

tion, breaks down to form formaldehyde and methylamine. Chuck was unable to identify formaldehyde or formic acid among the reaction products. He did not look for carbon dioxide.

Benzyl alcohol heated in a similar manner with sodium azide and dilute sulfuric acid was found to yield benzaldehyde, benzoic acid and aniline in liberal quantities. Considerable amounts of a tarry oil, the nature of which remains unknown, were formed at the same time.

A liquid ammonia solution containing methylamine and an excess of ammonium azide was heated in a closed tube at 200° for twelve hours. Nitrogen and guanidine were found among the products of the nitridizing action of ammono nitric acid on this ammono alcohol. The yields, which were abundant, were not determined quantitatively.

Guanidine was obtained by similarly heating liquid ammonia solutions of hexamethylenetetramine with ammonium azide and with sodium azide. A dimer of methylene nitride, which is as near the nitrogen analog of formaldehyde as the

trivalency of nitrogen permits, is nitridized to an ammono carbonic acid.

When heated in liquid ammonia solution with ammonium azide benzylamine is nitridized to a product, either benzamidine or phenyl cyanide, which on hydrolysis yields aquo benzoic acid.

Among the products formed by heating hydrobenzamide with ammonium azide in liquid ammonia solution benzonitrile and lophine were identified. Benzonitrile, which is the anammonide of benzoic acid, is formed by the nitridizing action of ammono nitric acid on the benzaldehyde-acetal. Lophine has long been known as a product of the oxidation of hydrobenzamide.

The action of hydrazoic acid on certain aldehydes and ketones as reported by Schmidt¹⁸ involves the nitridizing action of ammono nitric acid.

Summary

An account is given of experimental work which supports the assumption that hydrazoic acid is an ammono nitric acid.

(18) Schmidt, *Ber.*, **57**, 704 (1924); *Chem. Abst.*, **19**, 3248 (1925).
STANFORD UNIV., CALIF. RECEIVED OCTOBER 18, 1933

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Kinetics of the Decomposition of the Trichloroacetates in Various Solvents¹

BY FRANK H. VERHOEK

The decomposition of trichloroacetic acid is reported in the literature to follow the equation



A marked change in the rate of decomposition with change in concentration indicated that the reaction was not a simple unimolecular decomposition of the acid molecule. The decomposition of salts of the acid had not been studied quantitatively. Extension to several solvents seemed to offer interesting possibilities for studying the effect of solvent on reaction rate. For these reasons the present investigation was undertaken.

Trichloroacetic acid decomposes in water, and in aniline and related solvents^{2a,b} where the trichloroacetate of the amine is formed. On the other hand, trichloroacetic acid does not decom-

pose in relatively non-basic solvents; there is no decomposition in benzene, carbon bisulfide, carbon tetrachloride, ethyl ether, acetone, nitrobenzene, ethyl benzoate,³ in toluene and chloroform.⁴ In methyl⁴ and ethyl^{4,5} alcohols, the only reaction is that of ester formation.

Procedure

Qualitative work in connection with the present investigation showed that the presence of the ion is always necessary for decomposition. A large number of salts of trichloroacetic acid—with aniline, piperidine, pyridine, triethanolamine, ammonia, sodium, barium, copper—were prepared and their behavior studied in various solvents, chiefly at 70°. It was found that the free acid and all the salts decompose in water at practically the same rate, and that the salts decompose, also, in isoamyl alcohol, ethyl acetate, aniline, ethyl alco-

(1) Further details concerning this work may be obtained from a thesis prepared under the direction of Farrington Daniels and submitted by the author to the University of Wisconsin in 1933 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) (a) Silberstein, *Ber.*, **17**, 2864, (1884); (b) Goldschmidt and Brauer, *ibid.*, **29**, 109 (1906).

(3) Timofeev, *Chem. Zentr.*, **11**, 1651 (1925).

(4) Pearce and Nelson, *Proc. Iowa Acad. Sci.*, **26**, 251 (1929).

(5) Lichty, *Am. Chem. J.*, **18**, 597 (1896).

hol, acetic acid and acetone. In every case where the salts dissolved, they decomposed at elevated temperatures.

