MECHANISM OF THE SELECTIVE FORMATION OF CYCLOHEXANONE IN THE DECOMPOSITION OF CYCLOHEXYL HYDROPEROXIDE BY CHROMIUM STEARATE

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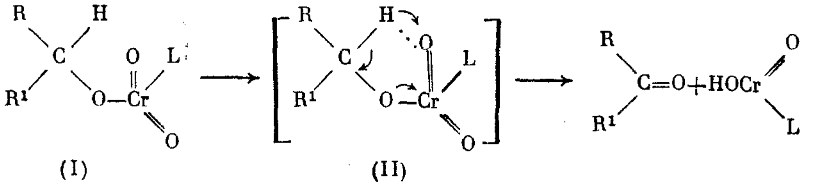
From a comparison of the rates of formation of cyclohexanone and 2-decanone in cyclohexane solutions of cyclohexyl hydroperoxide or tert-butyl-hydroperoxide in the presence of chromium(III) stearate and a mixture of cyclohexanol and 2-decanol in an atmosphere of argon at 350 K, it is concluded that the direct breakdown of cyclohexyl hydroperoxide by chromium stearate leads to selective formation of cyclohexanone. The contribution of the oxidation of cyclohexanol to ketone formation at a cyclohexanol concentration comparable with the hydroperoxide concentration (~0.1 M) is ~10%.

EXPERIMENTAL

Experiments on the decomposition of hydroperoxides and the oxidation of secondary alcohols were conducted in a thermostatically controlled glass reactor in a solution of cyclohexane in an atmosphere of argon at 350 K. All the reagents except for the catalyst were subjected to purification by fractional distillation before the experiment. The catalyst, chromium(III) stearate ($CrSt_3$), a preparation from the Kiev Chemical Reagent, Indicator Dye, and Analytical Preparations Plant, pure grade, was introduced into the reactor in the form of a chlorobenzene solution with a concentration of $1.8 \cdot 10^{-2}$ M. The content of cyclohexyl hydroperoxide (CHHP) and tert-butyl hydroperoxide (TBHP) in the samples collected was determined iodometrically. The content of cyclohexanol (COL) and cyclohexanone (CON), 2-decanol (DOL), and 2-decanone (DON) was analyzed gas chromatographically on a column filled with Chromaton N-AW with 15% polyethylene glycol adipate, at 381 K. Before GLC analysis, triphenyl phosphite was added to the samples for complete breakdown of the hydroperoxides which interfere with the analysis.

RESULTS AND DISCUSSION

Questions of the selective formation of ketones from secondary hydroperoxides in the case of their breakdown by chromium compounds were first raised in [1-3]. A mechanism of selective decomposition has been proposed [3], including the oxidation of secondary alcohols with synchronous electronic transition to a cyclic transition state (II) of the organochromium ester (I), as a well known intermediate step [5], has been proposed:



A key part of the mechanism [4] is the postulation of the formation of an organochromium ester directly from the secondary hydroperoxide and chromium compound during the oxidation of the latter.

An alternative to this mechanism of ketone formation in the case of decomposition of the secondary hydroperoxide consists of a possible intermediate formation of a secondary alcohol and subsequent oxidation of the alcohol to a ketone. Lauterbach et al. [6] see this

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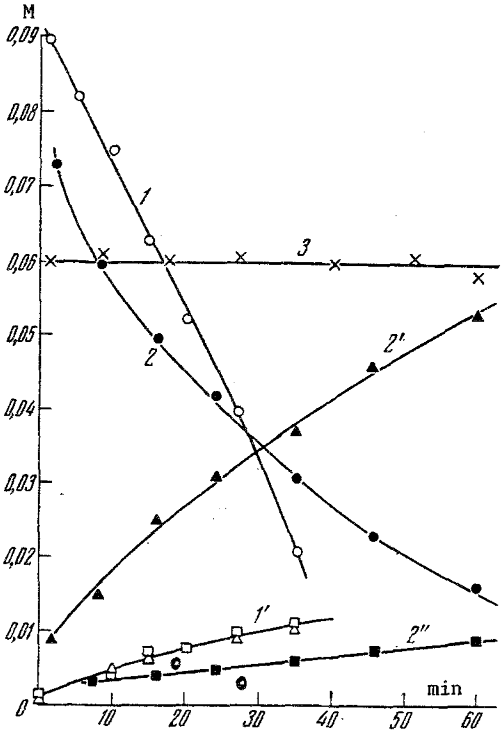

Fig. 1. Kinetic curves of hydroperoxide consumption and ketone accumulation in cyclohexane at 350 K, argon: 1) TBHP consumption; 1') accumulation of CON and DON at $[CrSt_3] = 1.6 \cdot 10^{-3}$, $[COL]_0 = [DOL]_0 = 0.095$ M; 2) CHHP consumption, 2') CON consumption; 2") accumulation of DON at $[CrSt_3] = 4.7 \cdot 10^{-4}$, $[COL]_0 = 0.06$, $[DOL]_0 = 0.104$ M; 3) CHHP without catalyst.

pathway of ketone formation in the experimental observation of the formation of CON from COL, oxidizable by the system tert-butyl hydroperoxide + chromium stearate (acetylacetonate). The contribution of these two mechanisms of ketone formation in the decomposition of hydroperoxides, catalyzed by chromium compounds, is of interest.

