

The Kinetics of Oxidation of Aldehydes to Acids and Acid Anhydrides

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In an attempt to obtain a closer insight into the mechanism of the catalytic autoxidation of aldehydes to acids and their anhydrides a study was undertaken in which the individual phases of the process were separately investigated, namely:

- a) the noncatalytic and catalytic decomposition of peracids,
- b) the noncatalytic and catalytic interaction of peracids with aldehydes, and
- c) the noncatalytic and catalytic hydrolysis of acid anhydrides.

The acetates and butyrates of heavy metals (e. g. of manganese, cobalt, copper, iron and nickel) were used as catalysts while as aldehydes were used acetaldehyde and butyraldehyde and as acids the peracetic and perbutyric acid.

It was found that the decomposition of peracids into acids and molecular oxygen proceeds kinetically according to an unsuspected empirically found relation

$$k t^n = \ln \frac{a}{a-x}$$

where the mean value of n is 0.5.

According to this equation various catalysts showed the following order of activity (with decreasing k): manganese, iron, cobalt, copper and nickel.

A mechanism of the catalysis is proposed and the order of the catalyst activity based on the free energy change during the transition from the lower to the higher oxidation state is evaluated. This order is in good agreement with that found experimentally.

An explanation of the inhibitory effect of the copper catalyst is also given.

The hydrolysis rate of acid anhydrides was found to be relatively very slightly influenced by the presence of oxidation catalysts.

INTRODUCTION

The oxidation of aldehydes with molecular oxygen (autoxidation) can be represented by the total equation:

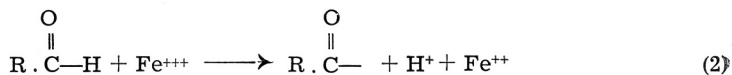


In this equation it is not clear how the molecular oxygen performs the oxidation at room temperature by splitting itself into atoms involved in this reaction.

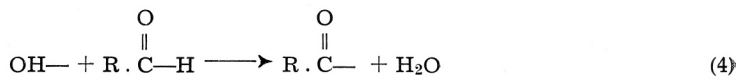
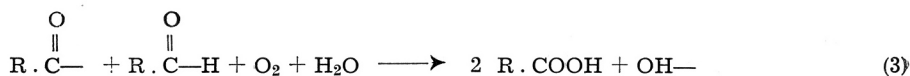
The older theories suppose the formation of a molal adduct and have to be rejected, as it was pointed out by G. Wittig¹.

Haber and Willstätter² represented the process of the aldehyde by the following chain mechanism:

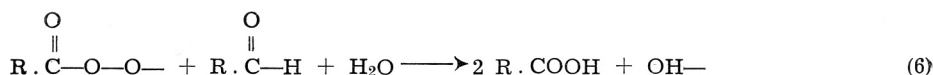
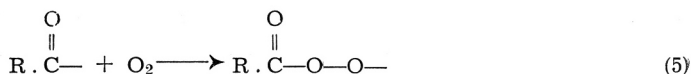
Start reaction:



Reaction chain:

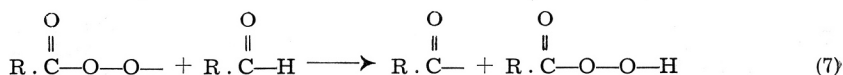


The triple collision, according to the equation (3) is improbable. Haber and Willstätter propose the formation of an addition product, according to the theory of Engler and Wild, and Bach.



G. Wittig cannot agree with this mechanism because it assumes the formation of hydroxyl radicals. He has found³ that unsaturated hydrocarbons subjected simultaneously with benzaldehyde to autoxidation did not transform to glycols. This transformation may, however, be expected if the reaction chain would proceed over hydroxyl radicals.

Wittig proposes a reaction mechanism which would start with the reaction (5) followed by



This reaction chain also explains the peracid formation which always occurs in this autoxidation. Similar reaction schemes have also been proposed by other investigators⁴.

In 1934 a new fact was discovered which has to be included in any satisfactory aldehyde oxidation theory, namely the formation of anhydrides⁵ which eventually hydrolyze into acids. We gave a contribution to the knowledge of the anhydride formation in a previous note⁶.

There is not only the mechanism of the anhydride formation to be explained but also the specific activity of various catalysts used for this oxidation.

In the technical literature⁷ it has been mentioned that a mixture of cobalt and copper salts gives higher yields of anhydride than manganese salts.

H. Meerwein⁸ assumes the formation of an unstable intermediate during aldehyde oxidation, namely the peresteraldehydehydrate which decomposes, depending on conditions, either into anhydride and water or directly into acid.

Concerning the formation mechanism of anhydrides the opinion put forward by A. H. Elce, M. Stanley and K. H. W. Tuerck⁹ should be mentioned.

namely that anhydrides are primary oxidation products and are not formed from the interaction of aldehydes with any intermediate oxidation product.

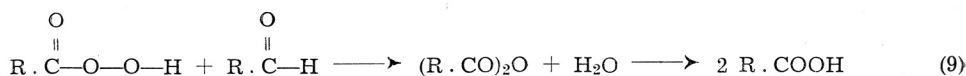
Trying to obtain a closer insight into the oxidation mechanism of aldehydes as promoted by various catalysts we have studied:

a) The catalytic and noncatalytic decomposition of peracids according to the total equation



into acid and molecular oxygen and

b) The catalytic and noncatalytic interaction with aldehydes, according to a tentatively supposed equation



with the formation of the acid anhydride as an intermediate, and the acid as a final product.

c) The possibility of a catalytic influence of heavy metal salts on the hydrolysis rate of acid anhydrides, according to the equation



was also separately studied.

