ratio C_2H_6/CO was too much lower than for the case of "continuum" light only.

It should be pointed out that most of the drop in C_2H_6/CO ratio with increasing intensity occurs at intensities not attainable with filtered light. It is possible that the same effect would take place with "continuum" light of sufficiently high intensity.

The general conclusion from the present study is that there is no evidence which definitely indicates that the decomposition by light of 3130 Å. is anything but a free radical reaction, just as for shorter wave lengths. In the "continuum" region, either of the two mechanisms is satisfactory as far as its ability to explain the known facts is concerned. The scheme of Spence and Wild is more cumbersome in that it requires an additional step which can also be objected to on theoretical grounds. One test which might have decided between the two free radical mechanisms, the variation of the yield of CO with pressure at high intensity, was inconclusive because of the polychromatic nature of the light. The generally higher C_2H_6/CO ratios as a result of decreasing the reaction cell size, while not very pronounced, favor the use of a wall process for biacetyl formation as opposed to the supposition of pressure dependence for the decomposition of acetyl radical. One of those alternatives is sufficient to explain the general pressure effects.

Summary

1. The quantum yield of acetone decomposition falls off with increasing intensity at 3130 Å. just as it does around 2500 Å.

2. With all other conditions and techniques held constant, a decrease in the reaction cell size causes a rise in the C_2H_6/CO ratio regardless of the choice of intensity, pressure, and wave length.

3. The reported increase in the C_2H_6/CO ratio with increasing pressure at high intensity was not confirmed. The reverse effect resulted for all intensities.

4. Our previously modified mechanism is found to be adequate for correlation of the definitely established facts. Particularly, the use of reactions of excited acetone molecules at 3130 Å. seems unnecessary.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

The Ionization Constants of Very Weak Acids. Acetoxime, Methyl Ethyl and Diethyl Ketoximes

BY CECIL V. KING AND ALEXANDER P. MARION

Difficulty has always been encountered in determining the ionization constants of very weak acids or bases. The conductance method fails when ionization is so small that conductance of water and its normal impurities become comparatively large, and the interpretation of conductivity in buffered solutions is uncertain. Hydrogen or other electrode measurements are useful in special cases, but usually only with very careful planning and interpretation. Rate measurements in which hydrogen or hydroxyl ion concentrations are determined from their catalytic effect on a suitable reaction have been often used. This method is capable of considerable refinement, and while not as accurate in general as other methods for the ordinary weak electrolytes, may be the best available for exceedingly weak ones. In the past salt effects have generally been ignored or inadequately treated. The purpose of the present work was to develop a method for determining acid dissociation constants of the order of 10^{-12} to 10^{-13} as a function of ionic strength with a reasonable degree of precision.

The Method.—A solution of acetoxime, unless in exceptionally pure water, would have an indefinite hydrogen ion concentration because the ionization is so small. A reaction sufficiently sensitive to hydrogen ion to be used in buffered solutions would probably be sensitive to general acid catalysis. The best procedure in such a case is to add the weak acid to a solution of strong base, and measure the extent of neutralization by means of a reaction only moderately sensitive to hydroxyl ion. From the rates the "hydrolysis constant" of the salt may be calculated.

For this purpose the catalyzed decomposition of nitrosotriacetonamine was chosen. The reaction has been studied in some detail by Francis and his co-workers,[1] by Brönsted and King[2] and by Kilpatrick.[3] The hydroxyl ion determination was first standardized by using solutions of sodium hydroxide, with sodium chloride to make up the ionic strengths desired. The previous work indicates that anions of even exceedingly weak acids do not catalyze the reaction, and the present work confirms this. The assumption is also made that in the specific salt effect, differences due to chloride, hydroxyl and weak acid anions are negligible.

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[1] Francis, *et al.*, *J. Chem. Soc.*, **101**, 2358 (1912); **103**, 1722 (1913); **107**, 1651 (1915).

[2] Brönsted and King, THIS JOURNAL, **47**, 2523 (1925).

[3] Kilpatrick, *ibid.*, **48**, 2091 (1926).

