

the very large distance σ^* will be mysteriously drawn together to the very much smaller distance σ and will then fly apart in deactivated states.

We have called attention to the foregoing difficulties, recognizing that Fowler and Rideal have themselves been cognizant of difficulties, and not in any way to disparage the useful and beautiful theoretical work which they have done.

¹ See, for example, Tolman, *J. Amer. Chem. Soc.*, **47**, 1524 (1925), where references to other work will be found.

² Fowler and Rideal, *Proc. Roy. Soc.*, **A**, **113**, 570 (1927).

³ Hirst and Rideal, *Ibid.*, **A**, **109**, 526 (1925).

⁴ This figure is used in order to agree with the calculations of Fowler and Rideal. It is, however, apparently the number of molecules at 273°K. rather than that at 300°K. which was approximately the actual temperature of the experiments of Hirst and Rideal.

⁵ Stuart, *Zts. Phys.*, **32**, 262 (1925).

A CASE OF NEGATIVE CATALYSIS IN A HOMOGENEOUS SYSTEM

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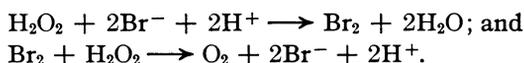
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Introduction.—The purpose of a series of studies² made recently has been to elucidate the mechanism of the so-called promoter action on reactions taking place in homogeneous systems. The reactions chosen for this purpose were the catalytic decompositions of hydrogen peroxide as effected by various salts. Hydrogen peroxide was selected because its decomposition products, oxygen and water, have no effect upon the reaction, and because the mechanism of some of its catalytic decompositions are well enough known to admit of the study of the anomalous effects observed when two or more catalysts are present at once. Sometimes the effect of mixed catalysts is the sum of their separate effects, as when hydrogen peroxide is decomposed by sols of platinum and gold.³ However, in many cases, the total effect is much greater than the sum of the individual effects; one of the catalysts being then said to exert a promoter action. In other cases, the resultant effect is less than the sum of the individual effects, and one of the substances is then said to produce negative catalysis.

These effects are well illustrated by the reactions involving hydrogen peroxide. The catalytic decomposition of this substance usually involves two interdependent simultaneous reactions, by one of which an intermediate compound is formed, and by the other of which it is decomposed.

Thus Bray and Livingston⁴ have shown that when hydrogen peroxide is decomposed by hydrobromic acid the two following reactions take place simultaneously:



These two reactions soon come to a steady state in which the reactions producing and decomposing the intermediate substance, bromine, proceed with equal rates.

Promoter action has been shown to be due to the formation of a second intermediate compound which is more rapidly acted upon by the hydrogen peroxide, with the evolution of oxygen, than is the first intermediate compound, so that the observed rate of the reaction is increased thereby. Thus it was shown⁵ that cupric salts, which promoted the catalytic decomposition of hydrogen peroxide by ferric salts, were converted into cupric acid, and that the subsequent rapid reaction between this substance and hydrogen peroxide accounted for the observed increase in rate.

It is evident that the converse effect, that of negative catalysis, might exist in the case where there is the possibility of the formation of a second intermediate substance which is more slowly acted upon by the hydrogen peroxide than the first intermediate. It has been found that the decomposition of hydrogen peroxide under the joint influence of potassium dichromate and vanadic acid is a reaction of this kind; and it is the purpose of this paper to present briefly the results of its investigation.

Method of Reaction-Rate Measurements.—The reaction rates were measured by the gasometric method, in an improved form of apparatus based upon the original design of Walton.⁶ An auxiliary buret, with a flask containing no reactants, has been added to make it possible to apply without computation a correction for any change in the barometric pressure occurring during the course of a slow reaction.

The vanadic acid used was prepared by adding acetic acid to a solution of ammonium vanadate since vanadium pentoxide is difficult to prepare in the pure state and shows a distressing tendency to form sols upon dissolving in water. The ammonium acetate formed thereby, being neutral in reaction, does not change the hydrogen-ion concentration of the solution; its neutral salt effect is doubtless small. Vanadic acid, as shown by the yellow color produced upon acidification, seems to be so weak an acid as to be nearly quantitatively displaced by acetic acid.

Experimental Results.—The rate $-dc/dt$ of the decomposition of the peroxide in all mixtures was found to be only approximately proportional to its concentration, c ; however, the data give fairly good constants when calculated according to the expression $K_R = 0.4343(10^4/t)(\log c_0/c)$. The data plotted in figure 1 show the effect upon the values of K_R of

changing the initial concentration of hydrogen peroxide. Because of this effect the initial concentrations were kept as nearly constant as possible and a small correction was applied to the values of reaction rates to reduce them to an arbitrary initial concentration of 187 millimols per liter of hydrogen peroxide when they differed from this value.

