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541.128.34 : 542.941.8 : 547.26

The Energies of Activation of the Catalytic Dehydrogenation of Primary and Secondary Alcohols

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Received January 16, 1956

The activation energies of dehydrogenation of primary and secondary alcohols were determined on Raney-copper catalyst in the temperature interval between 150 and 250°C. The values obtained are presented in Figures 2 to 8 and Table 2. By comparison of the influence of methyl groups on the change of the activation energy of dehydrogenation and dehydration as well as by taking into consideration the difference in the behaviour of hydrocarbons and alcohols the opinion is supported that the primary act of alcohol dehydrogenation consists in the breaking of the O-H bond of alcoholic hydroxyl group.

INTRODUCTION

There are few publications dealing with the activation energy of the catalytic dehydrogenation of alcohols to aldehydes and ketones.^{1,2,3} H. Dohse⁴ determined the activation energies for the dehydration of primary, secondary and tertiary alcohols and discussed the dependence of these energies on the chemical structure of alcohols.

We considered that it would be interesting to make a systematic determination of the activation energies of alcohol dehydrogenation on various alcohols believing that therefrom certain conclusions could be drawn about the mechanism of catalytic dehydrogenation.

EXPERIMENTAL

We used a somewhat modified apparatus (Figure 1) described first by G. M. Schwab⁵. Schwab studied the decomposition of formic acid into carbon dioxide and hydrogen whereby no liquid reaction products were formed which would mix with the original formic acid.

In the course of dehydrogenation of alcohols liquid aldehydes or ketones were formed in all cases except in the case of methanol which decomposes according to the equation



without aldehyde formation.

At first sight it might seem incorrect to make determinations of activation energies with alcohols which mix continuously and in all proportions with reaction products. The individual determination were therefore interrupted after approximately 1% of alcohol originally present was dehydrogenated. Such a small percentage of aldehyde or ketone mixed with the alcohol has no appreciable influence on the reaction velocity.

The reaction rate was determined by the volume of the gas evolved in a definite time interval. The gas was collected and measured in a 50 ml. burette divided into 1/10 ml.; during the reading off the gas pressure in the apparatus was brought to atmospheric pressure by adjusting the level bottle.

The rate of evaporation of alcohol as well as the temperature of the catalyst were controlled by adjusting the electrical heating by means of two transformers. During all determinations the evaporation rate of alcohol was such that per pass no more than one or two per cent of it was dehydrogenated. These very low concentrations were always far from the equilibrium concentrations which for the dehydrogenation of ethanol were calculated from free energy data as follows from Table I.

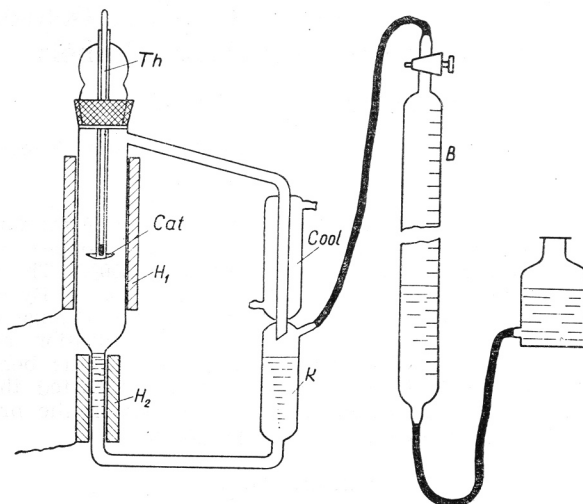


Fig. 1. *Th* — thermometer; *Cat* — catalyst; *H*₁ — heating of the catalyst; *H*₂ — heating of the evaporation section; *Cool* — cooler; *R* — recipient; *B* — burette.

TABLE I
Equilibrium constants and conversions for the dehydrogenation of ethanol calculated from thermodynamic data^a

Temp. °C	180	200	220	250	300
K_p	0.058	0.115	0.218	0.550	1.91
conversion %	24.4	32.0	42.1	59.5	80.4

Similar values were also obtained for the other alcohols.