In this paper we shall briefly denote the reaction (8) as »decomposition« and designate it with **I**, the reaction (9) as »interaction« **II**, and finally the reaction (10) as »hydrolysis« **III**.

EXPERIMENTAL

A. The decomposition of peracids with and without catalysts (Reaction I)

The noncatalytic reaction **I** has been studied only in comparatively concentrated aqueous solutions. In more dilute solutions, which were usually used in our experiments, it proceeded too slowly for kinetic studies. It is represented in Fig. 1.

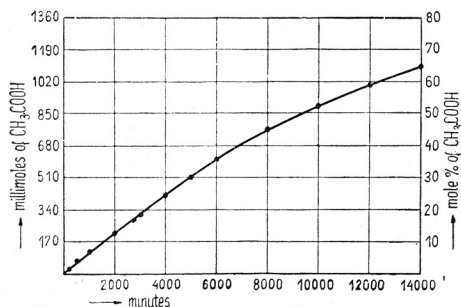


Fig. 1. The noncatalytic decomposition of the peracetic acid in an aqueous solution at 30°C.

The decomposition rate may be described by a reaction of the first order with a reaction rate constant $k = 7.214 \times 10^{-5}$ at 30°C.

In the presence of catalysts its kinetics were studied on the peracetic acid at 20°C and on the perbutyric acid at 40°C in the presence of manganese, iron, cobalt, mixture of cobalt and copper, copper and nickel as acetates and butyrates respectively.

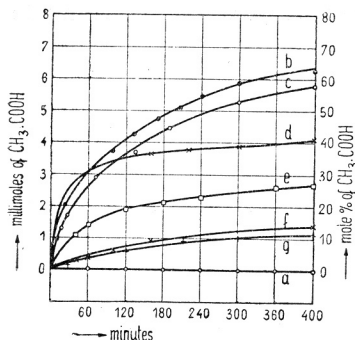


Fig. 2. The decomposition of peracetic acid at 20°C; a without catalyst, b in the presence of acetates of Mn (II), c Fe (II), d Co (II), e Co (II) + Cu (II) in the ratio 1 : 4, f Cu (II) and g Ni (II).

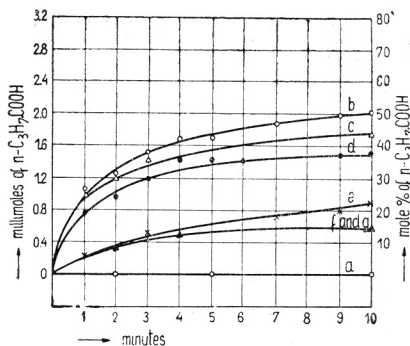


Fig. 3. The decomposition of perbutyric acid at 40°C; a without catalyst, b in the presence of butyrates of Mn (II), c Fe (II), d Co (II), e Co (II) + Cu (II) in the ratio 1 : 4, f Cu (II) and g Ni (II).

Figures 2 and 3 show the decomposition rates of the peracetic and the perbutyric acid in the presence and absence of catalysts.

In the absence of catalysts but *ceteris paribus* no decomposition could be observed during eight hours, this interval being considerably longer than the duration of one experiment.

Further it was proved by analysis that the decomposition of peracids in the presence of catalysts yields neither anhydrides nor hydrogen peroxide but only acids and molecular oxygen, as indicated in equation (8).

Trying to express the kinetics of the catalytic reaction I by some well known physico-chemical law we first applied the equations for the mono- and bimolecular reaction rates but no constant values either for k_{mono} or for k_{bi} were obtained. (See Tab. I, where data for the peracetic acid decomposition are given.)

TABLE I

Minutes	$k_{\text{mono}} \times 10^3$	$k_{\text{bi}} \times 10^4$	$k_{\text{I}} \times 10^2$
30	9.00	1.002	4.93
90	5.15	0.654	4.90
150	4.11	0.568	5.00
210	3.53	0.525	5.11
270	3.05	0.475	5.01

$k_{\text{I average}}$ at 20° = $5.01 \cdot 10^{-2}$
catalyst: Mn (II) acetate.

Applying instead the empirically found expression

$$k t^n = \ln \frac{a}{a-x} \quad (11)$$

satisfactory results for k_{I} were obtained (see Table I).

With various catalysts the values for n vary only very slightly from 0.374 to 0.638. As a mean value we took $n = 0.5$, so that the equation (11) can be written in the following way:

$$k t^{1/2} = \ln \frac{a}{a-x} \quad (12)$$

By squaring equation (12) and differentiating the obtained expression we come to the relation

$$+ \frac{dx}{dt} = \frac{k^2}{2} \frac{a-x}{\ln \frac{a}{a-x}} \quad (13)$$

Inserting the value for $\ln \frac{a}{a-x}$ from equation (12) into (13) we obtain the expression

$$+ \frac{dx}{dt} = k' \frac{a-x}{\sqrt{t}} \quad (14)$$

Supposing therefore that at the beginning the value $a-x$ is approximately equal to a , we receive after integration the equation of a parabola

$$x = a k \sqrt{t} \quad (15)$$

The catalytic peracid decomposition should, therefore, follow at the beginning of the process a parabolic equation, this being in good agreement with calculated values.

The k_I values calculated according to the equation (12) are constant for every individual catalyst but they differ from catalyst to catalyst. In Table II there are summarized the k_I values for decomposition of the perbutyric acid in the presence of various catalysts.

TABLE II

Catalysts as butyrates	Mn	Fe	Co	Co + Cu	Cu
$k_I \times 10^2$	26.25	22.80	19.40	6.54	5.50

Temperature = 40°C
Exponent $n = 0.5$

The order of the decreasing k_I values corresponds quite well with the actual order of the catalytic activity as represented in Fig. 3.