The reaction rate K_R at 30° (time expressed in minutes) was found to be 105–108 when the peroxide solution contained 0.5 mM./l. (millimols per liter) of potassium dichromate, as it did in all the experiments with mixed catalysts here considered. It was found to have the small value 7 or 5

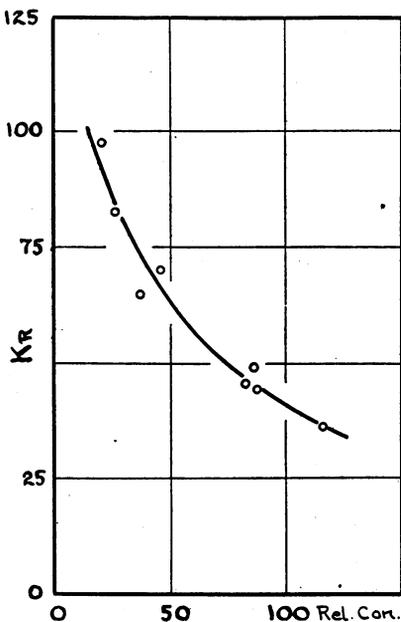


FIGURE 1

Variation of reaction rate with hydrogen peroxide concentration. Dichromate, 0.5 mM./l.; vanadic acid, 5 mM./l.

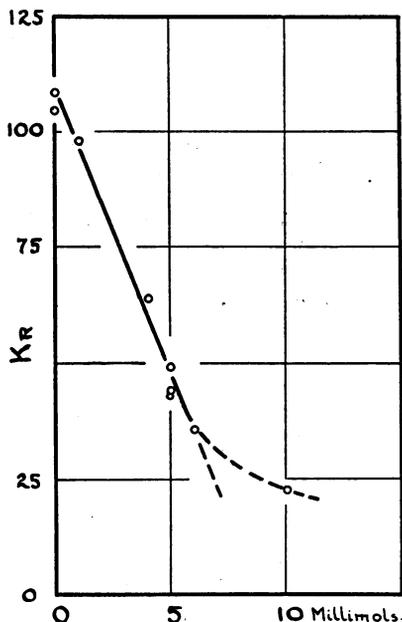


FIGURE 2

Effect of acetic acid upon a mixture containing dichromate (0.5 mM./l.) and ammonium vanadate (5 mM./l.)

when the solution contained no dichromate, but 20 mM./l. of ammonium vanadate or of vanadic acid, respectively. This is a larger quantity of ammonium vanadate than was ever present in the experiments with mixed catalysts.

An experiment with a mixture containing 0.5 mM./l. of dichromate and 20 mM./l. of neutral ammonium vanadate gave a reaction rate substantially identical with that produced by the dichromate alone. This showed that vanadate when neutral has no promoter action; in other words, that it does not influence the catalytic effect of the dichromate.

Experiments were then made with solutions all of which contained the dichromate at 0.5 and the vanadate at 5 mM./l., but which contained varying concentrations of acetic acid. The results are shown in figure 2. It is seen that the decrease in rate is almost proportional to the amount of acid added. When more than equivalent amounts of acetic acid were added, the straight-line relationship no longer held. This arose from the fact that reduction then took place, as was shown by the changed color of the solution after the peroxide had been decomposed.

Experiments with solutions containing 0.5 mM./l. of dichromate and 1 mM./l. of vanadic acid, but with varying amounts of ammonium vanadate gave the following results:

Ammonium vanadate in mM./l.	0	5	10	20
Reaction rate K_R	97	98	96 $\frac{1}{2}$	107

These experiments show that increase in vanadate has little effect unless accompanied by an increase in the acid concentration. The following results, which correspond to the data plotted in figures 2 and 3, also show this to be true.

$\text{NH}_4\text{VO}_3 = 5$	CH_3COOH	1	2	4	5
	K_R	98	(85)	64	45
$\text{NH}_4\text{VO}_3 = 0$	HVO_3	1	2	4	5
	K_R	94	70	(52)	45

The results indicate, therefore, that only free vanadic acid molecules affect the rate of decomposition; and they show further that acetic acid displaces nearly equivalent quantities of the vanadic acid from its salt.

A series of experiments was made with solutions containing the usual amount of dichromate and varying quantities of vanadic acid. These gave the results shown in figure 3. In this figure the abscissae represent the number of millimols of vanadic acid per liter on two scales (shown at the foot of the figure) corresponding to the upper and lower curves, respectively. It will be seen that the first very minute amounts of vanadic acid increase the rate from its normal value of about 108 to above 120, but that even at 0.80 millimolar the rate has fallen to below 100 and that at 25 millimolar it has dropped to about 35, after which it decreases further only very slowly with increasing amounts of added vanadic acid. The principal effect of the vanadic acid cannot be to remove the hydrogen peroxide from the reaction, since the amount of vanadic acid which halves the reaction rate can react with only about 1.5% of the hydrogen peroxide originally present.

The optical properties of perchromic and pervanadic acids are so similar that it was not possible to obtain even semi-quantitative values as to the extent to which the perchromic acid reacts with the vanadic acid to form pervanadic acid. However, examination at a suitable concentration of

reactants showed that much more pervanadic acid was formed by hydrogen peroxide in the presence of potassium dichromate than in its absence. Werther⁷ found, moreover, that a blue ethereal solution of perchromic acid after shaking with an aqueous vanadic acid solution, was decolorized with the simultaneous formation of pervanadic acid; it seems probable that the red perchromic acid reacts in an analogous manner.

