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The Catalytic Activity of Copper, Silver and Gold in Dehydrogenations*

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The activation energies of the catalytic dehydrogenation of formic acid and ethanol have been determined for metals of the Ib group (Cu, Ag and Au). The results given in Tables I and II show that the catalytic mechanism does not depend only on the free energy levels of *s*-electrons of these metals. For the dehydrogenation of ethanol on copper-silver mixtures an *S*-shaped curve was obtained having a horizontal part between 20 and 60 atomic % Cu.

Soon after the introduction of the electronic theory attempts were made to explain the properties of the contact catalysts by their electronic structure. We shall deal here only with those metals which catalyze the hydrogen transfer, *i. e.* the hydrogenation-dehydrogenation reactions. These reactions are catalysed by some of the transition metals, which have only partially filled *d*-bands, as for example Fe, Co, Ni (partially filled 3*d*-bands), Ru, Rh, Pd (4*d*-bands) and Os, Ir and Pt (5*d*-bands). Some catalytic activity for these types of reactions is shown also by metals of the Ib group of the periodic system (Cu, Ag and Au), with *d*-bands completely filled and with *s*-bands only partially filled. There is however some difference of opinion about the electronic structure of metallic copper to which L. Pauling¹ for example attributes a certain *d*-character.

The connection of the catalytic activity of the transition metals with their empty *d*-band levels is considered to be proved by the fact that their alloys with metals with completely filled *d*-bands show a fall of catalytic activity parallel to the fall of their magnetic susceptibility.^{2, 3}

The metals of the Ib group (Cu, Ag, Au), which in the periodic table follow the transition metals, have neither empty *d*-levels nor are they paramagnetic, but they exhibit notwithstanding in hydrogenation-dehydrogenation reactions a catalytic activity, although a weaker one than the transition metals. Schwab⁴ explained their activity by the partly filled *s*-band, in view of the fact that their electric resistance and energy of activation rise parallel after being alloyed with metals from the II to VI group of the periodic system.

The findings of Schwab⁵ and of Rienaecker⁶ about the dehydrogenation activation energies of copper and of silver on the formic acid apparently do not agree with the well known activities of these metals for the hydrogenation

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of olefins⁷: although a lower activation energy was found for silver than for copper, the former is a much weaker catalyst and is not used technically either for the hydrogenation of olefins and carbonyls or for the dehydrogenation of alcohols. It is of course doubtful if such simple analogy between the catalytic activity on formic acid dehydrogenation and the activity for dehydrogenation of alcohols and the hydrogenation of olefins and carbonyls is permissible.

As a contribution to the elucidation of this question we undertook to determine the activation energies of the same catalysts (copper, silver and gold) for the dehydrogenation of formic acid and of alcohols.

The results obtained for the dehydrogenation of formic acid agree fairly well with those obtained by previous investigators, already quoted.^{5, 6} Our results are represented in Table I and Fig. 1.

TABLE I
Dehydrogenation of formic acid

	Cu	Ag	Au
activation energies kcal/mol	19.3	16.7	16.3

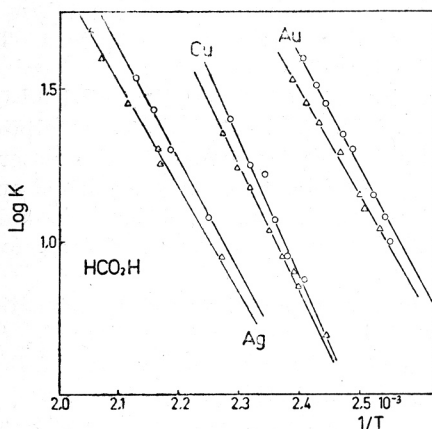


Fig. 1

The activation energies found by us for the dehydrogenation of ethanol showed, on the contrary, a different trend (Table II and Fig. 2):

TABLE II
Dehydrogenation of ethanol

	Cu	Ag	Au
activation energies kcal/mol	9.8	22.8	20.6

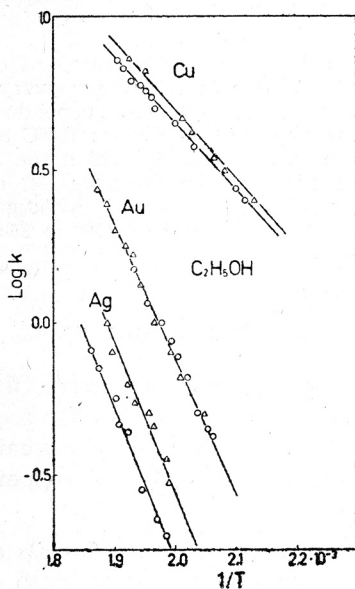


Fig. 2

It was also interesting to investigate the activation energies of mixed copper-silver catalysts. The results are represented in Table III and Fig. 3.

