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Oxidation of Organic Compounds
Medium Effects in

by

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U.K. Pergamon Press Ltd., Headington Hill Hall,
Oxford OX3 0BW, England

U.S.A. Pergamon Press Inc., Maxwell House, Fairview Park,
Elmsford, New York 10523, U.S.A.

CANADA Pergamon Press Canada Ltd., Suite 104,
150 Consumers Road, Willowdale, Ontario M2J 1P9, Canada

AUSTRALIA Pergamon Press (Aust.) Pty. Ltd., P.O. Box 544,
Potts Point, N.S.W. 2011, Australia

FRANCE Pergamon Press SARL, 24 rue des Ecoles,
75240 Paris, Cedex 05, France

FEDERAL REPUBLIC
OF GERMANY Pergamon Press GmbH, Hammerweg 6,
D-6242 Kronberg-Taunus, Federal Republic of Germany

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First edition 1984

British Library Cataloguing in Publication Data

Emanuel, Nikolai Markovich

Oxidation of organic compounds.

1. Oxidation

2. Chemistry, Organic

I. Title II. Zaikov, G E

III. Maizus, Z K

547'.23 QD281.09 80-40511

ISBN 0-08-022067-3



This monograph deals with the rôle of phase states in radical-chain processes compounds. To begin with, data are given of the medium in chain-initiation, branching reactions. Problems are examined on a series of radical reactions, in particular. On the basis of a knowledge of elementary reactions (including chain-propagatory reactions) of the medium on the rate and course of the reaction is treated. In this manner the reaction may valuable oxygen-containing compounds and products formed.

The monograph is intended for scientific field of radical reactions and in particular compounds. It will also be of interest to logists employed in chemical works and 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
		0.0655
85	1.5 ± 0.11	1.4 ± 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.

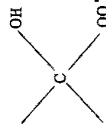
It is now evident that ions can participate in chain-propagation reactions and also inhibit radical chain processes of oxidation of a number of organic compounds. In particular examples exist (67,68) of a negative catalytic effect by the bicarbonate ion on the radical chain process involved in the oxidation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

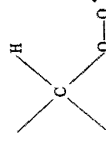
(Fig. 102) Measurements of the electrical conductance have shown that the

compound can be considered an ideal inhibitor during inhibition as opposed to, for example, the constancy of the inhibition rate over inhibition by bicarbonate ions of the oxidation of negative homogeneous catalysis in a reaction substance (negative catalyst) which is consumed (*).

Inhibition of oxidation by bicarbonate ion hydroxy-peroxy radicals :

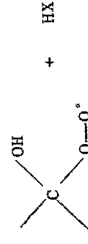


When C_6H_{12} is oxidised, a



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

The difference between the α -hydroxyl peroxides consists in the fact (68) that it can act as a reducing agent and take part in reactions



(*) It has been shown that it is the bicarbonate ion which acts as the inhibitory agent in the reaction, since the inhibitory action of bicarbonate solution is acidified

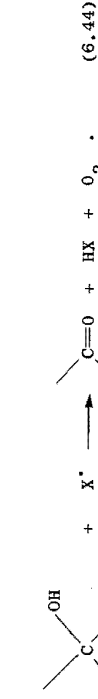


TABLE 79

The Influence of Sodium Bicarbonate on the Oxidation of Cyclohexanone and Cyclohexanone compounds. Temperature $[NaCO_3] = 1.4 \times 10^{-2} \text{ mol } \ell^{-1}$

System	Structure of peroxide
91% I — 9% H ₂ O	
94.3% II — 5.7% H ₂ O	
89.3% II — 5.7% H ₂ O H ₂ O — 5.0% I	
84.3% II — 5.7% H ₂ O H ₂ O — 10.0% I	
74.3% II — 5.7% H ₂ O — 20.0% I	
89.3% II — 5.7% H ₂ O — 5.0% iso-C ₄ H ₇ OH	
94.3% II — 5.7% H ₂ O — 0.15 mol \ell^{-1} H ₂ O ₂	
74.3% II — 5.7% H ₂ O — 20.0% tert-C ₄ H ₉ OH	

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. $[NaHCO_3] = 4 \times 10^{-5} \text{ mol } \ell^{-1}$
Temperature 75°C
 $k_{inh} = 6.9 \times 10^{-7} \text{ mol } \ell^{-1} \text{ s}^{-1}$

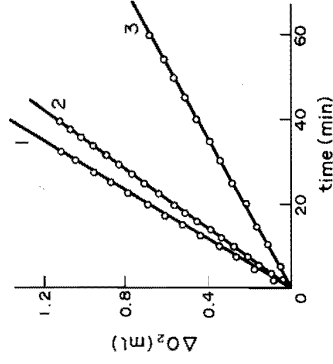
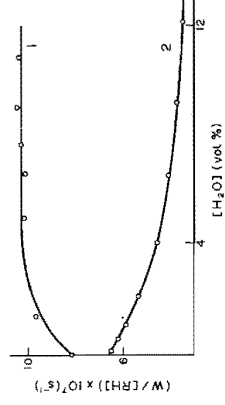


Fig. 103

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

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



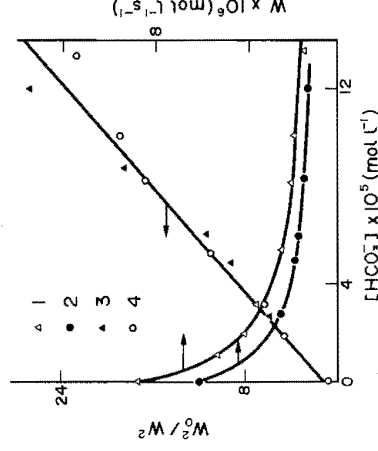
The twofold reactive capacity of the oxidant is, in principle, to inhibit any desirable reaction of the substrate with the oxidant.

The dependence of the rate of reaction on the concentration of the oxidant is shown in Figure 103.

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.



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

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 :

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

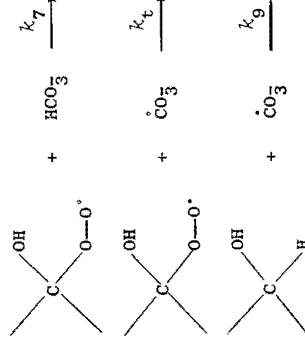
in which W_0 is the rate of oxidation in the absence of sodium bicarbonate.

$$W_0 = \frac{k_p [\text{RH}]}{\sqrt{k_t}} \sqrt{W_{inh}} \quad (6. LXXII)$$

$$W = \frac{b \sqrt{W_{inh}}}{1 + a [\text{HCO}_3^-]} \quad (6. LXXIII)$$

$a = 1.8 \times 10^5 \text{ l mol}^{-1}$ and $b = x_{PI} [\text{RH}]$ (see Fig. 104).

The kinetic relations which were obtained scheme :



Assuming

$$k_7 [\text{HCO}_3^-] [\text{RO}_2^{\cdot}] = k_9 [\text{RH}] [\overset{\cdot}{\text{C}}\text{O}_3^-]$$

the following expression is obtained for

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

or

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

From these equations

$$a = k_7 k_8 / k_9 k_t [\text{RH}] = 1.3$$

Since $[\text{RH}] = 8.75 \text{ mol l}^{-1}$ and k_t is $2.33 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$.

Addition of hydrogen peroxide weakens the inhibitory effect of sodium bicarbonate; this is most probably connected with the formation of hydroperoxide.

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