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The Kinetics of Oxidation of Aldehydes to Acids and Acid Anhydrides. II*

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Continuing our studies on the catalytic decomposition of peracids into acids and on the interaction of peracids with aldehydes into acids and acid anhydrides, we examined the influence of other mixed catalysts, i. e. manganese and copper butyrates and iron and copper butyrates on reaction rates.

They were found to be in good accordance with thermodynamic data.

The anhydride formation in the presence of a mixture of manganese and copper catalyst was investigated and found to be slightly inferior to the yield obtained with a pure manganese catalyst.

Continuing our studies[1] on the catalytic decomposition of peracids into acids, and on the catalytic interaction of peracids with aldehydes into acids and acid anhydrides we used two new catalyst mixtures not investigated previously.

In the first study we investigated the influence of a mixture of cobalt and copper butyrates and we found that copper slowed down the cobalt catalyzed decomposition of the peracid considerably, while the cobalt catalyzed interaction in the presence of copper was affected only to a minor degree (see Table 5 in the previous paper[1]).

Now we examined the influence of copper to both manganese and iron catalysts on reactions **I** and **II** in an attempt to find out the catalytic behaviour of manganese and iron in the presence of copper.

From our previous investigations as well as from theoretical considerations, only manganese and iron seemed to be worth investigating in combination with copper**. The decomposition rates in the presence of these catalysts were higher than those in the presence of cobalt, i. e. $k_{\text{I}} = 26.2$ for manganese, 22.8 for iron and 19.4 for cobalt, whereas the corresponding interaction rate constants (k_{II}) amounted to 34.9 for manganese, 29.4 for cobalt and 9.7 for iron. A mixture of cobalt and copper gave an extraordinary high k_{II} value of 42.3 which we interpreted as an inhibition of the decomposition due to copper.

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* Paper I: reference[1].

** All metals used as catalysts in these experiments were in the bivalent state.

EXPERIMENTAL

The experimental technique and the apparatus were described in our previous paper.[1]

Figure 1 represents the decomposition of perbutyric acid in the absence of catalysts as well as in the presence of copper, manganese, and manganese and copper butyrates respectively. The amount of catalyst used was 10 mg/100 ml of a solution of perbutyric acid in ethylacetate.

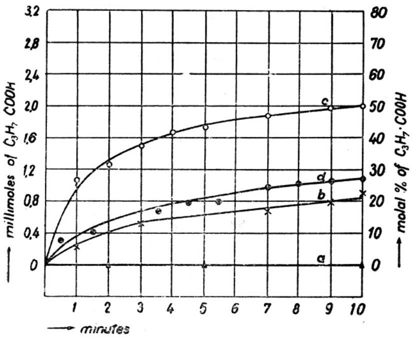

Fig. 1.

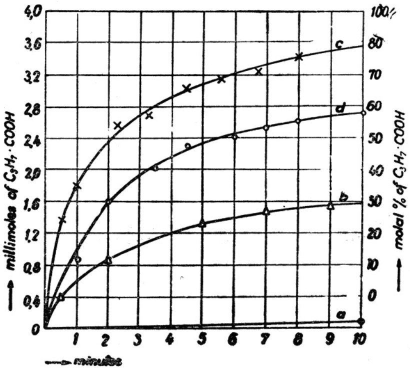

Fig. 2.

Fig. 1. The decomposition of perbutyric acid at 40°C; *a* without catalyst; *b* with copper (II); *c* with manganese (II); *d* with a mixture of copper (II) and manganese (II) in the ratio of 2 : 1, as butyrates.

Sl. 1. Razgradnja permaslačne kiseline kod 40°C; *a* bez katalizatora; *b* u prisutnosti bakrenog (II)-, *c* u prisutnosti manganovog II)-; *d* u prisutnosti smjese bakrenog (II)- i manganovog (II)-butirata u omjeru 2 : 1.

Fig. 2. The total reaction (decomposition and interaction) at 40°C; *a* without catalyst, *b* with copper (II); *c* with manganese (II); *d* with a mixture of copper (II) and manganese (II) in the ration of 2 : 1, as butyrates.

Sl. 2. Ukupna reakcija (razgradnja i interakcija) kod 40°C; *a* bez katalizatora; *b* u prisutnosti bakrenog (II)-; *c* u prisutnosti manganovog (II)-; *d* u prisutnosti smjese bakrenog (II)- i manganovog (II)-butirata u omjeru 2 : 1.

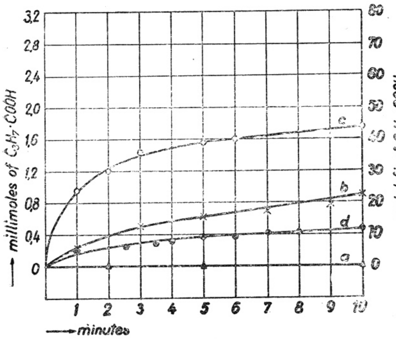

Fig. 3.

