COUPLED REACTIONS OF DECOMPOSITION OF HYDROPEROXIDES AND OXIDATIVE ISOMERIZATION OF OLEFINS WITH CATALYSIS BY RHODIUM COMPLEXES

L. D. Tyutchenkova, L. G. Privalova, Z. K. Maizus, and I. M. Émanuél'

In an investigation of the catalytic action of complexes of metals of variable valence in the oxidation of higher \( \alpha \)-olefins, it was established that bis(triphenylphosphine)carbonylrhodium chloride \( \text{Rh}(\text{PPh}_3)_2\text{COCl} \) and tris(triphenylphosphine)rhodium chloride \( \text{Rh}(\text{PPh}_3)_3\text{Cl} \) catalyze a new reaction pathway — the oxidative isomerization of \( \alpha \)-olefins [1, 2]. It was suggested that the isomerization occurs under the influence of a form of the catalyst modified during oxidation, representing a complex of Rh(II) with oxygen, peroxide free radicals, or hydroperoxides.

In this work, to confirm these hypotheses, we investigated the decomposition of hydroperoxides in the presence of \( \text{Rh}(\text{PPh}_3)_2\text{COCl} \) in olefin medium.

EXPERIMENTAL METHOD

Technical cumene hydroperoxide (CHP) was purified according to the method of [3]. 1-Nonene hydroperoxide (NHP) was accumulated in the low-temperature oxidation of 1-nonene by molecular oxygen. The oxidate obtained was concentrated under vacuum by congealing the unreacted olefin at \( \sim 20^\circ \text{C} \).

The decomposition of cumene and 1-nonene hydroperoxides in a mixed solvent 1-nonene—chlorobenzene (1:1 by volume) was conducted in an atmosphere of argon at 120\(^\circ\)C.

The ESR spectra were taken on a Varian E-4 spectrometer. A solution of the hydroperoxide in toluene was placed in one of the branches of a two-horned ampoule, and a solution of the catalyst in the other. The ampoule was thoroughly evacuated, after which the solutions were mixed and frozen with liquid nitrogen (in the resonator of the spectrometer). The hydroperoxide concentration was \( \sim 7 \times 10^{-1} \text{ M} \), catalyst concentration \( \sim 5 \times 10^{-3} \text{ M} \).

DISCUSSION OF RESULTS

The ratio of the rates of consumption of the hydroperoxide and the inhibitor N-phenyl-\( \beta \)-naphthylamine (neozone D) introduced into each of the systems permits a quantitative estimation of the fraction of decomposition of hydroperoxides into free radicals. Special experiments show that the rate of consumption of the inhibitor does not depend on its concentration, and, consequently, the inhibitor reacts only with the free radicals formed in the decomposition of hydroperoxides.

An addition of \( \text{Rh}(\text{PPh}_3)_2\text{COCl} \) leads to a substantial increase in the rate of decomposition of NHP in comparison with the uncatalyzed reaction (Fig. 1). The catalytic decomposition of CHP and NHP occurs at practically the same rate. The mechanism of the decomposition of the two hydroperoxides, however, differs. From an examination of Fig. 1 it is evident that the rate of consumption of the inhibitor in the decomposition of CHP is greater than for NHP. From the ratio of the rate of formation of free radicals \( W_p \) to the rate of summary decomposition of CHP, it is evident that \( \sim 90\% \text{ ROOH decomposes to form free radicals. In the decomposition of NHP, chiefly molecular products are formed, and only \( \sim 20\% \) of the total amount of the hydroperoxide breaks down to free radicals.} \)

©1975 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for $15.00.
Fig. 1. Kinetic curves of the consumption of hydroperoxides and the inhibitor N-phenyl-β-naphthylamine in the case of catalysis by Rh(PPh₃)₂COCI (1·10⁻⁴ M) in oxygen-free medium, 120°. Solvent: mixture of nonene and chlorobenzene (1:1 by volume): 1 and 3) consumption of nonene hydroperoxide and inhibitor, respectively; 2 and 4) the same for cumene hydroperoxide; 5) consumption of nonene hydroperoxide in the absence of the catalyst.

Fig. 2. Kinetic curves of the catalyzed decomposition of cumene hydroperoxide (1) and consumption of 1-nonene in the case: 2) of cumene hydroperoxide; 3) of tert-butylhydroperoxide; 4) of nonene hydroperoxide. Concentration of Rh(PPh₃)₂COCI 5·10⁻⁴ M, solvent nonene—chlorobenzene, 120°.

The decomposition of CHP and tert-butyl hydroperoxide (TBHP) in 1-nonene medium, catalyzed by Rh(PPh₃)₂COCI, is accompanied by consumption of 1-nonene, with the formation, according to the data of gas—liquid chromatography, of 2-nonene and 3-nonene (chromatograph —katharometer, chromosorb G with 5% benton-34 and dinonyl phthalate, 100°).

From the kinetic curves of the decomposition of CHP in the presence of Rh(PPh₃)₂COCI and the consumption of 1-nonene as a result of its oxidative isomerization (Fig. 2, curves 1 and 2), it is evident that the isomerization of 1-nonene occurs at a substantial rate even after the complete consumption of CHP. In a system containing TBHP the rate of isomerization of nonene is lower than in the presence of CHP (curve 3). And finally, in the decomposition of NHF the isomerization of 1-nonene practically does not occur (curve 4). The data obtained are evidence that the structure of the hydroperoxide influences not only the mechanism of its catalytic decomposition, but also the reaction of isomerization of olefin coupled with it.

It should be noted that in the absence of hydroperoxides or oxygen, Rh(PPh₃)₂COCI does not catalyze the isomerization of olefin. Moreover, as has already been indicated, the isomerization of 1-nonene also occurs after the consumption of hydroperoxide (see Fig. 2). All this is evidence that a form of the catalyst modified during the decomposition of the hydroperoxide is responsible for the isomerization of the olefin.

A confirmation of this hypothesis was obtained with the aid of the UV and ESR spectra. The spectrum of Rh(PPh₃)₂COCI in a mixture of chlorobenzene and 1-nonene in oxygen-free medium has a characteristic absorption maximum at 365 nm (Fig. 3, curve 1). When CHP or NIIP is introduced into this system at 20°, the maximum disappears entirely (curve 2). An analogous change in the spectrum was also observed in the absence of ROOH in the case of purging of O₂ through the solution of the catalyst for ~1.5 h at 80°. Evidently the formation of a complex of the catalyst with hydroperoxides is accomplished more readily than with O₂.

Rh(PPh₃)₂COCI is diamagnetic. However, when CHP or TBHP is added to a solution of the catalyst, an ESR signal arises (Fig. 4).