

$$\tau = \frac{2d}{1,35 \times \frac{1}{2(1-b)}(q-1)^2}, \text{ hence } \tau(q-1)^2 = 3(1-b)d.$$

Now $1 + \tau(q-1)^2$ may be written for the factor $(1 + \tau q(q-2)) : (1-\tau)$ in (5) for small values of τ , which in view of the above approximated relation becomes $1 + \frac{3(1-b)d}{q-1}$.

Now $q = 3(1-b') \frac{r}{r-1}$ for small values of x . This being about 6,

$2,5(1-b') \frac{r}{r-1}$ may be put for $q-1$, so that we get approximately

$1 + \frac{6}{5} \frac{r-1}{r} d$ for the factor in question. Hence the factor θ in

$R T_c = \frac{2}{1+x} \frac{8}{27} \frac{a_c}{b_c} \times \theta$, referred to in the first part of this paper, will evidently according to (5), when for d its value is substituted, amount to:

$$\theta = \frac{2(r-1)^2}{(1-b')r^2} \times \frac{27}{8} \left[1 + \frac{6}{5} \frac{r-1}{r} \left\{ 1 - \frac{3+\beta}{2(1-b')} \frac{r-1}{r} \right\} \right],$$

holding for very small values for x . Only a small value of r , e.g. $r = 1,5$, satisfies this. If β has then become $= 0$, and $b' = 1/2$, θ becomes

$$\theta = 1 \left[1 + \frac{2}{5} (1-1) \right] = 1,$$

while with $r = 1,5$ (see the first part of this Paper in these Proceedings, § 8, p. 278) θ should be exactly $= 1$. Possibly x is not small enough to justify the above approximations and the neglect of certain values, and then it is possible that $r > 1,5$ drops out. But the calculations get very intricate then.

At any rate the formulae (4), (5), and (6) contain the full solution of the problem put by us.

La Tour près Vevey, spring 1920.

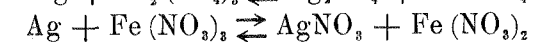
Chemistry. — “*Catalysis*” VIII. By NIL RATAN DHAR (with A. K. DATTA and D. N. BHATTACHARYA). (Communicated by Prof. ERNST COHEN).

(Communicated at the meeting of September 25, 1920).

a. Reaction between silver nitrate and ferrous-ammonium sulphate.

I tried to determine the kinetics of the reaction between ferrous ammonium sulphate and silver nitrate. The reaction seems to be very rapid.

When $N/_{50}$ silver nitrate and $N/_{50}$ ferrous ammonium sulphate are mixed at 25° , a bimolecular velocity coefficient of 0.0007 is obtained, but unfortunately this coefficient falls off as the chemical reaction proceeds. Since the metallic silver formed reacts on the ferric salt produced and we get an equilibrium of this nature



$$\text{or } \frac{(\text{Fe}^{++})(\text{Ag}^+)}{\text{Fe}^{+++}} \text{ at equilibrium} = 0.128$$

(cf. NOYES en BRAUN, Jour. Amer. Chem. Soc. 1912, 34, 1016) the reaction between ferrous ammonium sulphate and silver nitrate is rapid even at 0° and has a small value for its temperature coefficient.

The reaction is markedly accelerated by acids; nitric, sulphuric, citric, tartaric, and acetic acids have been tried; the greater the concentration of hydrogen ions, the greater is the velocity. This catalytic activity may be utilised in determining the concentration of hydrogen ions.

Magnetic force has practically no effect on this reaction. It is extremely sensitive to the influence of dirt etc.

Potassium nitrate appreciably retards the reaction, so do manganese salts very markedly.

Carbonic acid markedly accelerates the reaction. Boric acid is practically without any influence. So is phenol, which is probably slightly retarding in its effect. Glucose markedly accelerates the reaction. This is a case of induced reaction. A mixture of excess of silver nitrate and very little of ferrous ammonium sulphate was prepared and divided into equal parts, to one of which glucose was

added, whilst the other was left as it is; in a short time, more silver was deposited in the tube containing glucose, though a neutral solution of glucose cannot reduce silver nitrate. This is another case of an induced reaction already studied. (DHAR, Trans. Chem. Soc. 1917, **111**, 690).

Summary: *a.* The reaction between silver nitrate and ferrous ammonium in dilute solutions is bimolecular. The reaction is very rapid even at 0° and the temperature coefficient has a small value.

b. When the chemical change has proceeded up to a certain extent, an equilibrium is set up:



c. Acids accelerate this change; in case of nitric, sulphuric, citric, tartaric acetic acids, the greater the concentration of H⁺ ions, the greater is the acceleration. Carbonic acid markedly accelerates, whilst boric acid and phenol are without action. Manganese sulphate and potassium nitrate are retarders.

d. A neutral solution of glucose cannot reduce silver nitrate at about 20°; the reaction between ferrous ammonium sulphate and silver nitrate induces the chemical change between glucose and silver nitrate.

b. Oxidation of sodium sulphite by atmospheric oxygen.