To the list of solvents in which free trichloroacetic acid does not decompose were added isoamyl alcohol, ethyl acetate, acetic acid and 6 *N* sulfuric acid; it is likely that a negligible quantity of trichloroacetate ions is present in such solutions. It was found that trichloroacetic acid dissolved in acetic acid did not decompose even at the boiling point of the solvent, a temperature at which an inorganic salt in the same solvent reacts rapidly. The non-ionizing ethyl ester of trichloroacetic acid, also, was completely stable in alcohol solution.

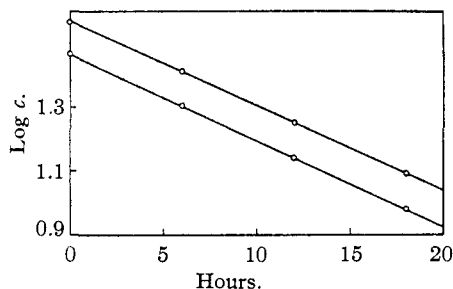


Fig. 1.—The velocity of decomposition of sodium trichloroacetate in water at 70°. (The ordinate scale for the upper curve has been displaced 0.1 unit for convenience in graphing.)

The salts were prepared by neutralizing weighed quantities of trichloroacetic acid, crystallizing, and drying over phosphorus pentoxide in a vacuum desiccator.

The course of the reaction was followed by acid and base titration, and by evolution of carbon dioxide gas. In studying aqueous solutions, the salts were weighed out to give tenth molar solutions. Ten cc. portions were pipetted into 50-cc. Pyrex flasks, which were then loosely covered with tin-foil caps and small inverted beakers. They were immersed in large thermostated oil-baths, sufficient air space remaining under the inverted beaker to prevent oil from seeping into the flasks. After allowing thirty minutes for temperature equilibrium the flasks were removed, at intervals, from the bath and cooled quickly in ice water. The contents were then titrated with standard acid or base, as the particular salt required. The initial concentration was always determined by titrations of two samples left in the bath until the decomposition was complete. The original weight served as a check.

After each titration the solution was analyzed with standard silver nitrate and potassium chromate indicator in order to correct for the formation of hydrochloric acid. This correction varied from 10% at the highest temperature in water to 3% and less at the lower temperature, while in alcohol the correction amounted to less than 1%. By analyses of the gaseous products and the determinations of the ratio of acid to chloride, it was found that the chloride was not due to a competing hydrolysis of the

trichloromethyl group, but to a following reaction—the oxidation of the reaction product, chloroform, to phosgene, followed by hydrolysis of the latter to carbon dioxide and hydrochloric acid. Only the oxidation of chloroform could give the observed reaction products, namely, carbon dioxide and a one to one ratio of acid to chloride. These same oxidation products were obtained also in a solution of chloroform alone, containing no trichloroacetate. The formation of some chloride then offers no complication in the kinetics of the primary reaction—the decomposition of the trichloroacetate.

The gas-evolution apparatus was so constructed that the solution could be shaken in the thermostat and the gas led off to a buret to be collected and measured at atmospheric pressure. It was made entirely of glass to avoid any action of the solvent vapors on rubber tubing. The shaker was of the lever type previously used in this Laboratory,⁶ but the connection to the gas buret was made through a simple arch made by bending a 1.2-meter length of 4-mm. tubing into a smooth curve so that the diameter of the arch was about 40 cm. The reaction flask was held at the bottom of the shaker arm by a glass-blower's clamp, so that it twisted back and forth as the shaker moved. With this construction the flask can vibrate through a large arc without breaking the arch; the original arch is still in use. As soon as the solution had come to the temperature of the bath, a by-pass stopcock at the top of the gas buret was closed, and the time of closing taken as zero time for the reaction. The total gas evolved at the completion of the reaction measured the concentration at the moment of closing the stopcock. The alcohol was saturated with dry carbon dioxide at room temperature before making up the solution.

Decomposition in Water Solution

Sodium Trichloroacetate.—The reaction was followed by titration of the sodium bicarbonate formed with standard sulfuric acid to two-thirds completion at the three higher temperatures. It was found to follow the first order equation as shown by the straight line of Fig. 1 in which $\log c$ is plotted against time. The concentrations c are obtained by subtracting the titrations in cc. of 0.0333 *N* sulfuric acid from the final titrations. The data are shown in Table I, where k represents first order velocity constants calculated from the slopes of lines similar to those of Fig. 1, and E , the energy of activation, is calculated in the usual manner. When exactly the same solution was used at two different temperatures, the corresponding value of E is recorded separately and an average of the E 's is taken. When different stock solutions were used at the different temperatures, E was calculated from the averaged values of the k 's.

