

EFFECT OF RING SIZE ON THE RATE OF DEHYDROGENATION OF CYCLOALKANOLS OVER COPPER CATALYST

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Received September 8th, 1977

The initial rates of dehydrogenation of C₅, C₆, C₇, C₈, C₁₀ and C₁₂ cycloalkanols have been measured at 200°C on a copper/kieselguhr catalysts. The observed dependence of rate on ring size shows a minimum for C₆, in agreement with published data on other reactions of cyclic compounds requiring a *sp*³ to *sp*² hybridization change in bonding orbitals.

The studies of structure effects on the reaction rate are a powerful tool for the elucidation of reaction mechanisms in general. Vast experimental material has been accumulated especially on homogeneous reactions in solution which can serve as a basis for comparison and interpretation of results with heterogeneous catalytic reactions. Whereas the effects of substituents on the rate of catalytic reactions have been used frequently relatively little attention has been paid to the influence of ring size on reactivity of cyclic compounds¹⁻⁵, mostly in the hydrogenation of cyclic alkenes²⁻⁵.

The purpose of the present work was to apply this approach to the dehydrogenation of cyclic alcohols to ketones where a comparison with homogeneous reactions would be more straightforward. Another goal was to supplement the previous findings on substituent effects on rate of the dehydrogenation of aliphatic secondary alcohols over a copper catalysts⁶.

EXPERIMENTAL

The same copper/kieselguhr catalysts but from an other batch (44% Cu after reduction, surface area 25 m²/g) and the same procedure for the measurement of initial reaction rates have been used as in the preceding paper from this Laboratory⁶. The cyclic alcohols were chromatographically pure specimens with properties corresponding to the published values. At the conditions used the dehydration of alcohols was negligible.¹

RESULTS

The found values of the initial reaction rates of the dehydrogenation are summarized in Table I. A minimum of rate appears at C₆ in agreement with the prediction of a general influence of ring size on the reactivity in reactions which require a change

from sp^3 to sp^2 hybridization of bonding orbitals in the product or in the transition state leading to a change in ring strain⁷. The same trend has been observed in the dehydration of cyclic alcohols over alumina¹; the data are given also in Table I. In contrast, a maximum should appear at C_6 in reactions with opposite change of hybridization (sp^2 to sp^3)⁷; this actually has been found for the hydrogenation of cycloalkenes over palladium³.

It is evident that the influence of ring size on reactivity in heterogeneous catalytic reactions is governed by the same general rules as in homogeneous transformations of cyclic compounds. For comparison, Table I contains also rate data of two relevant homogeneous reactions. The hydride reduction of cyclic ketones^{8,9}, in which the change in hybridization is reverse to our case, shows a maximum at C_6 .

Our results allow to draw some conclusions on dehydrogenation mechanism. It follows from the dependence of the rate on ring size that the rate-determining step must involve the change of hybridization at C_α . The only possibility is the splitting of the $C_\alpha-H$ bond. This finding is in agreement with the evidence brought by deuterium kinetic isotope effect of the dehydrogenation of 2-propanol on chromia¹⁰. We suggest that also on copper catalyst the dehydrogenation consists of a rapid loss of the hydrogen atom from the hydroxyl group after adsorption of the alcohol, resulting in the activation of the $C_\alpha-H$ bond by the bonding of the alkoxy rest to the metal. Such activation has been demonstrated by quantum chemical calculations¹¹. Its consequence is the slow loss of the second hydrogen atom (from the $C_\alpha-H$ bond) probably assisted by the electrophilic attack of the H^+ or surface copper

TABLE I
Found and Published Relative Rates of Various Reactions of Cyclic Compounds

Ring size	Present data 200°C ^a	Dehydration over Al_2O_3 200°C (ref. ¹)	Reduction of ketones with $NaBH_4$ (ref. ⁸)	Oxidation of cycloalkanes by CrO_3 (ref. ⁹)
5	1.2	1.9	0.0434	5.9
6	1.0	1.0	1.0000	1.0
7	3.4	2.3	0.0063	14.1
8	3.8	8.6	0.0005	40.1
10	4.9	—	0.0001	6.23
12	7.6	—	0.0011	4.9

^a Partial pressure of the reactant in the feed 0.17 bar, the balance to atmospheric pressure being nitrogen.

atom. An electrophilic attack on the C—H bond has been suggested as the decisive step in the oxidation of cycloalkanes by Cr_2O_3 in strongly acidic solutions⁹ the results of which are also given in Table I.

We are indebted to Dr K. Sporka, Institute of Chemical Technology, Prague, and to Dr J. Závada, Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague, for the gifts of C_{10} and C_{12} alcohols.

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