LUTHER (Zeit. phys. Chem. 1903, **45**, 662) advanced the idea that negative catalysis cannot take place in a reaction which is entirely free from positive catalysts and the phenomenon is really due to the destruction or otherwise rendering latent of these positive catalysts. TITOFF (ibid. 1903, **45**, 641) as a result of his studies of the combined effect of positive and negative catalysors on the rate of oxidation of sodium sulphite lends his support to LUTHER's theory. The effect of negative catalysts on this reaction was first studied by BIGELOW (ibid. 1898, **26**, 493), who found the oxidation of the salt in aqueous solution to be greatly retarded by the presence of minute quantities of benzaldehyde, iso-butyl alcohol, glycerol, phenol etc. BIGELOW also demonstrated that the effect of negative catalyst is not on the rate of solution of oxygen, but on the rate of the reaction between the sulphite and oxygen. A few years later TITOFF substantiated BIGELOW's results and in addition studied the simultaneous effect produced by copper sulphate, a powerful accelerator and manitol a strong retarder. He found that these two substances do not exert any additive effect but influence each other. YOUNG (Jour. Amer. Chem. Soc. 1901, **23**, 119; **24**, 1902, 297) found that small quantities of certain alkaloids

greatly retard this oxidation, specially if this solution is alkaline, and the inhibitory effect of sucrose, invert sugar, asparatic acid, etc., have been noted by SAILLAND (Zeit. Ver. Zuckerind. 1913, **63**, 1035). In 1912, we conducted some experiments on this line. From preliminary experiments it was observed that the velocity of the reactions depends greatly on the quality of the water used. Ordinary distilled water was found quite inefficient as it contained sufficient dissolved salts and gases to affect the course of the reactions materially. Freshly prepared conductivity water obtained according to the method of JONES and MACKAY (Zeit. Phys. Chem. 1897, **22**, 237) was always used. The salts used were purified by recrystallisation from conductivity water and dissolved in the same water in resistance glass bottles. Well steamed Jena flasks were used as vessels in which the reaction took place. In short every care was taken to ensure purity. But in spite of all this care, it was found that velocity coefficients of the reactions carried out under identical conditions but on different days and even at different times on the same day were slightly different. TITOFF also found similar results. The explanation is probably that the reaction is so susceptible to external conditions, that even the slight variation of circumstances that is inevitable when we carry out the same reaction at two different times are sufficient to affect the results. It is therefore clear that our comparison of the results tried on different days or with different concentration of the same catalyst, cannot give an accurate idea of their relative effect. To remove this difficulty, at least partially, we carried out a blank experiment in which no catalyst was added, simultaneously with the main one. Two similar ERLLENMEYER flasks of capacity 150 c.c. were arranged side by side. A definite volume of sulphite was put in each flask. The catalyst was added in one flask. The course of the reaction was determined and their coefficients calculated. The ratio of these two coefficients gives the measure of the catalytic effect of the substance under consideration. In this way it was found that the ratio between the coefficients of two similar pair of reactions carried out on different days were almost the same, though their absolute velocities varied appreciably. The flasks were exposed to the atmosphere whose oxygen served as the oxidising agent.

About $\frac{N}{100}$ iodine and thio sulphate solutions were used as titration liquids. A definite volume of the sulphite solution is pipetted in a flask containing an excess of standard iodine and the excess of iodine was titrated back with the standard thio sulphate.

The temperature of the experiments was about 30° C.

Substance	Concentration	$\frac{K_1 \text{ catalyst}}{K_1 \text{ blank}}$
Cane sugar	0.2 N	0.09
"	3.1×10^{-2} N	0.17
"	6.7×10^{-3} N	0.47
"	9.4×10^{-4} N	0.63
"	3.7×10^{-5} N	0.89
Lactose	0.15 N	0.084
"	3.1×10^{-2} N	0.15
"	9.4×10^{-4} N	0.55
"	3.7×10^{-5} N	0.85
Glucose	0.1 N	0.22
"	1×10^{-3} N	0.75
"	2×10^{-4} N	0.83

It will be evident from the above results that cane sugar, lactose, and glucose are very strong retarders. Cane sugar and lactose have almost similar effects, though lactose is slightly stronger in its effect.

It appears probable that sugars as a class will act as negative catalysts. It has been found that the sparingly soluble volatile substances like camphor and menthol have marked negative effect while naphthalene, anthracene etc. have no catalytic effect.