The influence of temperature on the decomposition rate of peracids

Fig. 4 shows the decomposition rates of perbutyric acid in the presence of a mixture of Co(II)- and Cu(II)-butyrate in ratio 1:4 at various temperatures.

The decomposition rate constants have been calculated according to equation (12); the obtained values are represented in Fig. 5.

In Fig. 5 the reciprocal values of the temperature are plotted on the abscissa, the logarithms of the corresponding k values are ordinates.

It can be seen that the points so obtained lie rather well on a straight line. By applying Arrhenius' equation, the activation energy $q = 6620$ cal and a frequency factor $A = 3.44$ may be calculated.

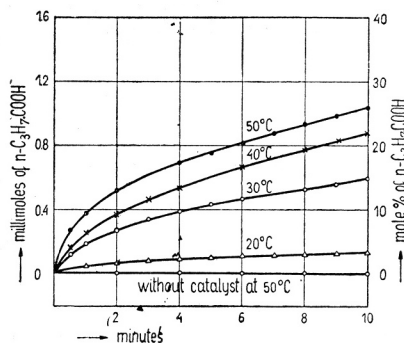


Fig. 4. The decomposition of perbutyric acid in the presence of Co (II) + Cu (II)— butyrates at various temperatures.

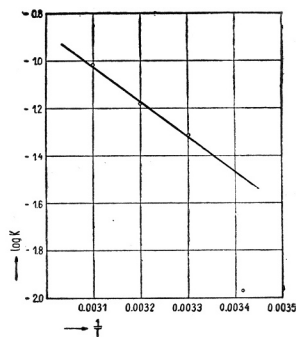


Fig. 5. The change of the reaction rate constant with temperature for the decomposition of perbutyric acid in the presence of Co (II) + Cu (II)— butyrates as catalyst.

The value at 20°C lies considerably below the straight line, but this is understandable since the catalyst used has a decreased activity at this temperature and therefore a quite different energy of activation must result.

The influence of the valence state of the catalyst on the decomposition rate of peracids

The Fig. 6 shows the decomposition of the perbutyric acid at 40°C in the presence of manganese (II)- and manganese (III)-butyrate respectively.

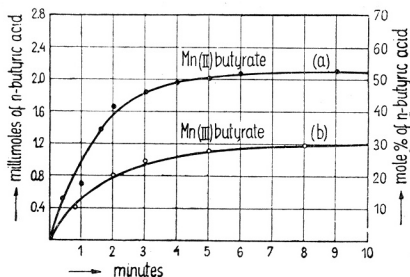


Fig. 6. The decomposition of the perbutyric acid in the presence of butyrates of Mn (II) (a) and Mn (III) (b) at 40°C.

The nearly colourless manganese (II) salt solution catalyzes the peracid decomposition considerably better than the dark coloured manganese (III) salt solution. This fact will be discussed later.

B. The interaction of aldehydes with peracids (Reaction II)

The noncatalytic interaction

The reaction II in the absence of catalysts is so slow to be negligible.

The Fig. 7 shows the reactions which proceed at 20° to 50°C. It was found that beside butyric acid a certain amount of butyric anhydride was formed; this is not shown in Fig. 7.

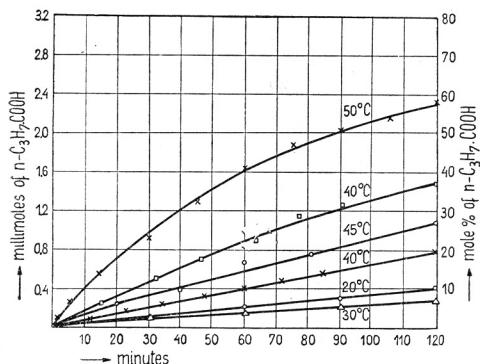


Fig. 7. The interaction curves of butyraldehyde and perbutyric acid in the absence of catalyst at various temperatures. The concentrations of reactants are equimolar (40 : 40 millimoles) at 20°, 40° and 50°C; and in the ratio 10 : 1 (40 : 4 millimoles) at other temperatures.

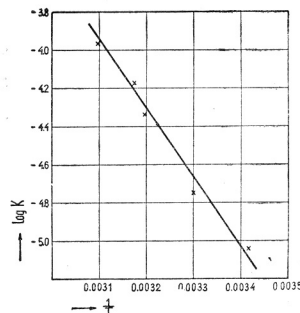


Fig. 8. The change of the reaction rate constant with temperature for the interaction of the butyraldehyde and perbutyric acid in the absence of catalyst.

The reaction rate could be well calculated using the equation for the second order reactions.

Table III gives the k'_{II} values for the interaction of perbutyric acid and butyraldehyde in equimolar concentrations.

TABLE III

Minutes	30	60	90	120	150	180
$k'_{II} \times 10^5$	0.890	0.877	0.926	0.936	0.910	0.890

k'_{II} average at 20° = 0.905×10^{-5}
catalyst: non

From the logarithms of the k'_{II} values at various temperatures a straight line could be constructed yielding an activation energy $q = 16\,570$ cal and a frequency factor $A = 7.29$ (Fig. 8).

Simultaneous catalytic decomposition and interaction (reaction I + II)

Since it was not possible to study the reaction II separately because the same catalysts promote also the reaction I, the total reaction I + II was kinetically investigated in the presence of catalysts. (Fig. 9.)

It can be seen that total reaction I + II proceeds much faster than the reaction I. This means that the reaction II is a much faster catalytic reaction than the reaction I.