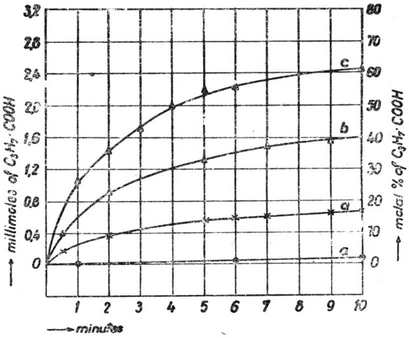

Fig. 4.

Fig. 3. The decomposition of perbutyric acid at 40°C; *a* without catalyst; *b* with copper (II); *c* with iron (II); *d* with a mixture of copper (II) and iron (II), in the ratio of 2 : 1, as butyrates.

Sl. 3. Razgradnja permaslačne kiseline kod 40°C; *a* bez katalizatora; *b* u prisutnosti bakrenog (II)-; *c* u prisutnosti željeznog (II)-; u prisutnosti smjese bakrenog (II)- i željeznog (II)-butirata, u omjeru 2 : 1.

Fig. 4. The total reaction (decomposition and interaction) at 40°C; *a* without catalyst; *b* with copper (II); *c* with iron (II); *d* with a mixture of iron (II), and copper (II) in the ratio of 1 : 2, as butyrates.

Sl. 4. Ukupna reakcija razgradnja i interakcija kod 40°C; *a* bez katalizatora; *b* u prisutnosti bakrenog (II)-; *c* u prisutnosti željeznog (II)-; u prisutnosti smjese željeznog (II)- i bakrenog (II)-butirata, u omjeru 1 : 2.

Figure 2 represents the total reaction (decomposition + interaction) of butyraldehyde and perbutyric acid in the absence of catalyst as well as in the presence of copper, manganese, and copper and manganese butyrates respectively. The concentration ratio of butyraldehyde to perbutyric acid was 10 : 1.

Figure 3 represents the decomposition of perbutyric acid in the presence of a mixture of iron and copper butyrates. For comparison the decomposition curves in the presence of iron and copper, and in the absence of catalysts are represented.

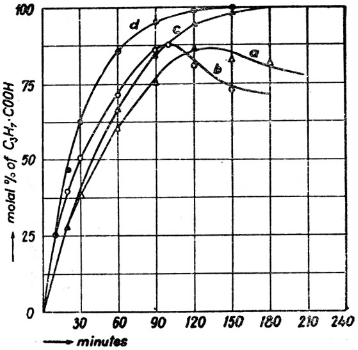

Fig. 5. The formation of butyric anhydride during the interaction of butyraldehyde with perbutyric acid and the corresponding total reaction curves (decomposition and interaction) at 40^{0}C; *a* the formation of anhydride in the presence of manganese (II)- and copper (II)-butyrates in the ration 1 : 2; *b* the same as *a*, but in the presence of manganese (II)-butyrate alone; *c* the total reaction curve (determined by the disappearance of perbutyric acid) in the presence of a manganese (II)- and copper (II)-butyrates catalyst mixture as given in *a*; *d* the total reaction curve in the presence of manganese (II)-butyrate alone.

Sl. 5. Stvaranje anhidrida maslačne kiseline za vrijeme interakcije butiraldehida i permaslačne kiseline te odgovarajuće krivulje ukupne reakcije razgradnja i interakcija kod 40^{0}C; *a* stvaranje anhidrida u prisutnosti manganovog (II)- i bakrenog (II)-butirata u omjeru 1 : 2; *b* isto kao *a*, ali u prisutnosti manganovog (II)-butirata samog; *c* krivulja ukupne reakcije određena nestajanjem permaslačne kiseline u prisutnosti smjese katalizatora manganovog (II)- i bakrenog (II)-butirata kao pod *a*; *d* krivulja ukupne reakcije u prisutnosti manganovog (II)-butirata samog.

Figure 4 represents the total reaction (decomposition + interaction) of butyraldehyde and perbutyric acid in the presence of a mixture of iron and copper butyrates. For comparison the corresponding curves in the presence of iron and copper butyrates respectively, as well as in the absence of catalyst are represented.

Figure 5 represents the concurrent formation of butyric anhydride in the presence of a mixture of manganese and copper butyrates, and in the presence of manganese butyrate alone. For comparison the total reaction curves in the presence of a mixture of manganese and copper butyrates, and in the presence of manganese butyrate alone are plotted.

DISCUSSION OF RESULTS

A. Decomposition of peracids

Copper showed a strong inhibitory effect on the catalytic activity of manganese and iron for the decomposition of peracids.

The computed k_I- values amounted for a manganese-copper mixture to 10.5 and for a iron-copper mixture to 2.6. The ratio of copper to manganese or iron was here 2 : 1.

In our previous study on this subject[1] we determined the k_I- values for a 4 : 1 copper-cobalt mixture. In order to correlate the above mentioned values obtained for 2 : 1 mixtures of manganese-copper and iron-copper catalysts, the k_I- value of a 2 : 1 copper-cobalt mixture was determined and all these values are represented in Table 1.

