[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

THE INFLUENCE OF NEUTRAL SALTS ON THE TEMPERATURE COEFFICIENT OF REACTION VELOCITY

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The reaction we studied is that between acetone and iodine in dilute aqueous solution, and our technique and methods are described in a previous paper.[2] The velocity constant used throughout this paper is the (calculated) number of moles of iodine disappearing per minute from 1 liter of a solution containing 1 mole of acetone, 1 gram equivalent of acid, about 0.01 *N* iodine, and a stated amount of neutral salt. The solution also contained 0.025 *M* potassium iodide to keep the iodine in solution. When this constant was determined at two temperatures for a solution of the same composition, the ratio is referred to as the temperature coefficient of the reaction. We are thus comparing the velocities at two temperatures for solutions containing the same concentration of total acid.

Lamble and Lewis[3] have attempted to calculate the temperature coefficient for solutions of equal hydrogen-ion concentration. Since, in the case of our solutions, there are no reliable data for making the necessary calculations, and there is not even agreement as to the nature of the catalyst,[4] we have not attempted to calculate the temperature coefficient for equal concentrations of catalyst.

The abnormal action of neutral salts is commonly ascribed to hydration effects and therefore, we made a preliminary study of the effect of lithium nitrate on the velocity and temperature coefficient of the reaction. We selected this salt because it shows very abnormal changes in solubility over the temperature range 20–30°. The solubility of lithium nitrate is almost doubled between 23° and 30°, and the salt also possesses a congruent melting point and a transition point, $3H_2O - {}^1/_2H_2O$, between these two temperatures. In previous investigations the salts used showed normal changes in solubility over the region investigated and we hoped, therefore, to find the velocity measurement affected by the abnormal hydration effects.

We crystallized the lithium nitrate twice from distilled water, and by a blank test showed that a 2 *N* solution of the salt absorbed no appreciable amount of iodine over a period of 4 hours. We also tested to see whether

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[1] The work included in this paper is summarized from the thesis presented by William Lemkin, submitted as part of the requirement for the degree of Doctor of Philosophy in New York University.

[2] Rice and Kilpatrick, THIS JOURNAL, **45**, 1401 (1923).

[3] Lamble and Lewis, *J. Chem. Soc.*, **105**, 2330 (1914).

[4] Kendall, *Proc. Nat. Acad. Sci.*, **7**, 56 (1921).

lithium nitrate alone had any catalytic activity. The results in Table I show that the neutral salt alone has no measurable catalytic action.

TABLE I

EFFECT OF LITHIUM NITRATE ON THE REACTION, $CH_3COCH_3 + I_2$

Concentration of acetone, 0.071 (*M*)

Salt present	None	None	2.2 *M* $LiNO_3$	2.2 *M* $LiNO_3$
N iodine, initial	0.01162	0.01162	0.01050	0.01050
After 300 min.	0.01161	0.01161	0.01047	0.01049

For the velocity measurement we used nitric acid as catalyst. By passing air through the acid for several hours we removed all traces of oxides of nitrogen, which would decompose the hydriodic acid formed during the reaction. Table II gives the results of our measurements at 23° and 30° with and without lithium nitrate.

TABLE II

VELOCITY CONSTANTS WITH AND WITHOUT LITHIUM NITRATE AT 23° AND 30°

Temp. ° C.	Constant per liter	Av.	Temp. ° C.	Constant per liter	Av.
	No salt present			2.102 *M* $LiNO_3$ present	
23.00	13.58		23.00	20.13	20.12
	13.60	13.58		20.11	
	13.56		23.00	20.09	20.05
23.00	13.62			20.02	
	13.59	13.58		20.05	
	13.55				
				2.103 *M* $LiNO_3$ present	
30.00	30.49	30.48	30.00	45.06	44.98
	30.48			44.91	
30.00	30.44		30.00	44.98	45.00
	30.30	30.35		45.03	
	30.32				

With no salt present. $k_{30}/k_{23} = 2.2393$, precision measure $= 0.20\%$.