The effect of several organic acids and their salts were also investigated. (See Table next page).

It is very peculiar that the weak acids like acetic, propionic, cacodylic etc. have comparatively small retarding effects. Their sodium salts also exert practically the same effect. On the other hand comparatively strong acids like oxalic, salicylic, benzoic etc. exert much greater retarding effect, and their salts too exert the same effect as the acids. Moreover it is found that the sodium salts of stronger inorganic acid have no marked effect.

We have found that hydroquinone has a very great negative effect on this reaction. For the same concentration, it exerts the greatest negative catalytic effect amongst the negative catalysts investigated up till now. We tried to determine the temperature coefficient of this heterogeneous reaction and see whether this becomes greater in presence of the powerful negative catalyst hydroquinone. Unlike most other heterogeneous reactions, we found that the temp-

Substance	Concentration	$\frac{K_1 \text{ catalyst}}{K_1 \text{ blank}}$
Oxalic acid	1.2×10^{-3} N	0.29
"	3×10^{-4} N	0.56
"	3×10^{-5} N	0.90
Benzoic acid	1.2×10^{-3}	0.25
"	2×10^{-4}	0.58
"	5×10^{-5}	0.83
Cacodylic acid	.02 N	0.75
"	.01 N	0.94
Sodium benzoate	1×10^{-3}	0.19
"	0.7×10^{-3}	0.25
"	1.5×10^{-4}	0.70
"	1×10^{-5}	0.90
Potassium oxalate	1×10^{-3} N	0.29
"	1×10^{-4} N	0.80
"	2×10^{-5}	0.96
Sodium salicylate	1×10^{-3}	0.23
"	1.5×10^{-4}	0.73
"	1×10^{-5}	0.95
Sodium citrate	1×10^{-3}	0.14
"	1×10^{-5}	0.85
Sodium acetate	3×10^{-3}	0.73
"	1×10^{-3}	0.85
Sodium propionate	3×10^{-3}	0.74
"	1×10^{-3}	0.89
Sodium butyrate	3×10^{-3}	0.74
"	1×10^{-3}	0.85

erature coefficient is about 2 (between 25°—40°) and it does not appreciably change in presence of hydroquinone (DHAR, Proc. Akad. Wet. Amsterdam 1919, 21, 1042). It has been found that so long as about one third of the substance is oxidised, the unimolecular velocity coefficient remains practically constant, but as the oxidation proceeds further, the velocity coefficient increases rapidly, and hence

it becomes very difficult to determine the temperature coefficient accurately. It appears therefore that the reaction is auto-catalytic.

MATHEWS and his colleagues (Jour. Phys. chem. 1913, **17**, 211; Jour. Amer. chem. Soc. 1917, **39**, 635) found that ultraviolet light markedly accelerates this reaction, and also established the fact that this is not a case of auto-oxidation. For this reaction, they could not find a positive catalyst; copper sulphate, which is known to be a powerful catalyst under ordinary conditions exerted no appreciable effect in ultra-violet light. On the other hand the negative catalysts like hydroquinone, phenol etc. exerted a retarding effect in presence of ultra-violet light. So it appears that there are very few positive catalysts, but very many negative ones for this reaction when carried out in light or darkness.

The explanation of the negative catalytic effect of organic substances in general on this reaction is this:

The reaction consists in the oxidation of SO_2 radical into SO_4 , and the sulphite ion is the active agent. It is well known that several organic substances form complexes with sulphurous acid and sulphites; these complexes are stable so far as oxidation is concerned and hence the organic substances act as negative catalysts by diminishing the concentration of sulphite ion by combining with it.

In foregoing papers I have proved that the phenomenon of negative catalysis is very common, whilst there are very few positive catalysts. According to LUTHER's view a negative catalyst must have a positive catalyst as its counterpart, but this is not probable since there are so few positive catalysts and so many negative ones. Hence it appears that LUTHER's view which emphasises that negative catalysis cannot take place in a reaction which is entirely free from positive catalysts, is not substantiated by experimental evidence.

Summary.

a. Cane sugar, lactose, glucose, camphor, and menthol are negative catalysts, whilst naphthalene, and anthracene are without action on the oxidation of sodium sulphite.

b. The weak organic acids and their sodium salts exert practically the same effect. Benzoic, oxalic, salicylic acids and their sodium salts exert greater negative effect than the weak acids and their salts. It is very peculiar that the acid and its salt should exert the same effect.

c. The temperature coefficient of the reaction is about 2 and it

does not change appreciably in presence of the strong negative catalyst hydroquinone.

d. The phenomenon of negative catalysis is very common in oxidation reactions. LUTHER's view which emphasises that negative catalysis cannot take place in a reaction which is entirely free from positive catalysts, is not substantiated by experimental evidence.

e. The organic substances act as negative catalysts by diminishing the concentration of the sulphite ion, which is the active agent in this oxidation; the diminution in concentration of sulphite ion is caused by the formation of a stable complex of the sulfite and the organic substance; this complex is not oxidized as readily as the sulphite ion.

c. Catalytic activity of the undissociated acid.