The determinations of the activation energies were made with the following alcohols: methanol, ethanol, propanol-1, propanol-2, *n*-butanol-1, *n*-butanol-2, 3-methyl-butanol-1.

For comparison two aldehydes, viz. formaldehyde as a 20% water solution and pure butyraldehyde were also subjected to the same procedure.

As catalyst we used Raney copper, prepared by treating a 50 : 50 copper-aluminum alloy with an approximately 8% sodium hydroxide solution, washing with water and keeping the active catalyst under water. Before its introduction into the catalyst chamber a part of the batch, which was always the same, was washed first with ethanol and then with the alcohol which was to be used for that dehydrogenation. The suspension of Raney copper in the alcohol was sucked into a pipette and left to settle down in it so that it was possible to use always approximately the same volume of sedimented copper, viz. 0.3 ml. which had a weight of approximately 0.3 g. Several determinations were made usually with the same portion of the catalyst.

The activation energies were determined in the temperature interval from 150 to 250°C.

The gas evolution at each definite temperature was fairly constant and independent of the evaporation rate of the alcohol. This means that in this case the reaction rate is independent of the reaction concentration and can be

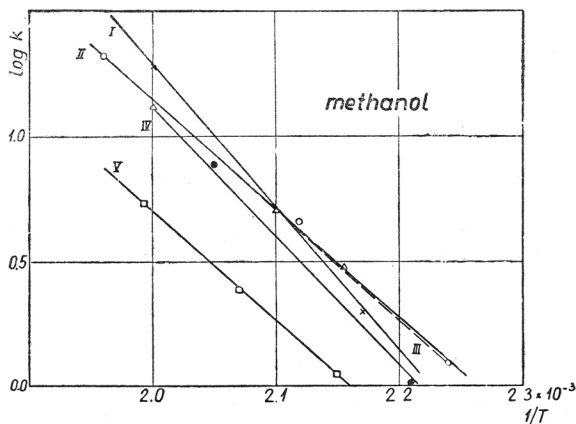


Fig. 2. Variation of dehydrogenation rate of methanol with temperature

considered as of zero order. The volume of the gas evolved per minute has been therefore taken as the reaction rate constant *k*.

By using the well known Arrhenius' equation

$$\log k = B - q/2.303 RT$$

and plotting the log *k* values against the reciprocal absolute temperatures fairly straight lines were obtained and from their slopes the activation energies were computed. The plots for individual alcohols are presented in Figures 2 to 8. For every alcohol the means were computed and are presented in Table II.

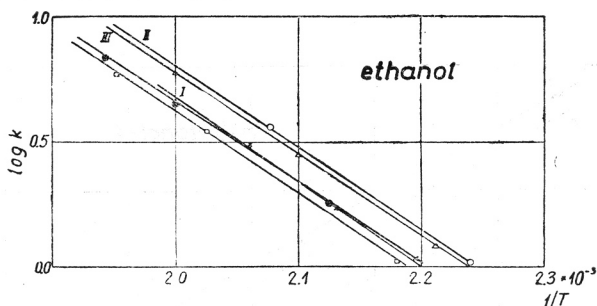


Fig. 3. Variation of dehydrogenation rate of ethanol with temperature

The mean reactivities of alcohols in comparison with methanol, at the arbitrarily chosen temperature of 182°C, are presented in Table III. As one mole of methanol gives three moles of gas and the other alcohols only one, the mean value of gas volume developed from methanol was divided by three.