With 2.10 *M* $LiNO_3$ present $k_{30}/k_{23} = 2.2401$, precision measure $= 0.20\%$.

The precision measure of a single experiment was taken to be 0.20%.

These solutions all contained about 0.1 *M* acetone, 0.1 *N* HNO_3, 0.01 *N* iodine and 0.025 *M* KI.

The result shown in Table II was entirely unexpected because, on the basis of the radiation theory, the great increase in the velocity should be accompanied by a smaller temperature coefficient. Our next step was to investigate whether this behavior was shown by other salts.

Effect of the Neutral Salts of Strong Acids on the Temperature Coefficient

We selected 23° and 25° as the two temperature limits, and measured the temperature coefficient by the method already described[1] which did not involve the measurement of the two velocity constants separately. However, in several cases we measured the velocity constants at the two temperatures and showed that the temperature coefficients, obtained in this manner, checked with those obtained by the shorter method. The neutral salts used were the highest grades that could be purchased, and in all cases were tested for absorption of iodine. Only those specimens that gave a negligible absorption over the period of an experiment were used. Table III contains the ratios obtained for 6 strong acids alone and in presence of various neutral salts.

TABLE III

TEMPERATURE COEFFICIENTS OF THE REACTION, $CH_3COCH_3 + I_2$, WHEN CATALYZED BY VARIOUS STRONG ACIDS ALONE AND IN THE PRESENCE OF NEUTRAL SALTS

Acid used	k_{25}/k_{23}	Acid used	Neutral salt M		k_{25}/k_{23}
HNO_3	1.2650	HNO_3	2.0	NaCl	1.2625
	1.2623	HCl	1.0	NaCl	1.2624
HCl	1.2623	HNO_3	2.0	KNO_3	1.2634
HI	1.2610	HNO_3	1.0	$Mg(NO_3)_2$	1.2624
$HClO_4$	1.2645	$HClO_4$	1.0	$LiClO_4$	1.2610
	1.2610	HNO_3	3.5	NaCl	1.2630
Benzenesulfonic	1.2613	HNO_3	2.1	$LiNO_3$	1.2670
Trichloro-acetic	1.2581	HNO_3	1.81	KNO_3	1.2642
β-Naphthalenesulfonic	1.2594				Mean = 1.2632
	Mean = 1.2617				

The acids were present at a concentration about 0.1 *N*.
0.025 *M* KI was present to keep the iodine in solution.
The precision measure of each experiment is 0.20%.

From Table III we see that the reaction has the same temperature coefficient when catalyzed by strong monobasic acids, and the temperature coefficient is unaffected by the presence of the salts of these acids. In one of our experiments with nitric acid as catalyst we had the solution saturated with sodium chloride and also some of the solid salt present. The temperature coefficient was the same as when no salt was present.

Effect of Moderately Strong Acids and Weak Acids on the Temperature Coefficient, in both the Presence and the Absence of Their Salts

We investigated first the temperature coefficient of the reaction using sulfuric acid alone and in the presence of various concentrations of sodium sulfate. In these cases we measured the velocities of the reactions. The results are given in Table IV.

It will be readily seen from Table IV that the presence of 0.434 *M* sodium sulfate hardly affects the velocity, yet the temperature coefficient is greatly diminished. In another experiment using less sodium sulfate we found that both the velocity and the temperature coefficient were lowered, which is the opposite of the effect predicted by the radiation theory.

In Table V we give the results for the other acids that we investigated. In the cases of the very weak acids the results are probably slightly higher

Table IV

Velocity Constants of the Reaction, $CH_3COCH_3 + I_2$, when Catalyzed by Sulfuric Acid Alone and in the Presence of Sodium Sulfate

Salt present	None	None	0.434 *M* Na_2SO_4	0.434 *M*	0.87 *M*	0.87 *M*
Temp., ° C.	23	25	23	25	23	25
Av.	12.52	15.56	12.98	15.87	15.56	18.93

For H_2SO_4, no salt present. $k_{25}/k_{23} = 1.2430$; hence $Q = 19{,}070$.
0.434 *M* Na_2SO_4 present. $k_{25}/k_{23} = 1.2225$; hence $Q = 17{,}610$.
0.87 *M* Na_2SO_4 present. $k_{25}/k_{23} = 1.2169$; hence $Q = 17{,}010$.