Constant values for the reaction rate constants $k_{(I+II)}$ could be obtained only by applying the empirical relation (11). Constant values for $k_{(I+II)}$ could also be obtained by application of the equation

$$k_{(I+II) \text{ bi}} t^n = \frac{1}{a-b} \ln \frac{b}{a} \cdot \frac{a-x}{b-x} \quad (16)$$

The concentration ratio of butyraldehyde to perbutyric acid was 10 : 1 in all our measurements and the concentration of butyraldehyde did not change appreciably during the experiment; thus both mono- and bimolecular equations could be applied.

The calculated values for the exponent n remain also reasonably constant and vary for various catalysts from 0.44 to 0.56.

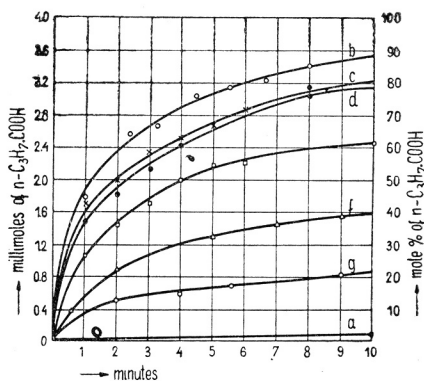


Fig. 9. The total reaction curves (the interaction and decomposition) of butyraldehyde and perbutyric acid in the absence and presence of catalyst at 40°C: a without catalyst, b in the presence of butyrates of Mn(II), c Co(II) + Cu(II) in the ratio 1:4, d Co(II), e Fe(II), f Cu(II) and g nickel(II).

Table IV gives the values of $k_{(I+II) \text{ mono}}$ and $k_{(I+II) \text{ bi}}$ at 40°C, according to equations (12) and (16).

TABLE IV

Minutes	$k_{(I+II) \text{ mono}} \times 10^2$	$k_{(I+II) \text{ bi}} \times 10^3$
0.24	45.40	11.48
1.00	51.10	13.03
3.56	48.40	12.60
7.16	51.80	13.55
9.80	51.20	13.51

$$k_{(I+II) \text{ mono average at } 40^\circ = 48.82 \times 10^{-2}$$

$$k_{(I+II) \text{ bi average at } 40^\circ = 12.88 \times 10^{-2}$$

Catalyst: mixture of Co(II) and Cu(II)-butyrates in the ratio 1:4.

Exponent $n = 0.5$.

The values for various catalysts are presented in Tab. V.

TABLE V

Catalyst as butyrate	$k_I \times 10^2$ by the eq. (12)	$k_{(I+II)} \times 10^2$ by the eq. (12)	$k_{II} \times 10^2$ by subtracting
Co+Cu	6.54	48.82	42.28
Mn	26.23	61.15	34.92
Co	19.43	48.82	29.39
Cu	5.50	16.38	10.88
Fe	22.80	32.49	9.69
Ni	5.50	8.70	3.20

Temperature = 40°C
Exponent $n = 0.5$.

The kinetics of reaction **II**.

We can assume the difference of the reaction rate constants for the total reaction and for the decomposition to be an approximate quantitative measure of the catalyst activity for the reaction **II** alone.

$$k_{II} = k_{(I+II)} - k_I \quad (17)$$

The reaction rate constants for the uncatalyzed interaction k'_{II} being very small can be neglected.

The values for k_{II} so obtained are shown in the last vertical column of Table V.

Fig. 10 represents the total reaction **I+II** of perbutyric acid and butyraldehyde in the presence of Co(II) + Cu(II)—butyrate in the ratio 1 : 4.

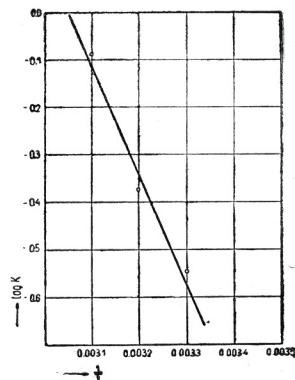
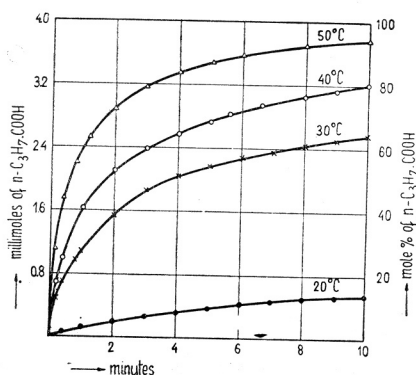


Fig. 10. The total reaction curves (the interaction and decomposition) of the butyraldehyde and perbutyric acid in the presence of Co (II) + Cu (II)-butyrates at various temperatures.

Fig. 11. The change of the reaction rate constant with temperature for the interaction of butyraldehyde and perbutyric acid in the presence of Co (II) + Cu (II)— butyrates.

From the values of the reaction rate constants for the total reaction **I+II**, calculated according to the equation (12), the formerly computed values of the constants k_I were subtracted, (Tab. VI).

TABLE VI

Temperature in °C	$k_{(I+II)} \times 10^2$	$k_I \times 10^2$	$k_{II} \times 10^2$
20	4.23	1.07	3.16
30	33.17	4.84	28.33
40	48.82	6.54	42.28
50	90.95	9.62	81.34

Catalyst: mixture of Co (II) + Cu (II) — butyrates in the ratio 1 : 4.
Exponent $n = 0.5$.

From the k_{II} values a straight line (Fig. 11) was constructed, indicating an energy of activation for the interaction $q=20600$ cal and a frequency factor $A=12.9$.

The point at 20°C is not situated on the straight line since at this temperature the catalyst has a decreased activity, and the activation energy has a different value.

In consequence of a considerably higher activation energy of the reaction **II** in comparison with the reaction **I**, 20.6 versus 6.62 kcal, a temperature increase

promotes much more the reaction **II** than the reaction **I**, giving at elevated temperatures a much higher yield of the anhydride as a direct product of the reaction **II**.

