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The Activity of Some Ib and VIII-group Metals for Hydrogenations and Dehydrogenations of Oxy-compounds*

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The energies of activation for the catalytic dehydrogenation of different alcohols (methanol, ethanol, propanol-2, butanol-1, butanol-2) as well as for the catalytic hydrogenation of acetone and butanone to alcohols were determined on the following metals: Ag, Cu, Ni, Co, Fe.

Furthermore, the energies of activation for the dehydrogenation of formic acid and of ethanol were determined over two mixed catalysts, Ni-Ag and Ni-Cu.

The results of these determinations are presented in Tables I and II and in Figures 1 and 2. They are found to be in agreement with the theory of formation of activated complexes between the reactants and catalysts if the influence of the resonance energy of these complexes is taken into consideration.

Some metals of the VIII and of the Ib group are well known as industrial catalysts for hydrogenation and dehydrogenation reactions. Nickel is widely used for the hydrogenation of alkene and carbonyl groups, iron for the synthesis of ammonia and the Fischer-Tropsch synthesis, while copper is used mainly for the dehydrogenations of alcohols to aldehydes and ketones and *vice versa*. Surprisingly, nickel is an unsuitable catalyst for dehydrogenation of alcohols or for the hydrogenation of fatty acids to their alcohols. These empirical facts induced us to make a comparative study of the kinetics of hydrogenation of carbonyl compounds to alcohols and of the dehydrogenation of alcohols to carbonyl compounds. We wanted to learn whether the activation energies, computed from the kinetic measurements, do agree with the current ideas about the causes of the activities of individual metals on one hand and with their practical activities on the other.

According to the theories, put forward by Schwab[1,2], Dowden and Reynolds[3] and Couper and Eley[4], the catalytic activity of the transition metals for hydrogen transfer reactions (hydrogenations-dehydrogenations) is due to their partly empty *d*-band. Adding various amounts of Ib-group metals to transition metals one can gradually fill the *d*-vacancies of these metals and

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according to the above mentioned theories the catalytic activity should decrease. This by the theory foreseen behaviour induced us to investigate systems which may contribute to a better understanding of the above mentioned theories. The exceptional catalytic behaviour of copper, in comparison with silver and gold, has been investigated previously[5].

We determined the activation energies for the dehydrogenation of methanol, ethanol, propanol-2, butanol-1, and butanol-2 over silver, copper, nickel-copper and nickel-silver. The results are given in Fig. 1 and 2.

TABLE I

Activation energies in kcal/mole for the dehydrogenation of alcohols

Catalysts / Reactants	Ag	Cu	Ni	Co	Fe
methanol	30,8	14,1	21,2	17,6	22,1
ethanol	22,8	9,8	15,3	13,4	17,0
butanol-1	17,1	8,7	13,7	12,0	16,1
propanol-2	13,7	6,4	12,2	9,9	15,8
butanol-2	14,7	7,2	12,6	9,7	14,8

On nickel and on iron sensibly higher activation energies have been found than over copper and cobalt. This is somewhat surprising as nickel is known to be the best hydrogenating catalyst of all the metals mentioned in Table I.

On the same metals we also investigated the activation energies of the inverse reaction, *viz.* the hydrogenation of the carbonyl group. The results (for acetone and butanone) are given in Table II.

TABLE II

Activation energies in kcal/mole for the hydrogenation of ketones

Catalysts / Reactants	Ag	Cu	Ni	Co	Fe
acetone	16,9	6,7	7,2	18,0	14,1
butanone	—	8,0	8,3	16,6	14,1

Here again copper shows an exceptionally good activity, especially if one compares it with silver. This is in agreement with the widespread use of copper for industrial hydrogenations of this class of compounds.

In another set of experiments we investigated the activation energies for the dehydrogenation of formic acid and ethanol on mixed catalysts, nickel-copper and nickel-silver. The results are given in Fig. 1 and 2.

EXPERIMENTAL

In the determination of the dehydrogenation activation energies the same apparatus and procedure were used as described previously[5]. The catalysts used were prepared by the reduction of their oxides as described[6].

The determination of activation energies for the hydrogenation of ketones was carried out as follows: over the catalyst which was placed in a glass tube hydrogen and the ketone were passed in the molar ratio 1:1, with different velocities in individual experiments, at constant temperature for one set of determinations. The same set of determinations was then carried out at different but always constant temperatures. The percentage of the hydrogenated ketone was plotted in a diagram *vs.* the reciprocal velocity. From the series of curves so obtained the values of temperatures and velocities were found (at the crossing points of the curves with the parallels to the abscissa) at which the conversions were identical. By plotting the logarithms of the so found velocities *vs.* the reciprocal temperatures a certain number of straight lines were obtained from which the energies of activation were calculated according to the Arrhenius equation; see Figs. 2a and 2b.