Anilinium Trichloroacetate.—The decomposition of anilinium trichloroacetate in water was fol-

(6) Eyring and Daniels, *THIS JOURNAL*, **52**, 1472 (1930).

TABLE I
DECOMPOSITION RATE OF SODIUM TRICHLOROACETATE IN WATER

Temp., °C.	<i>k</i> (sec. ⁻¹)	<i>E</i> (calories)
90	3.23 × 10 ⁻⁴	
	3.18	
	3.07	
	3.11	
80	7.71 × 10 ⁻⁵	
	7.70	<i>E</i> _{90-80°}
	7.70	36,180
	7.42	
70	1.701 × 10 ⁻⁵	<i>E</i> _{80-70°}
	1.725	36,380
	1.713	36,020
		36,200
60	3.53 × 10 ⁻⁶	
	3.48	<i>E</i> _{70-67°}
	3.42	36,180
	3.48	
50	6.18 × 10 ⁻⁷	<i>E</i> _{60-56°}
	6.18	36,940
	6.18	36,570
		36,750

lowed by titrating with 0.033 *N* sodium hydroxide the trichloroacetic acid left undecomposed in the solution. Air was bubbled through the solution for ten minutes before titrating to remove any carbon dioxide. The amount of chloride formed was much smaller than in the basic solutions resulting from the decomposition of sodium trichloroacetate. The results, calculated as before, are summarized in Table II. The points for the experiments at 90° do not lie satisfactorily on a line, a fact which indicates that the experimental

TABLE II
DECOMPOSITION RATE OF ANILINIUM TRICHLOROACETATE IN WATER

Temp., °C.	<i>k</i> (sec. ⁻¹)	<i>E</i> (cal.)
90	3.19 × 10 ⁻⁴	
	3.35	
	3.17	
	3.36	
	3.27	
80	8.06 × 10 ⁻⁵	<i>E</i> _{90-80°}
	8.12	35,420
	8.09	
70	1.770	<i>E</i> _{80-70°}
	1.742	36,870
	1.751	36,950
	1.754	36,910

technique was being pushed to the utmost at this higher temperature.

Barium Trichloroacetate.—Two determinations were made of the velocity of decomposition of barium trichloroacetate in water at 80°. The barium carbonate precipitates during the reaction and the reaction cannot be conveniently followed by titrating the base formed directly. The barium carbonate in each sample was therefore dissolved by adding a known quantity of nitric acid, and the excess acid titrated back with standard sodium hydroxide. The barium was later precipitated with sodium sulfate, and the solution titrated for chloride. The values of the velocity constants obtained were 7.34 and 7.52 × 10⁻⁵ sec.⁻¹.

Decomposition in Ethyl Alcohol

Anilinium Trichloroacetate.—The decomposition of anilinium trichloroacetate in alcohol was followed by measuring the volume, *v*, in cc. of carbon dioxide evolved. The reaction proceeds more rapidly toward the end of the reaction than is

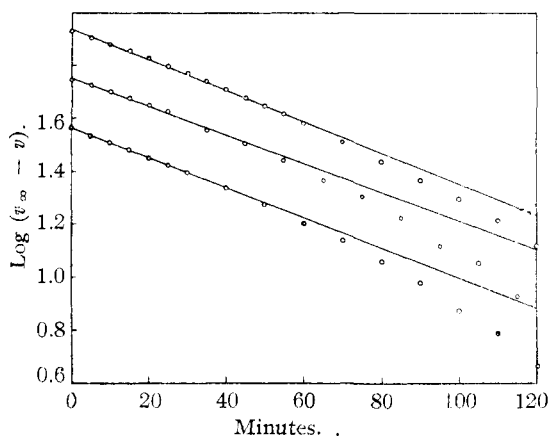


Fig. 2.—The velocity of decomposition of anilinium trichloroacetate in ethyl alcohol at 70°. (The two upper curves have been displaced upward by 0.2 and 0.4 unit, respectively, to avoid confusion of points.)

called for by the first order law. This can be seen in Fig. 2, in which log (*v*_∞ - *v*) is plotted against the time for three experiments with 0.1 *m* solutions. The curves are concave downward from the very beginning, showing that the reaction steadily accelerates. In order to have some standard for graphing, the points of the first two-fifths of the reaction were arbitrarily chosen and the best straight line was drawn through them. The constants calculated from these graphs are shown in Table III.