The hydrolysis of the so formed anhydride, which increases with rising temperature, should however be taken into account.

The formation of anhydrides during interaction

It was found by analytical determinations that the anhydride was always a constant byproduct of the catalytic as well as of the noncatalytic reaction **II**. As the reaction proceeds, its amount passes through a maximum (Fig. 12). Compare also the lit. cit.⁶

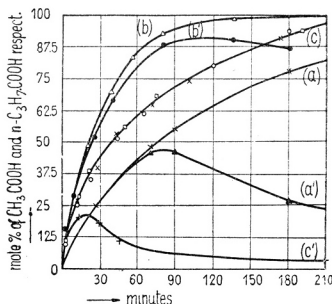


Fig. 12. The concurrent formation of acid anhydride during the oxidation of aldehydes by peracids in the absence and presence of catalysts at various temperatures: *a* the total non-catalytic reaction curve **I+II** for butyraldehyde and perbutyric acid at 40°C; *a'* the simultaneous formation of butyric anhydride; *b* the total reaction curve **I+II** for the butyraldehyde and the perbutyric acid at 40°C in the presence of Co(II) + Cu(II)-butyrates in the ratio 1:4; *b'* the simultaneous formation of butyric anhydride; *c* the total reaction curve **I+II** for the acetaldehyde and the peracetic acid at 20°C in the presence of Co(II) + Cu(II)-acetates in the ratio 1:4; *c'* the simultaneous formation of acetic anhydride.

The same form of anhydride curves as obtained here was also found previously for the aldehyde autoxidation with molecular oxygen.

The total reaction **I+II** was determined in three ways: (i) by determination of the acid formed, (ii) by determination of the unreacted aldehyde and (iii) by determination of the unreacted peracid. All points fall in the same curve what proves that one molecule of aldehyde reacts with one molecule of peracid.

The low percentage of the anhydride formed at *c'* in respect to *a'* and *b'* can be explained by the fact that at the temperature of 20°C the catalyst does not promote sufficiently the reaction **II**, whereas it considerably promotes the reaction **I**, resulting in the formation of the acetic acid and molecular oxygen which under these conditions oxidizes quantitatively the aldehyde into acid.

C. The kinetics of the anhydride hydrolysis (Reaction **III**)

This reaction was studied on acetic anhydride in the presence and absence of catalysts. Preliminary experiments showed that an anhydrous ethylacetate solution of acetic anhydride remains completely stable and unchanged even in the presence of catalysts at 40°C during 48 hours.

Fig. 13 shows the hydrolysis rates of the acetic anhydride. All these hydrolysis curves coincide perfectly at lower temperature what signifies that the catalysts used exhibit no catalytic activity. However, Co(II) and Mn(II) accelerate the hydrolysis at 40°C in a very slight degree.

The reaction rate constants calculated according to the equation for the bimolecular reaction rate are fairly constant and agree well with values found by other authors.

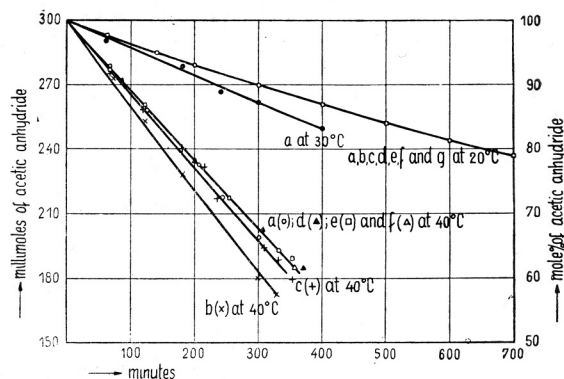


Fig. 13. The hydrolysis of acetic anhydride in the absence and presence of various catalysts at 20°, 30° and 40°C; a without catalyst; b in the presence of Mn (II); c Co (II); d Cu (II); e Ni (II); Fe (II) and g Co (II) + Cu (II) as acetates in the ratio 1 : 4.

From the k values for the noncatalytic hydrolysis at various temperatures a straight line has been constructed (Fig. 14), wherefrom an activation energy $q = 13.400$ cal and a frequency factor $A = 4.59$ resulted.

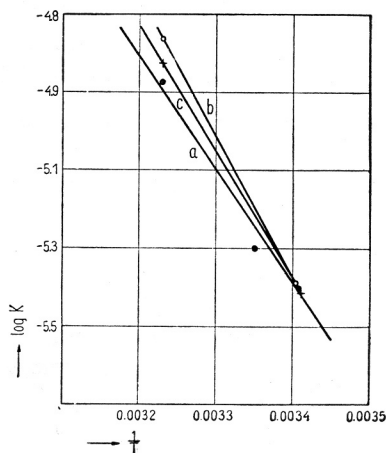


Fig. 14. The change of the hydrolysis rate constant with temperature for the acetic anhydride in the absence and presence of various catalysts; a without catalyst, b in the presence of Mn (II), c Co (II)-acetates.

D. Analysis and apparatus

The experiments were carried out on two systems: a) acetaldehyde, acetic acid, acetic anhydride, peracetic acid, and b) butyraldehyde, butyric acid, butyric anhydride, perbutyric acid.

The concentrations of reactants varied from 40 to 300 mgmoles in 100 ml of an ethylacetate solution.

The concentrations of the catalyst amounted from 2.5 to 60 mg in 100 ml solution, and the catalysts were introduced in an acetic or butyric acid solution, mainly in their lower oxidation state.

All reactants have been synthesized in this laboratory and their purity was from 99.0 to 99.5%.