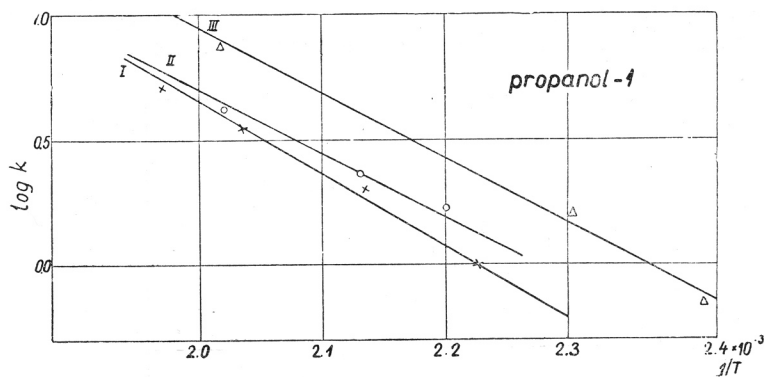


Fig. 4. Variation of dehydrogenation rate of propanol-1 with temperature

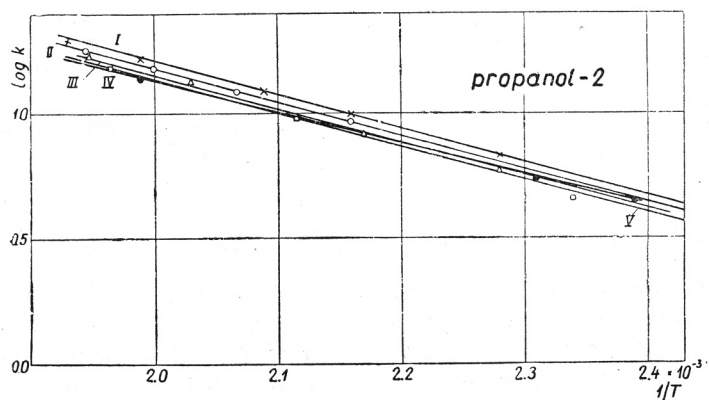


Fig. 5. Variation of dehydrogenation rate of propanol-2 with temperature

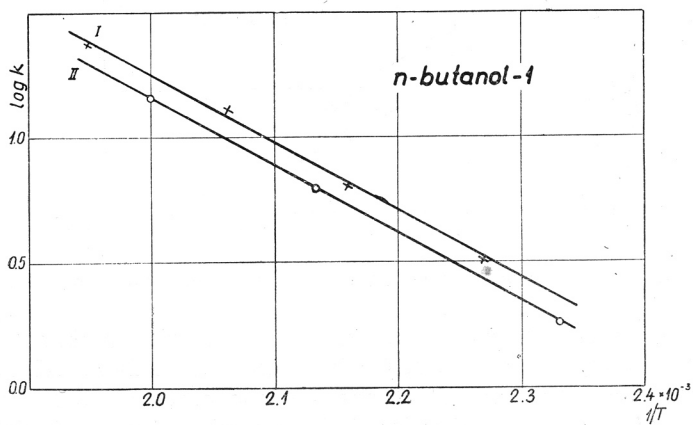
Fig. 6. Variation of dehydrogenation rate of *n*-butanol-1 with temperature

TABLE II

Activation energies for the dehydrogenation of alcohols on Raney copper

alcohol	methanol	ethanol	propanol-1	propanol-2	n-butanol-1	n-butanol-2	3-methylbutanol-1
activation energies cal./mole	21,860	15,010	12,140	6,030	12,420	5,920	12,160

The values give an approximate picture of the relative reactivity of each alcohol for the dehydrogenation on this catalyst.

Since methanol decomposes during the dehydrogenation on copper completely into carbon monoxide and hydrogen it seems important to determine the activation energy of the formaldehyde decomposition into carbon mono-