In recent years the question of acid catalysis has entered into a new period; and as a result of the accumulation of new observations and of increased exactitude in the measurement of the velocity of reactions, evidence has been obtained in support of the view that the catalysing power of an acid is not entirely due to the hydrogen ion, but that the undissociated acid also contributes to the observed effect.

This investigation had for its object the determination of the function of the undissociated parts of oxalic and picric acids in the hydrolysis of methyl acetate.

The experiments were all conducted at 45°. Dry pure potassium oxalate and sodium picrate were added in different quantities to diminish the ionisation of the respective acids. The former salt was crystallised from MERCK's pure sample, and the latter was prepared from pure materials and purified by repeated crystallisations.

The following summary of results is obtained ¹⁾

Oxalic acid.

Conc. of acid.	Conc. of $\text{K}_2\text{C}_2\text{O}_4$	Acid Conc. Salt. Conc.	K_1
·05 N	—	—	0·00091
"	·0038 N	13·16	0·00065
"	·0114 N	4·38	0·00044
"	·0174 N	2·37	0·00042
"	·0278 N	1·79	0·00038
"	·0590 N	1·02	0·00011

¹⁾ The experiments described here were finished in 1913.

Picric acid.

Conc. of acid.	Conc. of Sodium picrate.	Acid Conc. Salt. Conc.	K_1
0.03 N	—	—	0.00135
"	0.0031 N	9.67	0.00139
"	0.0050 N	6.00	0.00141
"	0.0513 N	0.58	0.00173
"	0.0778 N	0.38	0.00160
"	0.1161 N	0.25	0.00153
"	0.1597 N	0.18	0.00134
"	0.3066 N	0.09	0.00122

It will be evident from the foregoing tables that the velocity coefficients do not decrease proportionally with the decrease in the concentration of the hydrogen ions. In the case of oxalic acid the velocity coefficients fall off with the concentration of potassium oxalate; whilst in the case of picric acid the addition of sodium picrate produces at first an increase in the velocity coefficient and then when the concentration of sodium picrate reaches the value of 0.159 N, the velocity coefficients begin to fall off. This is explicable on the assumption that even undissociated acids are catalytically active in the hydrolysis of esters. But in view of the work of WALDEN (JOUR. Amer. Chem. Soc. 1912, 35, 1649) on the measurement of the di-electric constants of solutions, a different interpretation of these results is possible. WALDEN has shown with non-aqueous solutions that the di-electric constant and the ionising power of a solvent are enormously increased when electrolytes are dissolved in it. Naturally the degree of ionisation of the dissolved acid and along with it the concentration of hydrogen ions are also increased. Thus by the addition of salts of the same acids, there are two effects:

1. The diminution of hydrogen ions due to the increase of the common negative ion.

2. The increase in the concentration of the hydrogen ions due to the greater ionisation of the acid caused by the increase in the di-electric constant of the solvent.

It is evident that these two effects counteract each other.

In the case of potassium oxalate the first effect preponderates over the second and hence the velocity coefficient falls off with the concentration of potassium oxalate, whilst in the case of picric acid

the second effect predominates over the first and the velocity coefficient instead of decreasing, increases with the concentration of sodium picrate.

Moreover WALDEN has shown that there are two types of salts with regard to their effects on the di-electric constant of the solvent. He has observed that $N(CH_3)_4Cl$ markedly increases the di-electric constant of the solvent, whilst CH_3NH_2HCl affects this constant to a very slight extent. It is quite possible that even in aqueous solution salts like potassium oxalate, sodium acetate, etc. do not increase appreciably the ionising power of the solvent and the velocity of the reaction in its presence does not increase. In this way we can explain the negative effect of potassium oxalate and positive effect of sodium picrate on ester hydrolysis from the point of view of the change of the di-electric constant of the solvent due to the dissolution of electrolytes.

SUMMARY.

a. The hydrolysis of methyl acetate was investigated in presence of oxalic acid and picric acid and sodium picrate. In the former case, the velocity coefficient falls off, whilst in the case of picric acid, the velocity coefficient increases with the concentration of sodium picrate up to a certain extent and then decreases with the increase of the concentration of sodium picrate.

b. An explanation of these results is suggested on the basis of the increase of the di-electric constant and ionising power of the solvent observed by WALDEN when salts are dissolved in it.

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