In agreement with [6], we also observed oxidation of a mixture of two secondary alcohols (COL and DOL) by the system TBHP + $CrSt_3$ (Fig. 1, curves 1, 1'). The two secondary alcohols are oxidized at an equal rate, and the rates of accumulation of CON and DON are the same. Here the ratio of the initial rate of consumption of TBHP W_{ROOH} to the rate of formation of CON (oxidation of COL) ≈10, i.e., only ~20% of the TBHP is consumed for the oxidation of the two alcohols; the remaining 80% of the hydroperoxide is consumed catalytically. Taking the same two alcohols, cyclohexanol and 2-decanol, in a different experiment we measured the rates of accumulation of CON and DON in the presence of CHHP and $CrSt_3$. The kinetics of hydroperoxide consumption and ketone accumulation is presented on curves 2, 2', and 2" of Fig. 1. The initial rates of formation of the ketones differ by a factor of ~10. The rate of consumption of CHHP is in a 1.25 ratio to the rate of CON formation over the entire range of the reaction, i.e., the selectivity with respect to the ketone is very high, eight times as high as for TBHP. This fact alone is an indication of different mechanisms of CON formation in the catalyzed decomposition of CHHP and TBHP.

If we follow the hypothesis of [5] that both CON and DON are formed only in the oxidation of secondary alcohols in the systems ROOH + Cr(III), then with proportionality of the oxidation rate $W_{01} \sim k_1 \cdot [COL]$ and $W_{02} \sim k_2 \cdot [DOL]$, taking the alcohol concentrations into consideration (see Fig. 1), it follows from $(W_{01}/W_{02}) \approx 10$ that $k_1/k_2 = 17$, i.e., COL is oxidized 17 times as rapidly as DOL. This result contradicts the data obtained in the system TBHP + $CrSt_3$: Accumulation of the ketones occurs at virtually the same rate there (Fig. 1, curve 1').

We should mention that in the metal + hydroperoxide system either the metal in a high valence state or a metal-hydroproxide complex can serve as the oxidizing agent. The hypothesis that only hexavalent chromium is the oxidizing agent for alcohols in both our ROOH + Cr(III) systems should be refuted (compare curves 2', 2", and 1' in Fig. 1). The hypothesis of oxidation of alcohols by Cr—ROOH complexes is more acceptable; actually, the rate of alcohol oxidation may change as we go from CHHP—Cr to TBHP—Cr on account of a different nature of the hydroperoxides contained in the oxidizing agent. To test this hypothesis we conducted a series of experiments containing CHHP + $CrSt_3$ and increased the initial COL concentration from experiment to experiment. Although COL actually is rapidly oxidized by the CHHP—Cr system, an increase in [COL] should lead to a proportional acceleration of hydroproxide consumption. Measurement of the rate constant of the catalyzed decomposition of CHHP ($[CrSt_3] = 1.6 \cdot 10^{-4}$ M, 350 K, cyclohexane) in the presence of 0.01, 0.018, 0.05, and 0.087 M COL from the slope of the semilogarithmic plot gave values of $5.2 \cdot 10^{-5}$, $5.3 \cdot 10^{-5}$, $5.9 \cdot 10^{-5}$, $6.1 \cdot 10^{-5}$ sec^{-1}, respectively. The change in the rate constant is small (~20%), and assuming selective formation of CON only through the oxidation of COL by the CHHP—Cr system, we should have expected an eightfold increase. Zero order with respect to [COL] in these experiments can also be explained by ternary complex formation CHHP—Cr—COL(X); it is easy to show that if oxidation proceeds through the intermediate complex X, then when [COL] > [Cr...CHHP] independence of the specific rate of CHHP consumption from $[COL]_0$ can be observed. We ruled out this explanation by measuring the ratio of the rates of accumulation of CON and DON (W_{01}/W_{02}) at $[COL]_0 = 0.11$ M, i.e., almost twice as high as under the conditions of decomposition of CHHP (Fig. 1, curves 2, 2', 2"). If secondary alcohols give strong ternary complexes X, then by doubling $[COL]_0$ we should inevitably approximate halve W_{02} — the rate of oxidation of DOL to DON on account of competitive formation of X and X_1:

$$\mathrm{Cr}\ldots\mathrm{CHHP} + \mathrm{DOL} \rightleftarrows X_1$$
$$\mathrm{Cr}\ldots\mathrm{CHHP} + \mathrm{COL} \rightleftarrows X$$

As a result, we obtained the ratio $W_{01}/K_{02} = 10$, just as in the experiment shown in Fig. 1. In our opinion, the only explanation for the combination of these data requires a recognition that selective cyclohexanone formation in the decomposition of cyclohexyl hydroperoxide with catalysis by chromium salts occurs directly in the act of catalyzed decomposition, just as was previously suggested. There is a parallel reaction of alcohol oxidation; however, its contribution to ketone formation is minor. Judging by the experiments, in the system TBHP + $CrSt_3$ + DOL + COL, as well as in the presence of CHHP + $CrSt_3$, the oxidation of DOL and COL proceeds at an equal rate $W_{01}' \approx W_{02}$, where W_{01}' is the rate of accumulation of CON in the oxidation of the alcohol (Fig. 1, curve 1). And since $(W_{01}/W_{02}) = 10$ (see above), the contribution of the oxidation of COL with rate W_{01}' to the total ketone formation (W_{01}) is ~10%. The remaining 90% of the CON gives catalytic decomposition under the condition that $[COL]_0 \geq [CHHP]_0$. Earlier [1] a virtual 100% conversion of CHHP to the ketone was observed under the action of $CrSt_3$ in the absence of COL up to ~50% conversion in the decomposition of CHHP. It is clear that here COL oxidation could not play any appreciable role in CON formation. Precisely this circumstance was a weighty argument against the consideration of alcohol oxidation as a cause of selective ketone formation from secondary hydroperoxides in the presence of chromium-containing catalysts.

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