s^{-1}

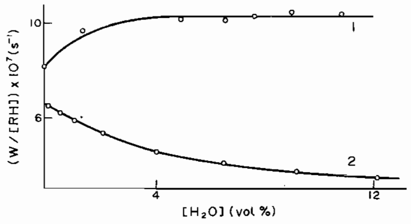


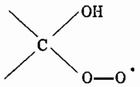
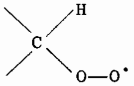
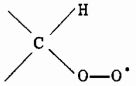
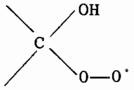
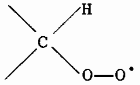
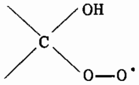
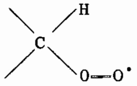
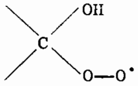
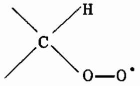
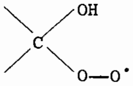
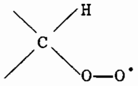
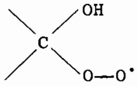
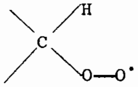
Fig. 103

The influence of water on the rate of oxidation of cyclohexanone.

1. no sodium bicarbonate present;
2. bicarbonate concentration $= 3 \times 10^{-5}$ mol^{-1} ℓ^{-1}

Temperature 75°C

TABLE 79 The Influence of Sodium Bicarbonate on the Oxidation of Aqueous Solutions of Cyclohexanol (I) and Cyclohexanone (II), and mixture of these compounds. Temperature 75°C $[NaCO_3] = 1.4 \times 10^{-4}$ mol ℓ^{-1}, $[AIBN] = 10^{-2}$ mol ℓ^{-1}

System	Structure of peroxyl radicals	$W_o \times 10^{-6}$ (mol ℓ^{-1})	W/W_o
91% I — 9% H_2O		8.52	0.21
94.3% II — 5.7% H_2O		3.3	0.95
89.3% II — 5.7% H_2O — 5.0% I	 ; 	4.74	0.64
84.3% II — 5.7% H_2O — 10.0% I	 ; 	5.72	0.55
74.3% II — 5.7 H_2O — 20.0% I	 ; 	7.70	0.42
89.3% II —5.7% H_2O — 5.0% iso-C_3H_7OH	 ; 	3.84	0.58
94.3% II —5.7% H_2O — 0.15 mol ℓ^{-1} H_2O_2	 ; 	2.92	0.61
74.3% II — 5.7% H_2O — 20.0% tert-C_4H_9OH	 .	3.00	1.00

The twofold reactive capacity of the α-hydroxyperoxyl radical makes it possible, in principle, to inhibit any desired number of chains from one particle of negative catalyst. The dependence of the rate of oxidation of cyclohexanol on the concentration of water in the presence and absence of sodium

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bicarbonate (Fig. 103) shows that, with increasing water content, the inhibitory effect of sodium bicarbonate also increases. This is evidently due to the increased degree of dissociation of the bicarbonate into ions. The increase in bicarbonate ion concentration results in a reduction in the rate of oxidation (Fig. 104).

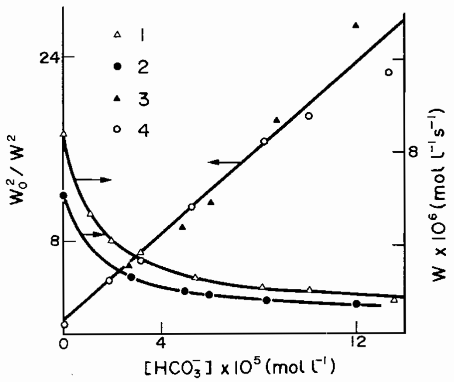


Fig. 104

Effect of sodium bicarbonate concentration on the rate of oxidation of cyclohexanone in the presence of 9 vol% water, and the variation of W_o^2/W^2 with increasing sodium bicarbonate concentration.(3,4)
1 and 4. 75°C and 2 and 3. 65°C.

W_{inh} = 6.9 x 10^{-7} mol ℓ$^{-1}$

The rate of oxidation of cyclohexane is related to the rate of inhibition (W_{inh}) and the concentration of bicarbonate ion by the following empirical expression :

$$W_o^2/W^2 = 1 + a\,[HCO_3^-] \qquad (6.LXXI)$$

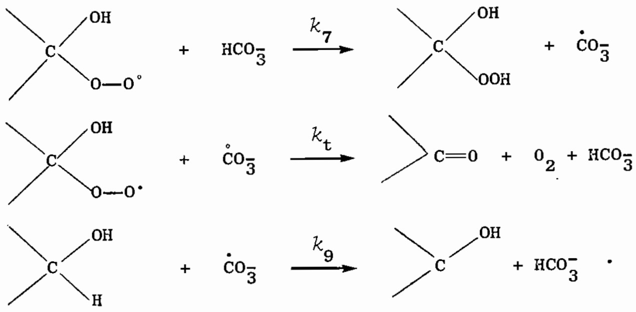
in which W_o is the rate of oxidation in the absence of sodium bicarbonate.

$$W_o = \frac{k_p}{\sqrt{k_t}}\,[RH]\,\sqrt{W_{inh}} \qquad (6.LXXII)$$

$$W = \frac{b\sqrt{W_{inh}}}{(1 + a\,[HCO_3^-])^{\frac{1}{2}}} \quad ; \qquad (6.LXXIII)$$

$a = 1.8 \times 10^5$ ℓ mol^{-1} and $b = r_{PT}[RH] = 1.0 \times 10^{-2}$ mol$^{\frac{1}{2}}$ ℓ$^{-1}$ s$^{-\frac{1}{2}}$ at 75°C (see Fig. 104).

The kinetic relations which were obtained are in good agreement with the scheme :



(6.45)

(6.46)

(6.47)

Assuming

$$k_7\,[HCO_3^-]\,[RO_2^{\cdot}] = k_9\,[RH]\,[\dot{C}O_3]$$

the following expression is obtained for fairly low concentrations :

$$\frac{W_o^2}{W_2} = 1 + \frac{k_7k_8\,[HCO_3^-]}{k_9k_t\,[RH]} \qquad (6.LXXIV)$$

or

$$W = \frac{k_p[RH]\;W_{inh}}{(k_t + k_7k_8\,[HCO_3^-]/k_9\,[RH])^{\frac{1}{2}}} \quad . \qquad (6.LXXV)$$

From these equations

$$a = k_7k_8/k_9k_t[RH] = 1.3 \times 10^5 \text{ ℓ mol}^{-1}.$$

Since $[RH]$ = 8.75 mol ℓ$^{-1}$ and k_t is 2.1 x 10^5 ℓ mol^{-1} s^{-1},(69) then $k_7k_8k_9$ = 3.3 x 10^{11} ℓ mol^{-1} s^{-1}.

Addition of hydrogen peroxide weakens the inhibitory effect of sodium bicarbonate; this is most probably connected with the reaction :

$$CO_3^{-\cdot} + H_2O_2 \longrightarrow HCO_3^- + HO_2^{\cdot} \quad , \qquad (6.48)$$

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