DISCUSSION OF RESULTS

As can be seen from Fig. 1 the activation energy for the formic acid dehydrogenation is much higher on pure copper and on pure silver than on nickel. Nickel-copper resp. nickel-silver mixtures containing up to 60 atom % of copper or silver have the same activities as pure nickel. The behaviour of these catalysts can be assumed to be in agreement with the *d*-band theory, namely that the *d*-band vacancies of nickel are responsible for

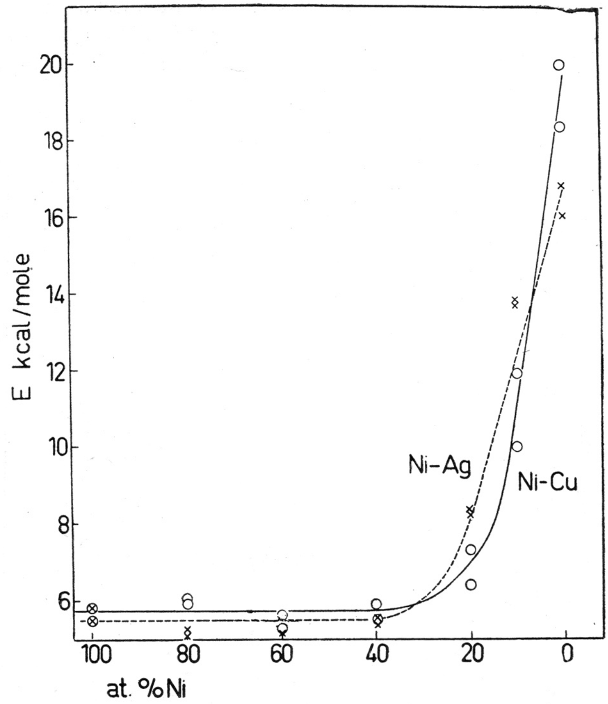
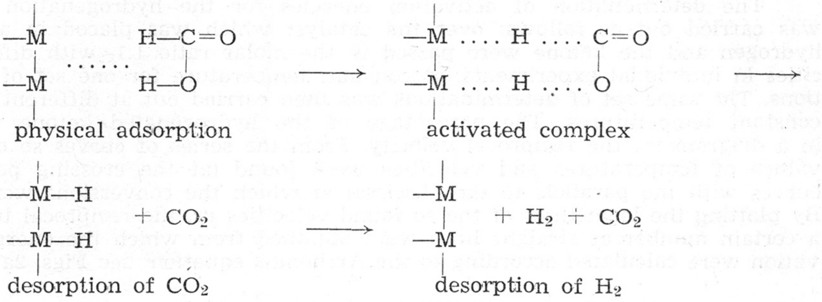


Fig. 1. Activation energies for the catalytic dehydrogenation of formic acid over Ni-Ag and Ni-Cu catalysts.

the catalytic decomposition based on an electron transfer from the formic acid to the catalyst. The mechanism of the catalytic decomposition of formic acid is assumed to be as follows[7]:



Quite different is the case of ethanol dehydrogenation, as can be seen from Fig. 2; addition of copper diminishes here the activation energy of nickel. This fact is in agreement with the exceptional low activation energy for the ethanol dehydrogenation over pure copper, as observed previously[6], but in disagreement with the d-band theory mentioned above, according to which copper with its filled d-band should show a higher activation energy for an electron transfer reaction than nickel.