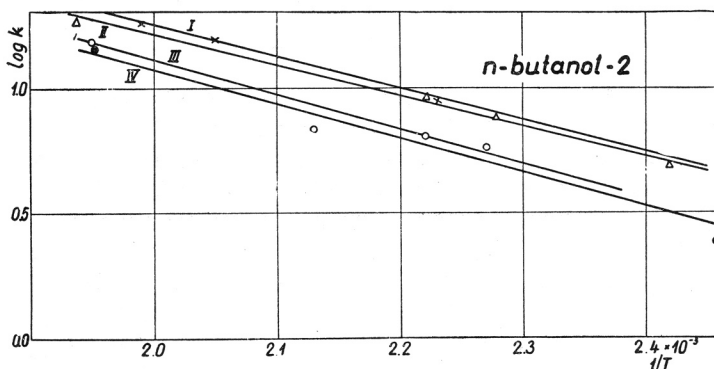


Fig. 7. Variation of dehydrogenation rate of *n*-butanol-2 with temperature

xide and hydrogen so to be sure that it does not interfere with the values of methanol. We, therefore, prepared an approximately 20% formaldehyde solution which was completely freed from methanol by fractional distillation and determined its activation energy for its decomposition into carbon monoxide and hydrogen on copper between 135 and 235°C; it was found to

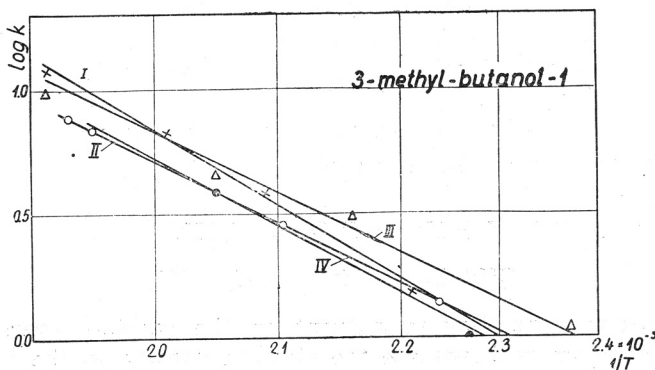


Fig. 8. Variation of dehydrogenation rate of 3-methyl-butanol-1 with temperature

TABLE III

The mean reactivities of alcohols on Raney copper at 182°C

alcohol	methanol	ethanol	propanol-1	propanol-2	n-butanol-1	n-butanol-2	3-methylbutanol-1
relative reactivity	100	219	340	1520	281	1560	336

be 8,300 cal./mole. The volume of the gas evolved from formaldehyde was approximately twice as great as that from methanol on the same catalyst at the same temperature in the same time. Hence it can be concluded that formaldehyde, if an intermediate product in methanol dehydrogenation at all, does not interfere with the determination of the activation energy for the methanol dehydrogenation.

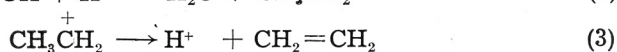
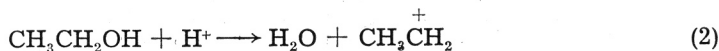
DISCUSSION OF RESULTS

The majority of experimental results for individual alcohols agree fairly well with each other except some which are higher and were obtained with fresh catalyst, especially in the case of methanol. The cause of these discrepancies cannot be ascribed with certainty to a definite effect, but the reduction of copper oxide — formed perhaps during the introduction of the catalyst into the apparatus in some cases — to metallic copper is a possible one.

The important conclusion to be drawn from these observations is the marked effect on the activation energies caused by the introduction of methyl groups on the alpha-carbon atom: the introduction of the first methyl group on the carbinol C-atom lowers the activation energy for approximately 6,800 cal./mole, the introduction of the second methyl group on this atom for approximately 9,000 cal./mole; the introduction of a methyl group into the beta position lowers the activation energy of normal primary alcohols for approx. 3,000 cal., whereas it has no effect on the activation energy of secondary alcohols. A gamma methyl substitution has practically no effect at all.

These findings agree fairly well with those of H. Dohse⁴ about the activation energies of dehydration of alcohols. He found that the activation energy decreased with the substitution of one methyl group for hydrogen in the alpha position by 5,500 cal., in the beta position by 2,500 cal. and in the gamma position by 500 cal.