Experimental

Eastman Kodak nitrosotriacetonamine, acetoxime and methyl ethyl ketoxime were used without further treatment (samples of the oximes redistilled before use gave no appreciable difference in rate). Diethyl ketoxime was prepared from diethyl ketone and hydroxylamine as described by Scholl.(4) The product was distilled under reduced pressure several times and finally the portion boiling at 75° at 15 mm. was retained. Various samples prepared in this way gave good agreement.

Fresh stock solutions of the oximes were prepared frequently by direct weighing into a volumetric flask, followed by addition of carbon dioxide-free water. Carbonate-free sodium hydroxide, kept in paraffin-lined bottles, was used throughout. Reagent grade sodium chloride was used and either weighed directly for experiments or made into stock solutions.

The rates were measured in an apparatus similar to that previously described.[3] In each experiment 60 cc. of solution was used, with 66 mg. of nitrosotriacetonamine (0.006 *M*). The thermostat was maintained at 24.9°. The first order rate constants were mostly evaluated as described by Guggenheim,(5) either graphically or by the least squares method.

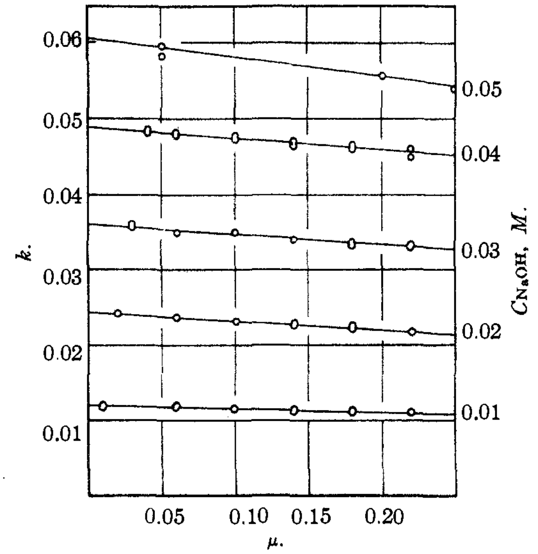

Fig. 1.—Salt effect (NaCl) in the catalytic decomposition of nitrosotriacetonamine.

The rate constants obtained in the standardization (*i. e.*, in solutions of sodium hydroxide and sodium chloride alone, $kt = 2.3 \log C_0/C$) are shown graphically in Fig. 1. The salt effect in this type of reaction is small and linear with ionic strength, and the straight lines represent the least square equations calculated from the experimental points

$$0.01\ M\ \text{NaOH} \quad k = 0.0120 - 0.0049\mu$$
$$.02\ M\ \text{NaOH} \quad k = .0243 - .0118\mu$$
$$.03\ M\ \text{NaOH} \quad k = .0360 - .0137\mu$$
$$.04\ M\ \text{NaOH} \quad k = .0488 - .0152\mu$$

The greatest deviation from these equations shown by any one experiment was 1.4%. Averaging the coefficients (divided by sodium hydroxide concentration) the general equation is obtained

$$k = (1.209 - 0.479\mu)C_{OH^-} \qquad (1)$$

which represents the rate satisfactorily in any solution used. The maximum deviation from the proceeding equations is 3% with 0.02 and 0.04 *M* sodium hydroxide at 0.22 ionic strength. In other solutions the divergence is 1% or less.

In Fig. 1 the straight line for 0.05 *M* sodium hydroxide represents equation (1) for this concentration, the circles a few check experiments made at a later date. In all succeeding work, equation (1) was used to calculate the hydroxyl ion concentration in any experiment.

The neutralization of a very weak acid by a strong base may be represented by the equation

$$HA + OH^- \rightleftarrows H_2O + A^-$$

The amount of hydroxyl ion which disappears may be taken as a measure of the amount of anion formed, and the unneutralized acid remaining can be found by difference. The "hydrolysis constant" of the salt (or its reciprocal) can then be calculated

$$1/K_h = K_{HA}/K_w = C_{A^-}/C_{OH^-}C_{HA} \qquad (2)$$

and if the water constant is known the dissociation constant K_{HA} follows. If K_{HA} is determined at various ionic strengths, suitable extrapolation will give K^0_{HA}, the true thermodynamic dissociation constant.