TABLE III
Dehydrogenation of ethanol over Cu-Ag mixtures

Cu atom. %	0	10	20	30	40	50	60	70	80	100
activation energies: kcal/mol	22.8	19.4	15.6	15.9	15.9	15.5	15.5	13.9	12.6	9.8

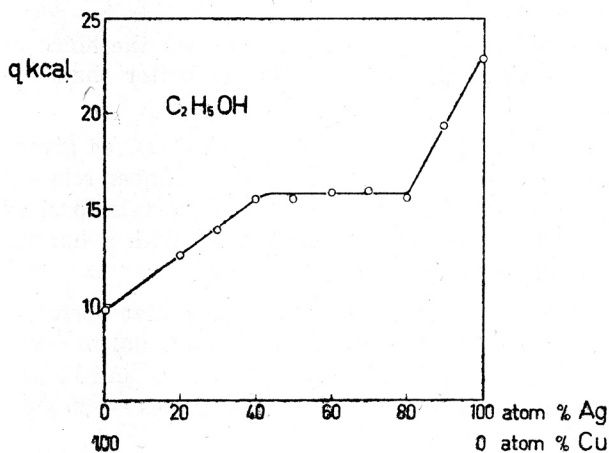


Fig. 3

EXPERIMENTAL

The catalysts were prepared by the precipitation of carbonates from aqueous solutions of the corresponding nitrates in which for every 10 milliatoms of metal or metal mixture 5 g. of calcined alumina was suspended. After the decantation and washing the carbonates were filtered, dried at 105°C and reduced with hydrogen at 200° to 210°C in the same apparatus in which the activation energies were determined. The apparatus, procedure and methods of computation have been described in a previous paper.⁸ Formic acid was investigated in the temperature interval of 130° to 180°C, and ethanol in that of 200° to 260°C. The formic acid and ethanol were *c. p.* and anhydrous.

DISCUSSION OF RESULTS

As it is evident from the results given above, the activity of catalysts depends greatly upon the substrate even for similar reactions. Silver and gold are for the dehydrogenation of formic acid somewhat better catalysts than copper, but for the dehydrogenation of alcohol copper is much more active than are gold or silver.

If the dehydrogenation mechanism by the metals of the Ib group should depend on the free energy levels of their *s*-electrons⁹, one should expect that metals with analogous electronic and crystal structures would show some parallelism between their electric conductivities and catalytic activities. In the case of the formic acid dehydrogenation, taking into account the relatively small differences between the activation energies and electric conductivities of the three metals, one could accept this as a first step working hypothesis. The electric conductivities at 0°C are for copper 64, for silver 66 and for gold 49.10⁴ cm.⁻¹ ohm⁻¹. From the results of the ethanol dehydrogenation it is evident, however, that no parallelism exists between the electric conductivity and catalytic activity. As can be seen from Table II, the catalytic mechanism does not depend only on the free energy levels of *s*-electrons, as the much higher activity of copper in comparison with gold or silver cannot be explained in this way. The different behaviour of copper in comparison to silver can be understood by taking into account that copper, contrary to silver, acts both as a mono- and bivalent element. It can therefore be assumed that the dehydrogenation of alcohols on copper proceeds via the holes in the 3*d*-band which for the dehydrogenation of alcohols act better than the free energy levels of 4*s*-electrons.

The activation energies of copper-silver mixtures, as given in Table III, are also rather interesting. Instead of the expected linear relationship between the activation energies and the composition, for metals so similar as copper and silver, an S-shaped curve has been obtained with a horizontal part between 20 and 60 atom. % of Cu.

The results of Table II seem to explain the better performance of silver in comparison with copper in the oxidation of methanol to formaldehyde; the latter decomposes during the process partially to CO and H₂ and this decomposition — as a result of different activation energies — is greater on copper than on silver.

REFERENCES

1. L. Pauling, *Proc. Roy. Soc. (London) A* **196** (1949) 343; cf. *Advances in Catalysis*, Vol. VII, p. 12.
2. A. Couper and D. D. Eley, *Discussions Faraday Soc.* **8** (1950) 172.
3. D. A. Dowden and P. W. Reynolds, *Discussions Faraday Soc.* **8** (1950) 184.
4. G. M. Schwab, *Discussions Faraday Soc.* **8** (1950) 166.
5. G. M. Schwab and E. Schwab-Agallidis, *Ber.* **76** (1943) 1226.
6. G. Riensaecker and Bade, cited in ref. 5, p. 1242.
7. R. N. Pease and L. Stewart, *J. Am. Chem. Soc.* **49** (1927) 2783.
8. I. Brihta and P. Luetić, *Croat. Chem. Acta* **28** (1956) 93.
9. G. M. Schwab, *Chim. e ind. (Milan)*, **35** (1953) 810.

IZVOD

Katalitička aktivnost bakra, srebra i zlata za dehidriranje*I. Brihta i P. Luetić*

Određene su energije aktivacije dehidriranja mravlje kiseline i etanola na metalima Ib-skupine (Cu, Ag i Au). Po rezultatima navedenim u tablicama I i II ne može se zaključiti, da bi katalitički mehanizam bio ovisan jedino o slobodnim energetskim nivoima s-elektrona u tim metalima. Osim na pojedinačnim metalima određene su energije aktivacije dehidriranja etanola i na smjesama bakar-srebro; dobivene vrijednosti leže na krivulji S-oblika, s horizontalnim dijelom između 20 i 60 atom. % bakra.

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