All experiments were carried out in specially purified ethylacetate solutions which did not contain any alcohol, acid or water and which had a titer of 99.95%.

The peracids were prepared according to the method of D'Ans and Mattner¹¹. The concentration of peracids was 75—80%. They were completely free of hydrogen peroxide and contained as impurities only a few percents of acid and water. Since all experiments were carried out in very dilute solutions (0.5—4.0%) the content of water never exceeded 1%.

The catalysts were prepared in this laboratory from chemicals of highest purity.

The aldehydes were determined by the hydroxylamine-chlorhydrate method with bromphenolblue as indicator.

The determination of acid anhydrides in the presence of acids and/or peracids in an ethylacetate solution was carried out according to a modified method of A. Leman and A. Johansson¹⁰ with thymolphthalein as indicator.

The acid content in the presence of peracids was determined from the difference of the total acid and peracid content.

The peracids were determined iodometrically. The presence of aldehyde did not affect the reliability of the method. Compare also the lit. cit.¹². The titration can be considerably speeded up by the addition of a few drops of chloroform to the solution¹³.

All titrations where aldehydes were present were carried out in a nitrogen atmosphere.

The acids and peracids in the presence of aldehydes were also determined comparatively by the method of Almquist and Brauch¹⁴. Both methods agreed well in their results.

Hydrogen peroxide and peracids were determined simultaneously according to the method of D'Ans and Kneip¹⁵.

The moisture in most reagents was determined by the K. Fischer reagent¹⁶, in aldehydes nephelometrically and in peracids indirectly by difference to 100.

A NEW CATALYTIC MECHANISM OF ALDEHYDE OXIDATION BASED ON THE RESULTS OF THIS INVESTIGATION

All possible reactions occurring during aldehyde autoxidation are represented in Fig. 15.

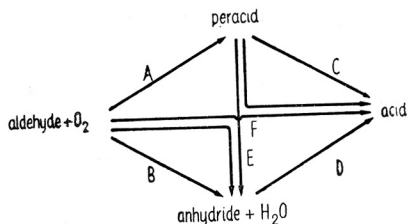
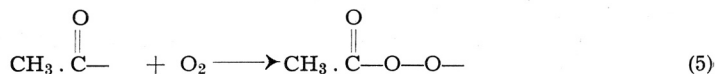
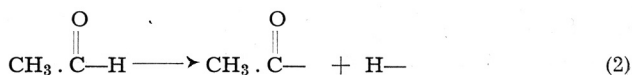
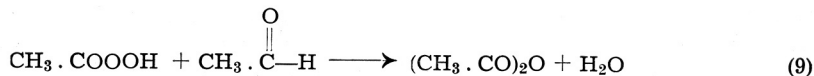
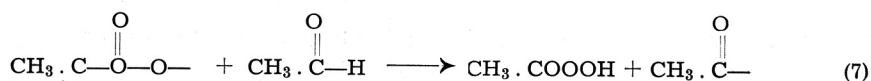


Fig. 15. The scheme of acid and anhydride formation at the aldehyde autoxidation by the molecular oxygen.

Now it is the question which of these ways occurs really. The anhydride can be formed alternatively by ways A+E or B.

The way A+E:

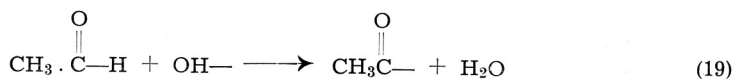
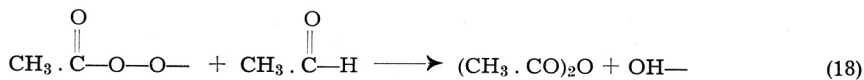




The way B:

The first step is same as in the way A+E (2)

The second step is same as in the way A+E (5)



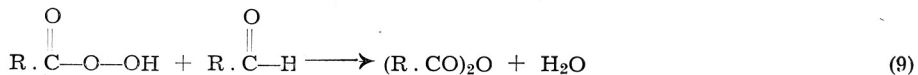
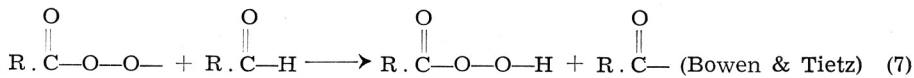
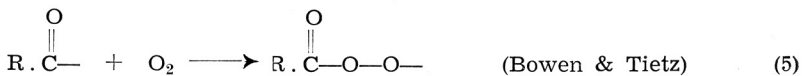
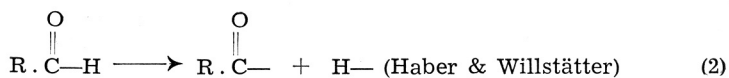
The step (18) in the way B involves a breaking of a O—O and a C—H bond, further the formation of a C—O and a O—H bond respect., while the corresponding step (7) in the way A+E involves only the breaking of one C—H bond and the formation of a O—H bond.

Thus, the way A+E leading to the anhydride comprises much simpler and therefore more probable steps.

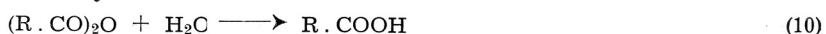
The formation of the peracid as the first product of the aldehyde oxidation can be considered as a firmly established fact resulting from experiments of many previous investigators^{17, 18, 1 and 4}.

The equation (7) can therefore be considered as being correct in so far as the quantity of the anhydride formed during the direct catalytic oxidation of the aldehyde corresponds exactly with that formed by the interaction of the peracid with the aldehyde.