The precision measure of each experiment is 0.20%, so that the precision measure of k_{25}/k_{23} is 0.28% and the precision measure of Q is 1.2%. For strong monobasic acids $Q = 20{,}540$.

Q was calculated from the Arrhenius formula as in the previous paper.[2]

than the true values, because the hydriodic acid liberated in the reaction probably took part in the catalytic action, and this would tend to raise the temperature coefficient slightly.

Table V

Temperature Coefficients of the Reaction, $CH_3COCH_3 + I_2$, when Catalyzed by Moderately Strong Acids and Weak Acids

Acid	Oxalic	Sulfuric	Phosphoric	Acetic
k_{25}/k_{23}	1.2509	1.2435	1.2410	1.2395
Q	19,630	19,110	18,930	18,820

The precision measure of $k_{25}/k_{23} = 0.20\%$, and that of $Q = 0.87\%$.

Effect of Small Quantities of Neutral Salts on the Velocity of Reaction

We investigated the effect of adding small quantities of neutral salts, especially those salts of the higher alkali metals which are not so extensively hydrated as lithium and sodium salts. We first tried the effect of rubidium nitrate on the reaction catalyzed by nitric acid. There was a distinct increase in the velocity. We then determined to try the effect of still smaller concentrations of salt. It must be remembered however, that in all our experiments it was necessary to have present 0.025 *N* potassium iodide in order to keep the iodine in solution. By using hydriodic acid as the catalyst we avoided the necessity of having potassium iodide present since iodine is soluble in aqueous hydriodic acid.

We therefore measured the velocity, with hydriodic acid as catalyst and with no neutral salt whatsoever present, and then measured the velocity again after the addition of small quantities of various neutral salts. We did these experiments in pairs, each pair being performed simultaneously in the same thermostat under similar conditions. The absolute velocities were not measured but the conditions were such that we obtained the relative velocities with a high degree of precision. In no case did we detect any fall in velocity due to the addition of neutral salt. If hydriodic acid was 95% dissociated, the addition of 0.01 *N* neutral salt should diminish the hydrogen-ion concentration about 0.5%, assuming that the simple mass-action law holds. These results, therefore, in conjunction with the temperature-coefficient measurements give some support to the complete dissociation theory for strong acids.

A theoretical discussion of the results obtained in the paper will be given in a succeeding communication.

TABLE VI

EFFECT OF VERY SMALL CONCENTRATIONS OF NEUTRAL SALT ON VELOCITY OF REACTION

Concn. *M*	0.079	0.053	0.01	0.01	0.01	0.01	0.1
Salt	$RbNO_3$	$RbNO_3$	KNO_3	KI	KI	$CsNO_3$	$CsNO_3$
Catalyst	HNO_3	HNO_3	HNO_3[a]	HI	HI	HI	HI
% incr. in *V*	1.9	9.1	2.7	0.16	0.10	0.32	3.0

In the two experiments with $RbNO_3$, 0.025 *M* KI was present to keep the iodine in solution. This was omitted in all the other experiments.

[a] In 30% C_2H_5OH.

Summary

1. We have measured the temperature coefficient of the reaction, $CH_3COCH_3 + I_2 = CH_3COCH_2I + HI$, when catalyzed by various acids alone and in presence of their salts.

2. The temperature coefficient of all strong acids is the same, and is unaffected by the presence of their salts.

3. The reaction has a lower temperature coefficient when catalyzed by weak acids. If the acids are arranged in descending order of their strengths this is also the order of diminishing temperature coefficients.

4. When the reaction is catalyzed by sulfuric acid the presence of one of its salts diminishes the temperature coefficient considerably. This is probably true for all weak acids.

5. Small quantities (about 0.01 *M*) of salts of the alkali metals increase the velocity slightly. There is no indication of any diminution such as we might expect on the basis of the mass-action law.

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