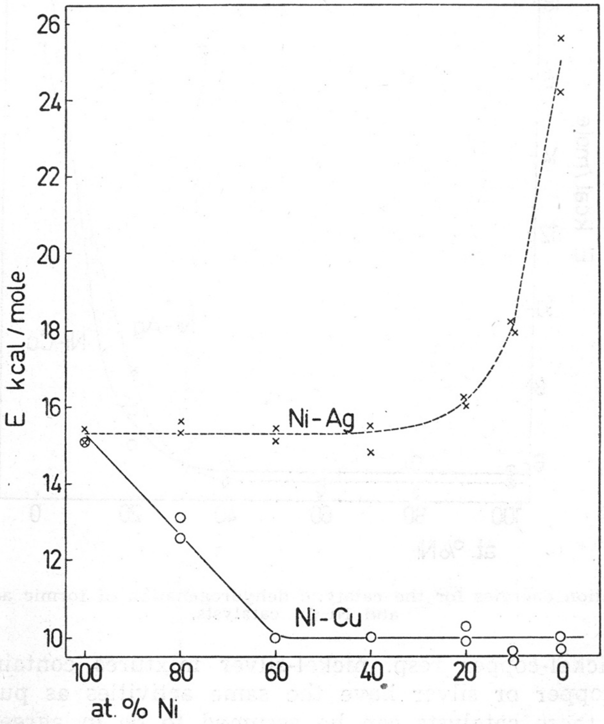
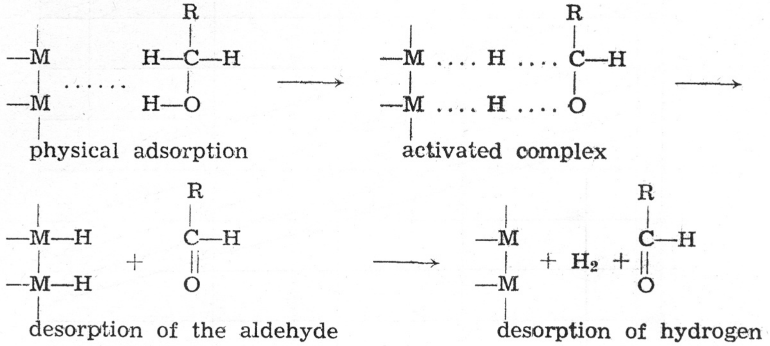


Fig. 2. Activation energies for the catalytic dehydrogenation of ethanol over Ni-Ag and Ni-Cu catalysts.

The reaction mechanism for the ethanol dehydrogenation can be represented in a similar manner as that mentioned above for formic acid, as was put forward already by Balandin.



In the experimental material exposed above there are several surprising features concerning the activity of individual catalysts. *E. g.* for such two similar reactions, as are the dehydrogenation of alcohols and that of formic acid, nickel and copper show just an opposite behaviour. While for formic acid dehydrogenation nickel is a very active and copper a poor catalyst, for the dehydrogenation of alcohols copper is much more active than nickel. Besides, it is well known that for the hydrogenation of the ethylenic bond nickel is considerably more active than copper while for the hydrogenation of the carbonyl group copper is at least as active as nickel.

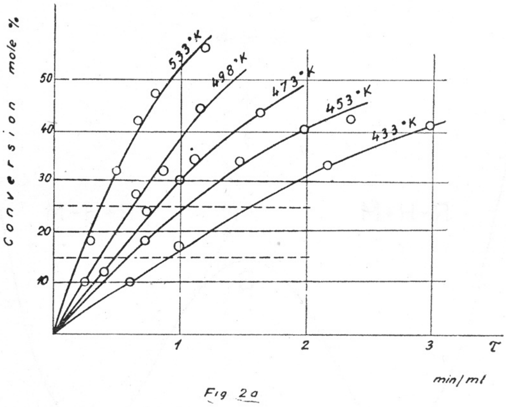


Fig. 2a. Kinetics of acetone hydrogenation to propanol-2 over nickel. Conversion of acetone *vs.* contact time (τ) (min/ml acetone)

The found facts of the influence of the structure of a reactant on its reactivity (see Table I) in a catalytic reaction can be well explained on the basis of the activated complex theory proposed by Ogg and Polanyi[8]. One of the factors influencing the catalytic activity is the resonance energy of the activated complex[9].

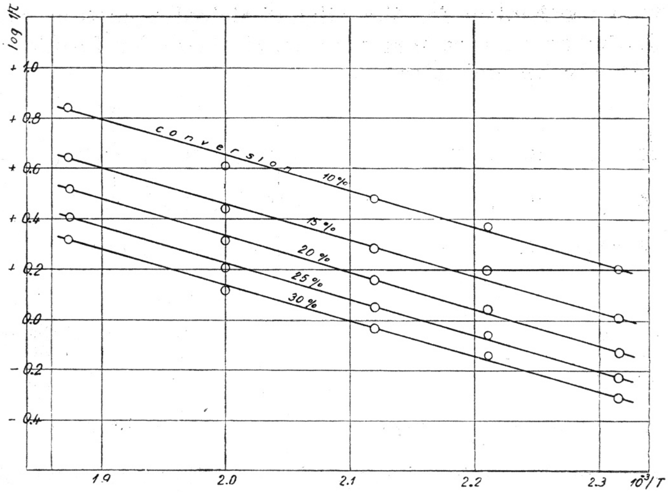


Fig. 2b. Kinetics of acetone hydrogenation. This diagram is obtained from Fig. 2a. Logarithms of $1/\tau$ *vs.* reciprocal temperatures.

