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# Oxidation of Organic Medium Effects

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*Academy of Sciences*

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This monograph deals with the rôle phase states in radical-chain process compounds. To begin with, data are of the medium in chain-initiation, reactions. Problems are examined on a series of radical reactions, pate. On the basis of a knowledge tary reactions (including chain-pr of the medium on the rate and cour ted. In this manner the reaction valuable oxygen-containing compound products formed.

The monograph is intended for scie field of radical reactions and in compounds. It will also be of int logists employed in chemical works problems of oxidation processes.

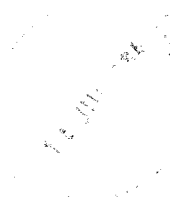


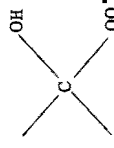
TABLE 78 Dependence of  $k_{\text{sec}}^{\text{H}}/k_{\text{cyclo}}^{\text{H}}$  on the relative concentration of cyclohexane and heptane

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

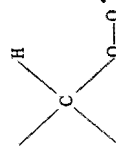
Specific

compound can be considered an ideal i during inhibition as opposed to, for The constancy of the inhibition rate inhibition by bicarbonate ions of the of negative homogeneous catalysis in the substance (negative catalyst) whi consumed(\*).

Inhibition of oxidation by bicarbonat hydroxy-peroxyl radicals :

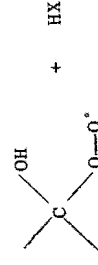


When  $\text{C}_6\text{H}_{12}$  is oxidised, a



radical is formed and no inhibition introduced (Table 79).

The difference between the  $\alpha$ -hydroxy calcs consists in the fact (68) that i a reducing agent and take part in re



Thus, sodium bicarbonate introduced at  $4 \times 10^{-5} \text{ mol}^{-1} \text{ l}$  in the oxidation of cyclohexanol, reduces the rate of oxidation at  $75^{\circ}\text{C}$  by a factor of 3. The

(\*) It has been shown that it is th

#### 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.

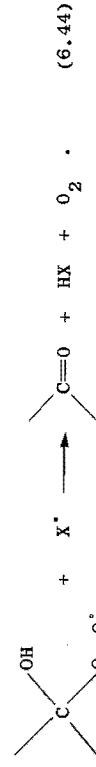


Fig. 102

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.  $[\text{NaHCO}_3] = 4 \times 10^{-5} \text{ mol}^{-1} \text{ l}^{-1}$   
Temperature  $75^{\circ}\text{C}$
3.  $k_{\text{inh}} = 6.9 \times 10^{-7} \text{ mol} \text{ l}^{-1} \text{ s}^{-1}$

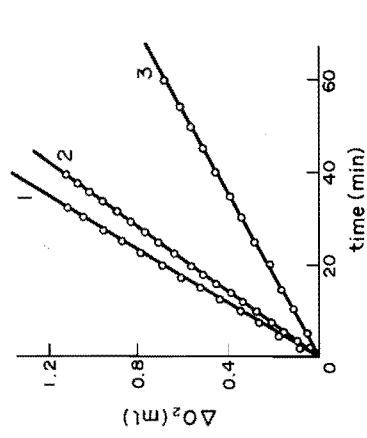
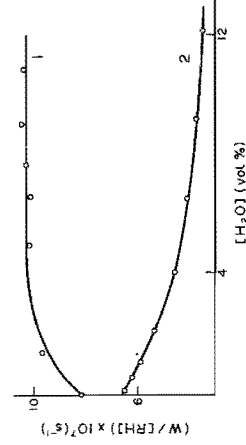


Fig. 103

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

1. no sodium bicarbonate present;
2. bicarbonate concentration =  $3 \times 10^{-5} \text{ mol}^{-1} \text{ l}^{-1}$   
Temperature  $75^{\circ}\text{C}$



System	Structure of
91% I — 9% H <sub>2</sub> O	
94.3% II — 5.7% H <sub>2</sub> O	
89.3% II — 5.7% H <sub>2</sub> O — 5.0% I	
84.3% II — 5.7% H <sub>2</sub> O — 10.0% I	
74.3% II — 5.7% H <sub>2</sub> O — 20.0% I	
89.3% II — 5.7% H <sub>2</sub> O — 5.0% iso-C <sub>3</sub> H <sub>7</sub> OH	
94.3% II — 5.7% H <sub>2</sub> O — 0.15 mol l <sup>-1</sup> H <sub>2</sub> O <sub>2</sub>	
74.3% II — 5.7% H <sub>2</sub> O — 20.0% tert-C <sub>4</sub> H <sub>9</sub> OH	

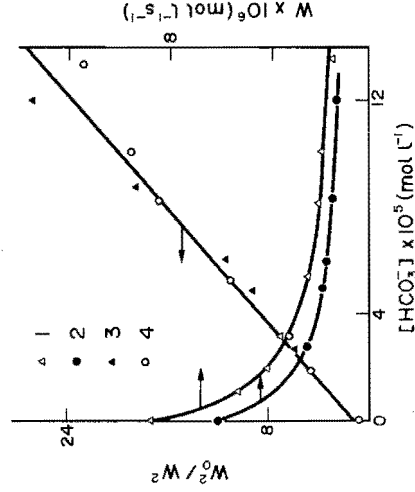
The twofold reactive capacity of th

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  $W_0^2/W^2$  with increasing sodium bicarbonate concentration, (3,4) 1 and 4. 75°C and 2 and 3. 65°C.

$$W_{0,65}^2 = 6.9 \times 10^{-7} \text{ mol l}^{-1}$$



The rate of oxidation of cyclohexane is related to the rate of inhibition ( $W_{inh}^2$ ) and the concentration of bicarbonate ion by the following empirical expression :

$$W_0^2/W^2 = 1 + \alpha [\text{HCO}_3^-] \quad (6.LXXI)$$

in which  $W_0$  is the rate of oxidation in the absence of sodium bicarbonate.

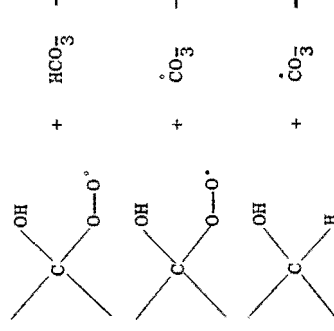
$$W_0 = \frac{k_p}{\sqrt{k_t}} [\text{RH}] \sqrt{W_{inh}}$$

$$(6.LXXII)$$

Specific

$\alpha = 1.8 \times 10^5 \text{ l mol}^{-1}$  and  $b =$  (see Fig. 104).

The kinetic relations which were observed are :



Assuming

$$k_7 [\text{HCO}_3^-] [\text{RO}_2^\cdot] = k_9 [\text{R}^\cdot]$$

the following expression is obtained

$$\frac{W_0^2}{W^2} = 1 + \frac{k_7 k_8 [\text{HCO}_3^-]}{k_9 k_t [\text{RH}]}$$

or

$$W = \frac{k_p [\text{RH}] W_{inh}}{(k_t + k_7 k_8 [\text{HCO}_3^-])/k_9}$$

From these equations

$$\alpha = k_7 k_8 / k_9 k_t [\text{RH}] =$$

Since  $[\text{RH}] = 8.75 \text{ mol l}^{-1}$  and  $k_t = 3.3 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ .

Addition of hydrogen peroxide weak

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