TABLE III

DECOMPOSITION RATE OF ANILINIUM TRICHLOROACETATE
IN ETHYL ALCOHOL AT 70°

Concn. (moles/liter)	k (sec. ⁻¹) × 10 ⁴
0.1	2.18, 2.06, 2.25, 2.00 ⁷
.05	2.11, 1.88
.033	2.28, 2.26, 2.32
.022	1.82
.125	2.04, 1.85
.0054	1.95

Although the results are somewhat discordant, it seems evident that there is no trend with changing concentration.

TABLE IV

INFLUENCE OF FOREIGN SUBSTANCES ON THE DECOMPOSITION RATE OF ANILINIUM TRICHLOROACETATE IN ETHYL ALCOHOL
AT 70°

Added substance	None	0.2 <i>m</i> aniline	0.73 <i>m</i> piperidine	0.1 <i>m</i> KI	5% H ₂ O
k (sec. ⁻¹) × 10 ⁴	2.12	2.88, 2.66, 2.84	3.98	2.36, 2.35	2.40, 2.43

If one assumes that the decomposition is that of the trichloroacetate ion, the increase in decomposition rate is readily explained by the fact that the ratio of trichloroacetate ion to molecular trichloroacetic acid increases as the reaction proceeds. The total amount of aniline in solution remains constant, while the amount of trichloroacetic acid steadily decreases; the relative excess of aniline over trichloroacetic acid becomes greater and the reaction of salt formation



is pushed farther toward the right. More of the trichloroacetic acid is thus present as ions at the end of the reaction than at the beginning, and the apparent velocity constant, which is calculated on the basis of the sum (trichloroacetic acid + trichloroacetate ion), is in consequence greater.

TABLE V

INFLUENCE OF TEMPERATURE ON THE DECOMPOSITION RATE OF ANILINIUM TRICHLOROACETATE IN ETHYL ALCOHOL

Temperature, °C.	70	60	E_{70-60}	50°	E_{60-50}
$k \times 10^4$ (sec. ⁻¹)	2.12 (av.)	5.33, 5.45	31,080	1.267	30,970 cal.

That the velocity constant does not change with change in initial concentration is due to the fact that at the beginning of the reaction, the aniline and trichloroacetic acid are always present in equimolecular proportions, no matter what the total concentration may be; hence the ratio of molecular trichloroacetic acid to trichloroacetate ion is not greatly changed by a change in initial concentration.

If the shift in the equilibrium (2) is the true explanation of the deviation from the first order law,

(7) By titration method instead of gas evolution.

it should be possible to increase the reaction velocity by adding some substance which would displace the equilibrium. The addition of an excess of aniline or of another base, of an inert electrolyte to increase the ionic strength, or of water to change the acidity and basicity constants, should have this effect. These predictions have been experimentally confirmed. Table IV shows the velocity constants, obtained by the titration method, for the decomposition of 0.1 *m* anilinium trichloroacetate in alcohol at 70° in the presence of foreign substances.

In the presence of the large excess of the strong base piperidine, the decomposition is first order for the full course of the reaction. In the other cases the reactions still deviate from the first order law.

It was also found possible to suppress ionization and decrease the reaction velocity by the addition of an excess of anilinium ion. A portion of the solution was made 0.2 *m* in aniline hydrochloride and the decomposition velocity of the trichloroacetate determined in the presence of this substance. The velocity constant at 60° was 3.89×10^{-5} as compared to 5.45×10^{-5} , indicating that the equilibrium (2) was displaced in the direction of fewer trichloroacetate ions by the excess of anilinium ion.

The decomposition of anilinium trichloroacetate in tenth-molar solution in alcohol at various temperatures is given in Table V.

An unexpected result was obtained when lithium chloride instead of potassium iodide was used as an inert electrolyte to increase the ionic strength. The reaction velocity was decreased rather than increased. A tenth-molar solution of anilinium trichloroacetate in alcohol, and also tenth molar in lithium chloride, gave a velocity constant at 70° of 1.77×10^{-4} sec.⁻¹. Two determinations in the presence of 0.5 *m* lithium chloride gave the still lower constants 1.33 and 1.42×10^{-4} ; with this large excess of lithium chloride the reaction also proved to be first order throughout. It was sup-

posed that a metathesis in the solution might result in the formation of unionized lithium trichloroacetate, reducing the ion concentration and the velocity constant. Reaction rate determinations for the decomposition in alcohol at 70° of lithium trichloroacetate prepared in the same manner as the barium salt, however, gave the first order constant 2.53 and 2.62×10^{-4} sec.⁻¹, practically the same as those for sodium trichloroacetate as shown in the following section.