If we assume the mechanism of the catalytic alcohol dehydration to be an ionic one (see for example D. A. Dowden⁷)



then every electron repelling substituent on the carbinol atom or on the adjacent carbon atom will increase the electron density on the oxygen atom and thus facilitate the dissociation of the hydroxyl ion from the alcohol mole-

cule. As there is a parallel and a numerical similarity between the effect of methyl groups on the activation energies of dehydrogenation and dehydration of alcohols, we can assume that the electron repelling effect of the methyl groups causes a weakening of the O-H bond as well as of the carbon-hydroxyl bond in the case of dehydration.

Relevant conclusions on the dehydrogenation mechanism of alcohols can be drawn by comparing their behaviour during dehydrogenation with that of corresponding hydrocarbons. Methane, for example, is completely stable under those conditions under which methanol decomposes completely into carbon monoxide and hydrogen. Independently of the conclusions made above from the similarity between the effect of substitution on the dehydration and dehydrogenation of alcohols we can ask again what inferences can be drawn from the very different behaviour of methane and that of methanol on the dehydrogenation mechanism of alcohols? Which bond is broken first, the C-H or the O-H bond?

The methyl group has, as is known, an electron repelling effect and the hydroxyl group an electron attracting one. As during the dehydrogenation the alcohol molecule loses a hydrogen atom which is covalently chemisorbed on the catalyst — the electron of the hydrogen entering into the empty conductivity levels of copper — it is probable that the presence of a hydroxyl group in the alcohol molecule makes the breaking of C-H bond more difficult in comparison with the energy required for its breaking in methane.

(The case of formaldehyde — owing to the agglomeration of electrons between the carbon and oxygen atoms — is a special one and no direct conclusions on the behaviour of methanol should be drawn from it.) It follows, therefore, that the primary act of alcohol dehydrogenation is more probably the breaking of the O-H bond than of a C-H bond. This breaking of the O-H bond is facilitated by the presence of the electron repelling influence of one or more methyl groups, and these theoretical conclusions agree fairly well with experimental findings.

From the bond energy values, however, a different conclusion could be drawn; the value for C-H is 87.7 kcal. and that for O-H is 110.2 kcal. We must, however, take into account that these values have been calculated for methane and water and that the presence of a methyl group weakens the O-H bond and the presence of a hydroxyl group strengthens the C-H bond.

From all these facts it can be concluded that very probably the primary act of alcohol dehydrogenation is the loosening of the O-H bond, followed by the chemisorption of hydrogen from this O-H group by the catalyst. The electrons of the remaining radicals rearrange themselves, making possible the severance of the second hydrogen atom. This hydrogen atom can collide with an already chemisorbed hydrogen atom forming a hydrogen molecule, or it can be chemisorbed on the vacant side of the catalyst and after that combine with an adjacent chemisorbed hydrogen atom to be finally desorbed as an hydrogen molecule.

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IZVOD

Energija aktivacije katalitičke dehidrogenacije primarnih i sekundarnih alkohola*I. Brihta i P. Luetić*

Određene su energije aktivacije dehidrogenacije na Raney-bakru u temperaturnom intervalu između 150 i 250°C za metanol, etanol, propanol-1, propanol-2, *n*-butanol-1, *n*-butanol-2, 3-metil-butanol-1. Dobivene vrijednosti prikazane su u dijagramima 2 do 8 i u tablici 2. Relativna aktivnost kod dehidrogenacije pojedinih alkohola prikazana je u tablici 3. Ako se uporedi upliv supstitucije vodika s metilnim skupinama na energiju aktivacije dehidrogenacije i dehidratacije, kao i ponašanje ugljikovodika, može se zaključiti, da se primarni akt dehidrogenacije alkohola vjerovatno sastoji u tome što se vodikov atom otcijepi iz hidroksilne skupine alkohola.

INSTITUT ZA INDUSTRIJSKA ISTRAŽIVANJA
ZAGREB

Primljeno 16. januara 1956.