TABLE I

	Co	Mn	Fe
k_I	12.0	10.5	4.0
Δk_I	7.4	15.7	18.8
ΔG kcal	41.7	34.8	17.8

The influence of the addition of copper to various catalysts is most pronounced for iron, less for manganese and still less for cobalt. The decrease of $k_I = \Delta k_I$ by the addition of copper is represented in the second row of Table 1. The third row shows for comparison the free energy changes for the reaction (23) in our previous paper.[1]

The question arises why the presence of copper influences the catalytic activity of the catalysts used in such a different degree.

The explanation is, we suppose, as follows. The decomposition rate depends on the concentration of Me^{++}-ions, according to the reaction (20) of our paper[1,*]. This concentration will be diminished in the presence of copper, according to the reaction (25), in a degree which depends on the equilibrium constant and, in consequence, on the free energy change of this reaction, i. e.

$$\frac{[Me^{+++}]\ [Cu^{+}]}{[Me^{++}]\ [Cu^{++}]} = K = e^{-\frac{\Delta G}{RT}} \qquad (31)$$

The more negative (or the less positive) are the ΔG values for each metal, the smaller will be the concentration of Me^{++}-ions and the slower, consequently, the reaction rate of (20). There exists evidently a strong parallelism between the determined k_I-values of Table I and the ΔG-values of the reaction (25).

The decreasing influence of copper on the catalytic activity of various metals in the order Fe > Mn > Co can, therefore, be understood from thermodynamic data on the basis of the equation (31).

The influence of the copper concentration on k_I-values for cobalt-copper mixture is seen from Table II.

TABLE II

	Co : Cu	
	1 : 2	1 : 4
k_I	12.0	6.5

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[*] There was a printing error in this reaction (20): the hydroxyl is, of course, an ion (OH^-) and not a radical (OH-).

This effect can be predicted from the relation (31) because an increased concentration of cupric ions causes a decrease in Me^{++}-ions and therefore a smaller decomposition rate.

B. Interaction of aldehyde with peracid

The inhibitory effect of copper on the catalytic activity of manganese and iron respectively was also observed for the interaction (reaction **II**). In the previous study this effect was investigated only for a cobalt-copper mixture 1 : 4. The k_{II}- values, obtained by subtracting k_I from k_{I+II}, as well as the quotient 100 $k_{II(Me+Cu)} / k_{II(Me)}$ are given in Table II.

TABLE III

	Co	Mn	Fe
k_{II}	42.3	26.7	2.1
$\frac{100\ k_{II(Me+Cu)}}{k_{II(Me)}}$	144.0	73.6	21.6

Remarks: Co : Cu = 1 : 4
Mn : Cu = 1 : 2
Fe : Cu = 1 : 2

Copper has, in this case too, the greatest inhibitory influence on the catalytic activity of iron, a smaller one on manganese, while cobalt is being enhanced in its activity.

C. Anhydride formation

Our previous investigations[1] into the formation of acid anhydrides in the presence of a mixture of cobalt and copper catalysts have now been extended to the study of the influence of manganese and a manganese-copper mixture as catalysts (see Figure 5).

Here, too, it was observed that the major part of the reactants was converted into acid anhydride. The amount of acid anhydride formed reached first a maximum and later decreased somewhat, probably owing to hydrolysis.

From Figure 5, comparing the curves *a* and *b*, we see that the presence of copper in a mixture with manganese has no appreciable influence on the anhydride formation. As the most important factor is the reaction rate constant k_{II}, we can compare now the k_{II}-value of pure manganese with that of a mixture of manganese-copper; we have for manganese $k_{II} = 34.9$ and for a manganese-copper mixture $k_{II} = 26.70$.

A mixture of manganese and copper butyrates should, therefore, be somewhat inferior to a pure manganese catalyst, but in no case better, as it was found for a mixture of cobalt with copper in comparison with pure cobalt (see[1]). This conclusion agrees well with the experimental data from Figure 5.

With this study we hope to have made a contribution to a better understanding of copper and the transition metals as catalysts at the decomposition of organic peracids and at their reactions with aldehydes. Thereby we hope to have filled up a gap as these catalysts were studied extensively only on other systems, such as in the decomposition of hydrogen peroxides[2, 3], and the oxidation of hydrocarbons (e. g. tetralin)[4].

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IZVOD

Kinetika oksidacije aldehida u kiseline i anhidride kiselina

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Nastavili smo svoje studije o katalitičkoj razgradnji perkiselina u kiseline kao i o interakciji perkiselina s aldehidima u kiseline i kiselinske anhidride, te smo ispitali utjecaj nekih drugih miješanih katalizatora na brzine tih reakcija. Rezultati sa smjesama manganovog i bakrenog butirata, te željeznog i bakrenog butirata dobro se slažu s termodinamičkim predviđanjima.

Nadalje smo ispitali proces stvaranja anhidrida u prisutnosti smjese manganovog i bakrenog katalizatora. Nađeno je, da ta smjesa djeluje nešto slabije od čistog mangana kao katalizatora.

INSTITUT ZA INDUSTRIJSKA ISTRAŽIVANJA
ZAGREB

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