We consider a three-center reaction of a molecule R—H with the atom M of a catalyst:

$$\mathrm{R{-}H + M \longrightarrow R\ldots H\ldots M \longrightarrow R + H{-}M}$$

One can represent, as usually, the potential energy of the atoms (resp. radicals) R, H and M for all separations of the linear complex R ... H ... M in terms

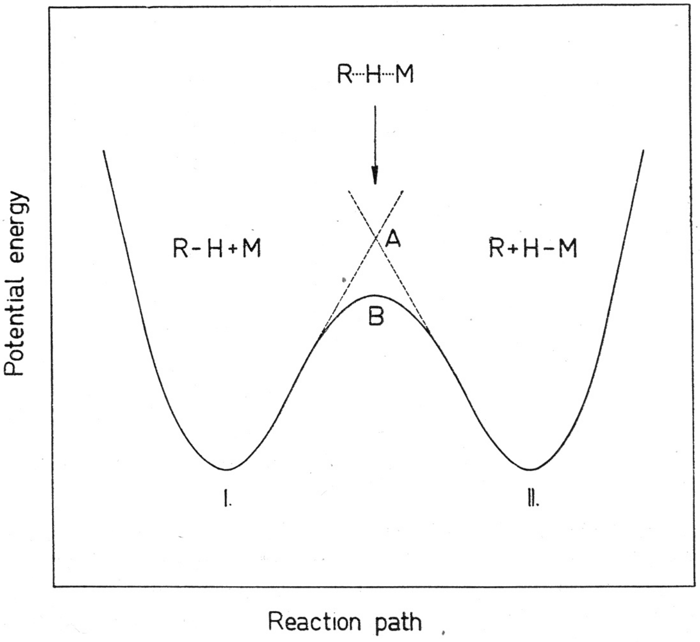


Fig. 3. An energy profile for a three-centre reaction.

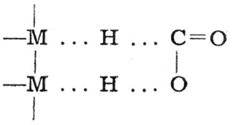
of a contour map. The reaction path is then the line of lowest potential energy from I to II (see Fig. 3).

At the crossing point of the two curves both states

$$R{-}H + M \quad \text{and} \quad R + H{-}M$$

have the same energy which is that of the transition state R . . . H . . . M. Because of the resonance between the states I and II the energy of the transition complex is lowered from the crossing point A to the point B of the alternative reaction route. As appreciable resonance can occur only between two structures of nearly the same energy, the lowering of the energy of the transition point from A to B will be the greater the nearer in magnitude are the bond energies R—H and H—M.

If we consider the following complexes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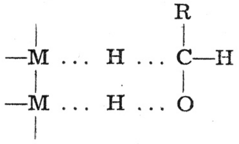
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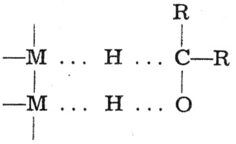
III

we see that the bond energies H—C and H—O decrease in the order I > II > III by virtue of the electron repelling effect of the R (alkyl) groups. For this reason the hydrogen atoms which separate from the molecule during dehydrogenation are more firmly bound in formic acid than in primary alcohols, and in primary acohols more firmly than in secondary alcohols. In consequence of this those catalysts which have a greater affinity towards hydrogen should be more active for formic acid dehydrogenation than for dehydrogenation of primary or especially secondary alcohols; the resonance energy of the activated complex in the case of formic acid dehydrogenation is higher on nickel than on copper, whereas in the case of alcohols this energy can be assumed to be higher on copper than on nickel. This is in good agreement with the found facts that *e. g.* nickel with its greater affinity towards hydrogen catalyzes the dehydrogenation of formic acid better than copper whereas copper catalyzes the dehydrogenation of alcohols better than nickel.

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IZVOD

Aktivnost nekih metala Ib i VIII grupe za hidriranje i dehidriranje oksi-spojeva

P. Fuderer-Luetić i I. Brihta

Određene su energije aktivacije za katalitičko dehidriranje različnih alkohola (metanol, etanol, propanol-2, butanol-1 i butanol-2) na ovim metalima: Ag, Cu, Ni, Co i Fe. Na istim metalima određene su energije aktivacije katalitičkog hidriranja acetona i butanona u alkohole. Konačno su određene i energije aktivacije za dehidriranje mravlje kiseline i etanola na miješanim katalizatorima Ni—Ag i Ni—Cu. Rezultati tih određivanja prikazani su u tablicama I i II kao i na slikama 1 i 2. Ustanovljeno je, da su rezultati u skladu s teorijom stvaranja aktiviranih kompleksa između reaktanata i katalizatora, ako se uzme u obzir utjecaj energije rezonancije tih kompleksa.

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