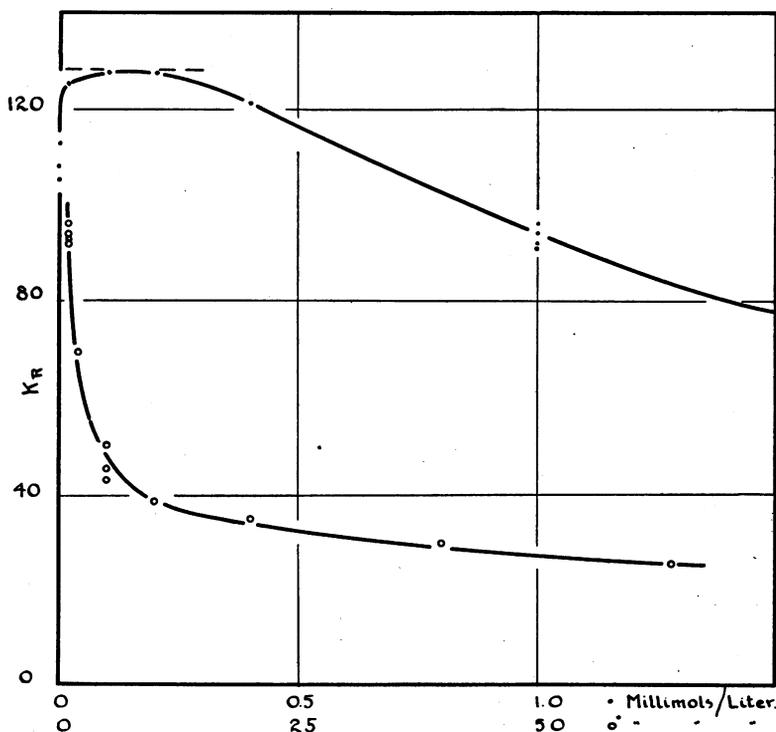


FIGURE 3
Reaction rate for added vanadic acid.

Theoretical Discussion of the Results.—The phenomenon of negative catalysis may be explained, in the same manner as promoter action, by the conception of a change in the path of the catalytic reactions.⁸ In this case the explanation is as follows: The catalytic decomposition of hydrogen peroxide by dichromate is doubtless due to the following reactions:

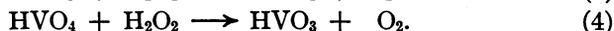
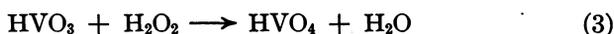


The compound formed in these reactions is no doubt K_3CrO_8 , but the formula KCrO_4 is used for the sake of convenience.

Reaction (1) proceeds rapidly at first and then reaction (2) becomes ef-

fective, and a steady state of catalysis is attained with a certain concentration of KCrO_4 present.

With vanadic acid the two corresponding reactions take place, as expressed by the following equations:



Reaction (4), however, takes place much more slowly than reaction (2) in conformity with the fact that the reactivity of pervanadic acid and hydrogen peroxide is much less than that of perchromic acid and hydrogen peroxide. However, when these two agents are simultaneously present with hydrogen peroxide, reaction (2) is in large measure replaced by reaction (4), because the following rapid reaction takes place to a large extent:



The result of this reaction is to diminish the proportion of the more reactive perchromic acid present, and thus to retard greatly the peroxide decomposition. This retarding effect should evidently increase as the concentration of vanadic acid is increased, and should approach a limiting value, as has been shown to be the case when most of the perchromic acid is converted by the rapid reaction (5) into pervanadic acid and but little of it is decomposed according to reaction (2).

A quantitative investigation of the shape of the curve, which should be analogous to a promotion curve,⁹ is rendered impracticable because of the complications caused by the slight acidity introduced by the negative catalyst.

Summary.—It has been shown in this investigation that vanadic acid greatly diminishes the rate of the catalytic decomposition of hydrogen peroxide by potassium dichromate. The "negative catalysis" is explained upon the basis of a change in the path of the reaction: the intermediate perchromic acid is converted into the less reactive pervanadic acid, whereby the total rate is decreased very largely. Another system is being sought where there are no complications which will interfere with the study of the shape of the curve.

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² Bohson and Robertson, *J. Am. Chem. Soc.*, **45**, 2512 (1923); Robertson, *Ibid.*, **47**, 1299 (1925); *Ibid.*, **48**, 2073 (1926).

³ Henri, *Compt. rend. soc. biol.*, **55**, 864 (1903).

⁴ Bray and Livingston, *J. Am. Chem. Soc.*, **45**, 1251 (1923).

⁵ Robertson, *J. Am. Chem. Soc.*, **47**, 1304 (1925).

⁶ Walton, *Z. phys. Chem.*, **47**, 188 (1904).

⁷ Werther, *J. prakt. Chem.*, **83**, 195 (1861).

⁸ Robertson, *J. Am. Chem. Soc.*, **48**, 2078 (1926).

⁹ Robertson, *Ibid.*, **48**, 2076 (1926).