Sodium Trichloroacetate.—The decomposition of sodium trichloroacetate in alcohol is a good first order reaction throughout the whole course of the reaction. It was studied in tenth-molar solution by the titration method used for the sodium salt in water. As the reaction proceeds, a white, crystalline precipitate, presumably sodium ethyl carbonate, $\text{NaO}(\text{C}_2\text{H}_5\text{O})\text{CO}$, is formed, which dissolves in water to form sodium bicarbonate. The data are summarized in Table VI.

TABLE VI
DECOMPOSITION RATE OF SODIUM TRICHLOROACETATE IN ETHYL ALCOHOL (k sec.⁻¹)

70°	70° +5% H ₂ O	70° +N/10 KI	60°	50°	<i>E</i> _(cal.)
2.48×10^{-4}	3.00×10^{-4}	2.40×10^{-4}	6.04×10^{-5}	1.338×10^{-5}	<i>E</i> _{70-60°}
2.44	3.06		5.82	1.351	31,810
2.31	2.97		5.95	1.354	
—	—	—	—	—	<i>E</i> _{60-50°}
2.41	3.01	2.40	5.94	1.348	31,710

Since the addition of potassium iodide does not affect the decomposition rate of sodium trichloroacetate, it may be concluded that it does not affect the degree of ionization of the latter. The ionization may already be fairly large.

Barium Trichloroacetate.—This substance was chosen as a salt of a valence type different from that of sodium trichloroacetate. It would be expected to be much less dissociated in alcohol than sodium trichloroacetate and its decomposition velocity consequently lower. This was found to be the case. The reaction, however, was not first order; on a graph $\log c$ against time it shows a curvature similar to that for the anilinium salt

shown in Fig. 2. In this case there is no equilibrium corresponding to (2) and the deviation from the first order law must be due to the increase in ionization with increasing dilution. This means that, contrary to the results with anilinium salt, a more dilute solution should decompose more rapidly than a concentrated one; this has been confirmed experimentally. If the ionization of barium trichloroacetate in alcohol is small, a marked increase in the ionization—and, consequently, in the decomposition velocity—should be observed on the addition of an inert electrolyte or of water. This prediction also was verified experimentally. The data are summarized in Table VII.

The Decomposition of Anilinium Trichloroacetate in Aniline.—The decomposition of anilinium trichloroacetate in aniline solution was followed by titration. Air caused the aniline solution to turn red and so the solutions were sealed off in glass tubes in an atmosphere of nitrogen. Two

tubes were titrated at the beginning, two at half completion and two at three-fourths completion. Velocity constants were calculated with the first order equation, k_1 for the first part of the reaction and k_2 for the last part, while k was calculated using all three points. The data are summarized in Table VIII and it is evident that here also the reaction goes relatively faster toward the end, and that the dilute solutions decompose faster.

Although the great excess of aniline might be expected to force equation (2) completely to the right, the dielectric constant may be so low as to permit the existence of some molecular trichloroacetic acid. As the concentration of trichloro-

TABLE VII
DECOMPOSITION RATE ($k_{\text{sec.}^{-1}}$) OF BARIUM TRICHLOROACETATE IN ETHYL ALCOHOL

70° 0.0167 <i>m</i>	70° 0.05 <i>m</i>	70° 0.05 <i>m</i> + 0.1 <i>m</i> KI	70° 0.05 <i>m</i> + 5% H ₂ O	60° 0.05 <i>m</i>	50° 0.05 <i>m</i>	<i>E</i> _(cal.)
3.19×10^{-5}	1.95×10^{-5}	6.95×10^{-5}	8.72×10^{-5}	5.40×10^{-6}	1.20×10^{-6}	<i>E</i> _{70-60°}
3.31	2.04	6.25	9.24	5.37	1.37	30,020
3.22	1.99		8.31			<i>E</i> _{60-50°}
—	2.11	—	8.67	—	—	30,630
3.24	2.02	6.60	8.74	5.38	1.28	