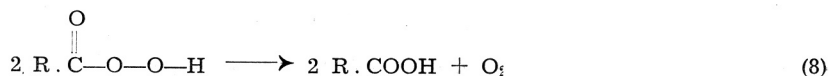
The whole reaction mechanism of aldehyde oxidation can therefore be considered as follows:



followed by:

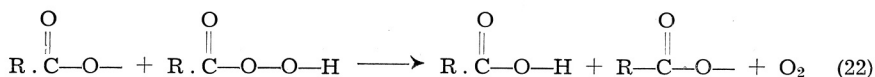
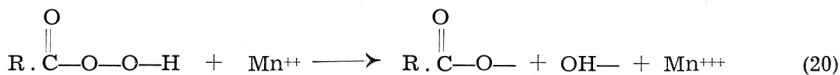


and



It is now to be elucidated by what mechanism the catalysts used promote the reaction rates in various stages of the reaction.

The decomposition of peracids proceeds much faster in the presence of the bivalent than in the presence of the trivalent manganese salt. The decomposition mechanism could therefore be represented according to a scheme which is analogous to that by which Haber and Weiss¹⁹ explained the decomposition of the hydrogen peroxide. In our case we can write:



If the reaction (20) occurs really, the peracid decomposition rate should directly be proportional to the free energy change of the reaction:



in which the catalyst delivers one electron.

From data collected by W. M. Latimer²⁰ we calculated the free energy changes presented in Table VII.

TABLE VII

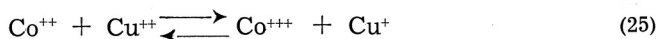
Reaction	Free energy change ΔG in kcal	Remarks
$\text{Fe}^{++} \longrightarrow \text{Fe}^{+++} + e$	+ 17.8	(estimated value)
$\text{Mn}^{++} \longrightarrow \text{Mn}^{+++} + e$	+ 34.8	
$\text{Co}^{++} \longrightarrow \text{Co}^{+++} + e$	+ 41.7	does not proceed in solutions
$\text{Ni}^{++} \longrightarrow \text{Ni}^{+++} + e$	—	
$\text{Cu}^{++} \longrightarrow \text{Cu}^{+++} + e$	—	

The relative order of the metals, with the only exception of manganese, agrees well with the determined k_1 values as recorded in table 2.

The Cu(II) ion has contrary to the Mn(II), Fe(II) and Co(II) ions the tendency to accept electrons according to the equation



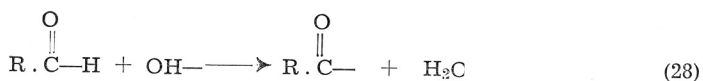
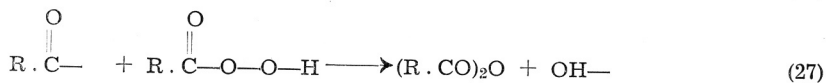
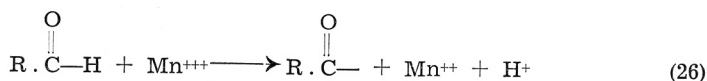
with a free energy decrease of $\Delta G = -3530$ cal. In the presence of Cu(II) ions Co(II) will therefore not be able to promote the peracid decomposition so easily as it does when present alone, since the reaction (23) is hindered by the reaction



which takes away the electrons needed for the reaction (20).

This theoretical conclusion agrees well with the relative position concerning the free energy change of a Cu(II)- and Co(II)- salts mixture in respect to other catalysts for reaction I and gives an indirect proof for the reaction (20).

We can now proceed to the examination of the catalytic mechanism of the interaction of peracid with aldehyde. We shall start by supposing the following reaction chain whose implications will be discussed:



Those catalysts which can very easily accept electrons, according to a reaction which is the reverse of equation (23), namely:



should therefore be the most powerful for the acceleration of the reaction II.

The calculated order of catalyst activities are: Co > Mn > Fe > Cu > Ni, whereas the observed orders are Mn > Co > Cu > Fe > Ni.

A remarkable success of the proposed theory consists in the fact that for the reaction II copper stands theoretically as well as practically before nickel, whereas for the decomposition both metals were theoretically and practically without any catalytic activities.

The nickel (II) ion cannot function as a catalyst either for the reaction I or for the reaction II, because there exists only one possible valence state of this metal in solutions. The Cu (II) ion, on the contrary, cannot function as a catalyst for the reaction I on account of the impossibility of transition to a higher valence state, but it does function as a catalyst for the reaction II as a consequence of the reaction (24).

We think that the unusually good catalytic properties of the mixture of the Co (II) and Cu (II) salts for the interaction can also be easily explained.

Cupric ions help in the formation of cobaltic ions which seem to be effective in the interaction according to the proposed mechanism (see equations 26—28). Moreover, cupric ions for their part, being always present in surplus, exhibit also certain catalytic activities on reaction II, although somewhat weaker.

Since reaction II is responsible for obtaining higher yields of anhydride during the oxidation of the aldehyde, it is easily understandable why a mixture of Co (II) and Cu (II) salts catalyses best the anhydride formation; this mixture is namely the weakest catalyst in the decomposition of peracid.

The proposed reaction chain for the reaction II supposes the formation of hydroxyl radicals, (equation 27). This is made in a contradiction to G. Wittig who found that olefinic compounds present in the mixture during the autoxidation of aldehydes do not yield glycols.

G. Wittig considers therefore that no chain mechanism involving the formation of such hydroxyl radicals is acceptable.

We cannot agree with this conclusion for following reasons:

The first step in a supposed glycol formation should be the reaction:



involving the formation of a new radical. Since the collision of the radical so formed with a hydroxyl radical, yielding the glycol, is an extremely improbable step, no chain mechanism can and does involve such improbable steps.

Moreover, if we do not accept the hydroxyl radical formation, we should, for the same reason, question the existence of acetyl radicals as no acetylation of olefinic compound present in the solution could be observed, since the dibiphenylenethylene changes only into fluorenone.