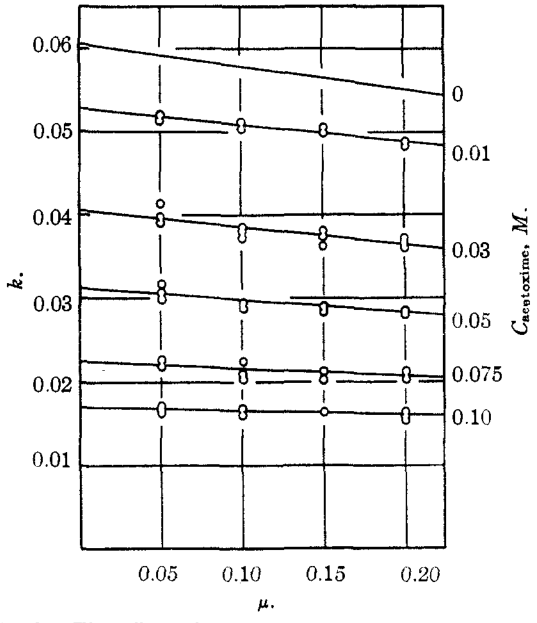

Fig. 2.—The effect of acetoxime and sodium chloride on the rate in 0.05 *M* sodium hydroxide.

The rate constants obtained for 0.05 *M* sodium hydroxide with various acetoxime concentrations are shown in Fig. 2. If dissociation constants are calculated from individual rate constants, the values vary widely—differences of 2% in rate constants lead to differences of approximately 20% in dissociation constants. In order to analyze the hundreds of experimental values obtained, each series was first plotted as in Fig. 2

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(4) Scholl, *Ber.*, **21**, 509 (1888).

(5) Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

and since the salt effect is, within experimental error, linear, what seemed to be the best straight line was drawn through the points. A few values falling 3% or more from these lines were discarded and a linear equation was calculated, by the method of least squares, for each concentration. Later all results with 0.01 M oxime were discarded, since the small degree of neutralization leads to large errors in K_{HA}.

All the least square equations retained are given in Table I. From these values and equation (1), hydroxyl ion concentrations were calculated for ionic strengths 0, 0.05, 0.10, 0.15 and 0.20 (the first being, of course, a hypothetical value); and K_{HA}/K_w calculated from equation (2). The complete set of values for acetoxime and average values for the other oximes are given in Table II.

TABLE I

SALT EFFECT ON THE DECOMPOSITION OF NITROSOTRIACETONAMINE IN SODIUM HYDROXIDE–OXIME SOLUTIONS AT 24.9°

C_{NaOH}	C_{oxime}	k
	Acetoxime	
0.01	0.03	$0.00604 - 0.00358\ \mu$
	.05	$.00444 - .00231\ \mu$
	.075	$.00331 - .00150\ \mu$
	.10	$.00270 - .00227\ \mu$
.03	.03	$.0215 - .00848\ \mu$
	.05	$.0164 - .00791\ \mu$
	.075	$.0118 - .00562\ \mu$
	.10	$.00900 - .00355\ \mu$
.05	.03	$.0402 - .0184\ \mu$
	.05	$.0315 - .0172\ \mu$
	.075	$.0228 - .0121\ \mu$
	.10	$.0169 - .00320\ \mu$
	Methyl Ethyl Ketoxime	
.01	.03	$.00538 - .00045\ \mu$
	.05	$.00455 - .00158\ \mu$
	.075	$.00347 - .00474\ \mu$
.03	.03	$.0219 - .0102\ \mu$
	.05	$.0169 - .00644\ \mu$
	.075	$.0121 - .00328\ \mu$
	.10	$.01055 - .00729\ \mu$
.05	.03	$.0414 - .0230\ \mu$
	.05	$.0327 - .0173\ \mu$
	.075	$.0246 - .0141\ \mu$
	.10	$.0199 - .0127\ \mu$
	Diethyl Ketoxime	
.01	.03	$.00685 - .00409\ \mu$
.03	.03	$.0234 - .0100\ \mu$
	.05	$.0195 - .0106\ \mu$
	.075	$.0143 - .00596\ \mu$
	.10	$.0130 - .0147\ \mu$
.05	.03	$.0430 - .0212\ \mu$
	.05	$.0359 - .0215\ \mu$
	.075	$.0281 - .00600\ \mu$

Although both K_{HA} and K_w vary exponentially with ionic strength, the ratio of the two shows only a small linear variation as is to be expected for weak electrolytes of the same valence type. Least square equations for average values of the ratio, valid at least to $\mu = 0.22$, are given in Table II.