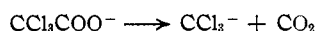
TABLE VIII
THE VELOCITY OF DECOMPOSITION OF ANILINIUM
TRICHLOROACETATE IN ANILINE

Temp., °C.	k_1	k_2	k	$E(\text{cal.})$
Concentration 0.2 <i>m</i>				
25	8.80×10^{-7}	9.16×10^{-7}	8.51×10^{-7}	
	8.84	9.10	8.63	
35	4.03×10^{-6}	4.09×10^{-6}	3.98×10^{-6}	25-35°
	4.00	4.17	3.84	27,700
45	1.64×10^{-5}	1.70×10^{-5}	1.56×10^{-5}	35-45°
	1.62	1.70	1.53	26,800
55	5.77×10^{-6}	6.20×10^{-6}	5.39×10^{-6}	45-55°
	5.79	6.33	5.34	25,780
Concentration 0.5 <i>m</i>				
25	7.54×10^{-7}	7.46×10^{-7}	7.64×10^{-7}	
	7.40	7.44	7.36	
35	3.31×10^{-6}	3.38×10^{-6}	3.22×10^{-6}	25-35°
	3.31	3.34	3.26	26,730
45 ^a	1.29×10^{-6}	1.38×10^{-6}	1.34×10^{-6}	35-45°
			1.36	27,750
55	4.91×10^{-6}	5.09×10^{-6}	4.71×10^{-6}	45-55°
	4.93	5.20	4.63	25,760

acetic acid is decreased, either initially or during the course of the reaction, the dissociation into trichloroacetate ions should increase. This suggestion accounts in part at least for the changes in decomposition rate noted in the table.

Discussion

As the mechanism for the decomposition, the reaction



is proposed. CCl_3^- is the anion of the *acid*, chloroform; as a very strong base it would immediately attach to itself a proton (from the solvent or the cation of the amine base) and form chloroform. In support of this hypothesis may be mentioned the decomposition of 2,4,6-trinitrobenzoic acid, which also splits off carbon dioxide. In this case the other product of the reaction, *s*-trinitrobenzene, is known to be acidic.⁹

That the reacting substance is the trichloroacetate ion is supported by the data for the decomposition in 95% alcohol. The decomposition velocity is less in water than in alcohol, and at first glance one would expect a water-alcohol mixture to give a velocity constant intermediate between those of the pure solvents. Actually, however, the velocity in 95% alcohol is for each salt greater even than that in pure alcohol. The addition of water to the alcohol probably increases the num-

(8) The values of k at 45° are taken from graphs of $\log c$ against time.

(9) Hegge, *Proc. Soc. Exptl. Biol. Med.*, **23**, 235 (1925).

ber of trichloroacetate ions without changing the chemical nature of the medium sufficiently to make them appreciably more stable than in pure alcohol.

Kappanna's constants¹⁰ for the decomposition rate of trichloroacetic acid in water increase with dilution but they are slightly less than the constants for the salts recorded here; 10% less when extrapolated to infinite dilution. However, the extrapolation may be uncertain, and corrections for chloride were not made.

The difference in the decomposition velocities in the various solvents may be explained by assuming that the ion is solvated in each solvent, and that the ions solvated by different substances and to a different extent show different degrees of stability. Thus we would expect the ion to be highly hydrated in water, not greatly alcoholated in alcohol, and still less solvated in aniline. If solvation exerts a stabilizing influence on the ion, in the same manner as, but to a less degree than, the addition of a proton to form the undissociated and completely stable trichloroacetic acid, the difference in reaction velocity is immediately accounted for. The more completely unsolvated the ion, the more rapidly would it decompose.

The hypothesis of solvation as the factor determining the stability of the ion is in agreement with the data on the temperature coefficients. Assuming that the solvation of the trichloroacetate ion is an exothermic reaction, "desolvation" must then be endothermic. When an ion decomposes it must also be desolvated, and enough heat must be added to take care of this endothermic reaction. This should appear in the energy of activation. A comparison of the values of E in water (36,045 cal.), alcohol (31,250 cal.) and aniline (26,760 cal.), shows that the decomposition of the stable, highly solvated ion in water has a higher energy of activation than the less solvated ion in alcohol, for which the energy of activation is in turn greater than for the slightly solvated ion in aniline.

The author wishes to express his gratitude for the helpful advice of Professor Farrington Daniels, under whose direction the work was carried out.