Studying the results of the interaction of peracids with aldehydes (Fig. 12) we came to the conclusion that acids are formed not only by the hydrolysis of acid anhydrides, the reaction way $A+E+D$ in Fig. 15, but also by the ways $A+C$ or $A+F$.* There is, namely, a remarkable difference in the amounts of the anhydride formed at 40°C (curve b' in Fig. 12) and at 20°C (curve c' in the same figure).

This difference can, however, be explained by supposing that one part of the peracid decomposes into the acid and molecular oxygen whereas the dissolved oxygen quantitatively oxidizes the equivalent amount of the aldehyde. This is in good accordance with the analytically found data, namely, that during the interaction unreacted aldehyde could never be found in amounts exceeding the amount of the decomposed peracid.

This difference in the amounts of anhydride formed by the interaction at various temperatures becomes still more understandable by taking into considerations the temperature coefficients of the reactions **I** and **II** respectively.

In Tab. VI is shown the great increase with the rising temperature of the interaction rate over the decomposition rate. Taking into account that during the interaction anhydride is the main primary product, while during the decomposition the acid represents the sole reaction product, all experimental data in Fig. 12 can now be elucidated and are well understandable.

Thus, at 20°C the main part of the peracid decomposes into the acid and molecular oxygen which in turn oxidizes the aldehyde, while at 40°C the interaction with the formation of anhydride predominates.

One phenomenon remains, however, to be explained. The ratio of the anhydride to the acid formed during the interaction at 40°C after approximately 100 minutes is 10 : 1. During the direct autoxidation of the aldehyde⁶ with molecular oxygen or air this ratio is at the beginning of the process approximately the same as during the interaction but after 100 minutes it falls to 1:1. We think that this fact can easily be explained in the following way.

The acetyl radicals during the direct oxidation, especially when the aldehyde concentration decreases at the end of the process, will have more often

* The hydrolysis rate of the anhydride is relatively low in comparison with the rate of the reaction **II** ($k_{III} = 1.6 \times 10^{-5}$, and $k_{II} = 2.9 \times 10^{-1}$ at 40°C in the presence of the cobalt).

the opportunity to react with oxygen, forming peracid radicals, according to Eq. (5) than to react with the already formed peracid, according to Eq. (27).

A higher concentration of peracid radicals and a lower concentration of the aldehyde will therefore favour the reaction (22) at the end of the process which yields only the acid but no anhydride.

In our studies on the decomposition of peracids as well as on the interaction of peracids with aldehydes no »induction period« was observed. This induction period is, however, very characteristic for the catalytic and non-catalytic autoxidation of aldehydes with molecular oxygen.

In all our experiments the catalyst was added (in form of its lower valence state, with exception of copper) to a reaction mixture always containing peracids, which oxidized the catalyst in turn (at least partially) to its higher valence state, noticeable by a marked change into deep colours. In this way, in the presence of a trivalent manganese, cobalt and iron salts the reaction **II** could start immediately, according to equation 26, without any induction period.

In a separate experiment it was also found that by adding a few drops of a peracid to a previously autoxidized solution containing the Mn(II)-acetate as catalyst no induction period has been observed. This is in good accordance with the Haber-Willstätter view of the reaction mechanism presented in equation 2.

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IZVOD

Kinetika oksidacije aldehida u kiseline i anhidride kiseline

T. Vrbaški i I. Brihta

Da bismo dobili točniji uvid u sam mehanizam katalitičke oksidacije aldehida u kiseline i kiselinske anhidride studirali smo posebno pojedine faze procesa t. j.

- a) nekatalitičku i katalitičku razgradnju perkiselina,
- b) nekatalitičku i katalitičku interakciju perkiselina i aldehida i
- c) nekatalitičku i katalitičku hidrolizu kiselinskih anhidrida.

Kao katalizatore upotreбили smo acetate odn. butirate nekih teških metala kao na pr. mangana, kobalta, bakra, željeza i niklja. Eksperimente smo izveli s etanalom i perocetenom kiselinom i butanalom i permaslačnom kiselinom.

Pronađeno je, da se razgradnja perkiselina u odgovarajuću kiselinu i molekularni kisik odvija po empiričkom kinetičkom izrazu

$$kt^n = \ln \frac{a}{a-x}$$

gdje srednja vrijednost za n iznosi 0,5.

Razni katalizatori pokazuju, računajući ovim izrazom, slijedeći red aktivnosti (uz padajuće k vrijednosti): Mn, Fe, Co, Cu i Ni.

Predložen je mehanizam djelovanja katalizatora na razgradnju perkiselina. Izračunate su aktivnosti katalizatora na temelju promjene slobodne energije kod prijelaza od nižeg na viši oksidativni stepen. Dobiveni se red aktivnosti katalizatora dobro slaže s onim, koji smo utvrdili eksperimentalno.

Protumačili smo inhibitorско djelovanje bakrenog katalizatora.

Zatim smo našli, da se kinetika interakcije perkiselina s aldehydima odvija po istoj zakonitosti kao i razgradnja perkiselina. Glavni reakcioni produkt kod interakcije, kod nešto povišene temperature, uvijek je kiselinski anhidrid.

Predložen je mehanizam djelovanja katalizatora na interakciju perkiselina i aldehida. Dobiveni se rezultati dobro slažu s termodinamskim proračunima na osnovu promjene slobodne energije kod prijelaza raznih katalizatora od višeg na niži oksidativni stepen.

Pronašli smo, da gornji katalizatori utječu samo u vrlo ograničenoj mjeri na brzinu hidrolize kiselinskih anhidrida.