Summary

1. The velocity of decomposition of anilinium trichloroacetate has been determined in water, ethyl alcohol and aniline, and that of sodium and barium trichloroacetates has been determined in

(10) Kappanna, *Z. physik. Chem.*, **158**, 355 (1932).

water and alcohol. The velocities increase in the orders given.

2. The decompositions in water, and the decomposition of the sodium salt in alcohol, follow the first order law, but the decompositions of the anilinium salt in aniline and alcohol, and of the barium salt in alcohol, show an increase in the specific reaction rate as the decomposition proceeds. These departures have been explained on the basis of changes in the degree of ionization.

3. The reaction velocity has been shown to be dependent upon the concentration of the trichloroacetate ion. It is suggested that the reaction is a

unimolecular decomposition of the trichloroacetate ion.

4. Temperature coefficients for the decomposition in the several solvents support the hypothesis that the stability of the ion is determined by the extent of solvation and the nature of the solvating substance.

5. The formation of chloride ion in solutions of trichloroacetates in water and alcohol has been shown to be the result of an oxidation of the chloroform which results from the decomposition of the trichloroacetates.

MADISON, WIS.

RECEIVED OCTOBER 18, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WORCESTER POLYTECHNIC INSTITUTE]

The Potentiometric Determination of Arsenates¹

BY W. E. HANSON, S. B. SWEETSER AND H. B. FELDMAN

During the titration of acid arsenates with silver nitrate, the nitric acid formed in the reaction prevents the potentiometric determination of the arsenate since it reacts with the insoluble silver arsenate.

Bedford, Lamb and Spicer,² using as buffers sodium bicarbonate, ammonium acid succinate and sodium phenolphthalate found that no end-points could be secured. By means of a secondary titration with sodium hydroxide during which the acid formed in the reaction was destroyed, they were able to carry out the potentiometric titration successfully. In addition to requiring the use of two burets, the above method of conducting the titration is exceedingly tedious since the acid formed after each small addition of silver nitrate must be neutralized by addition of base.

In the following work, it was found that under the proper conditions the potentiometric determination of arsenates could be accomplished by using sodium acetate as a buffer.

Apparatus and Materials.—The cell used in this work was composed of a saturated calomel electrode connected to the solution being titrated by a bridge containing agar saturated with potassium nitrate. In this solution was immersed a silver electrode. The voltage of this cell was determined using a Leeds and Northrup student potentiometer.

(1) The material presented in this paper is partly from the theses submitted by W. E. Hanson in 1932 and S. B. Sweetser in 1933 in partial fulfillment of the requirements for the degree of Bachelor of Science.

(2) Bedford, Lamb and Spicer, *THIS JOURNAL*, **52**, 583 (1930).

All solutions used in this work were made from recrystallized c. p. salts and were standardized by standard volumetric and gravimetric procedures.

Experimental

The fact that Bedford, Lamb and Spicer³ found in every case that more base was necessary for the titration than the amount theoretically necessary to neutralize the acid formed in the reaction suggested the addition of a large excess of free base before the titration with silver nitrate, thus eliminating the secondary titration. Accordingly, a series of experiments were carried out in which 1.5 to 3 times the theoretical amounts of sodium hydroxide necessary to neutralize the acid formed in the reaction were added to solutions of 25 cc. of 0.1004 *N* Na₂HAsO₄ which had been diluted to 225 cc. and these alkaline solutions were titrated with 0.1008 *N* silver nitrate. In every case it was found that the experimentally determined equivalence points indicated an amount of silver nitrate greater than that theoretically required, the deviation between the experimentally determined and theoretical equivalence points being about 2% when 1.5 times and about 4% when 3 times the theoretical amounts of base were used. The nature of these deviations indicated co-precipitation of silver oxide with the silver arsenate.

In order to avoid this precipitation of silver oxide and at the same time keep the hydrogen-ion concentration of the solution low enough to prevent the solution of the silver arsenate, it was decided to use sodium acetate as a buffer. A series of titrations was made in which the amount of acetate present corresponded to 2, 10, 50 and 100 times the amount necessary to react with the nitric acid formed in the reaction. The solutions containing 10, 50 and 100 times the theoretical amounts of acetate showed characteristic titration curves but the rate of change of voltage with addition of silver nitrate in the vicinity of the equivalence

(3) Ref. 2, p. 587.