TABLE II

THE RATIO K_{HA}/K_w FOR ACETOXIME AT VARIOUS IONIC STRENGTHS

C_{NaOH}	C_{oxime}	K_{HA}/K_w 0	0.05	0.10	0.15	0.20
0.05	0.03	38.3	38.7	39.4	40.2	40.9
	.05	35.6	35.6	37.2	38.1	39.1
	.075	37.7	38.0	38.6	39.1	39.7
	.10	40.5	39.5	38.9	38.1	37.4
0.03	.03	38.5	38.2	38.3	38.2	38.1
	.05	36.3	36.3	36.8	37.1	37.5
	.075	38.3	38.2	38.7	38.9	39.2
	.10	39.4	39.1	39.2	39.1	39.1
0.01	.03	40.3	40.9	41.9	42.9	44.0
	.05	39.7	39.8	40.3	40.7	41.2
	.075	39.4	39.3	39.5	39.6	39.8
	.10	38.0	38.8	40.2	41.4	42.9
Average, acetoxime		38.5	38.5	39.1	39.5	39.9
	$K_{HA} = K_w\,(38.3 + 7.6\ \mu)$					
Methyl ethyl		35.6	35.7	36.4	37.0	37.7
	$K_{HA} = K_w\,(35.4 + 11.0\ \mu)$					
Diethyl		25.4	25.9	26.5	27.0	27.7
	$K_{HA} = K_w\,(25.4 + 11.4\ \mu)$					

Rather than express K_{HA} as a semi-empirical function of ionic strength it seems more useful to calculate values of K_w from the data of Harned and Mannweiler[6] for sodium chloride solutions and tabulate corresponding values of K_{HA}. This is done in Table III. Although the values of K_w are given in terms of molalities ($m_H m_{OH}$) the deviation from molarities is very small up to 0.22 ionic strength.

TABLE III

IONIZATION CONSTANTS OF THE THREE KETOXIMES AS A FUNCTION OF IONIC STRENGTH AT 24.9°

μ	$K_w \times 10^{14}$	$K_{HA} \times 10^{13}$ Acetoxime	Methyl ethyl ketoxime	Diethyl ketoxime
0	1.00	3.83	3.54	2.54
0.01	1.22	4.68	4.33	3.11
.05	1.48	5.72	5.32	3.84
.10	1.63	6.37	5.95	4.33
.15	1.73	6.82	6.41	4.69
.20	1.80	7.17	6.77	4.98

No previous determinations of the ionization constants of methyl ethyl or diethyl ketoximes or of the "hydrolysis constants" of their salts were found in the literature. For acetoxime the value 6.0×10^{-13} at 25° has been cited by Scudder[7] based on the measurements by Lundén[8] of the

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[6] Harned and Mannweiler, THIS JOURNAL, **57**, 1873 (1935).

[7] Scudder, "Conductivity and Ionization Constants of Organic Compounds," D. Van Nostrand Co., New York, N. Y., 1914.

[8] Lundén, *Z. physik. Chem.*, **54**, 532 (1906).

rate of hydrolysis of ethyl acetate in solutions of barium hydroxide partially neutralized by the oxime. This agrees with our value at $\mu \sim 0.075$ but is based on $K_w = 1 \times 10^{-14}$ which is correct only at $\mu = 0$.

Summary

The rate of decomposition of nitrosotriacetonamine, catalyzed by hydroxyl ion, has been measured as a function of ionic strength at 24.9°, up to $C_{\text{OH}^-} = 0.05$ and $\mu = 0.22$ and may be expressed in the equation

$$k = (1.209 - 0.479\ \mu)\ C_{\text{OH}^-}$$

Using this catalytic reaction to measure hydroxyl ion concentration in solutions of sodium hydroxide partially neutralized by acetoxime, methyl ethyl and diethyl ketoximes, the acid dissociation constants of these oximes have been determined as a function of ionic strength.

WASHINGTON SQUARE COLLEGE
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Ternary System Silver Bromate–Sodium Bromate–Water

BY JOHN E. RICCI AND JACK J. ALESHNICK*

Introduction.—The formation of a compound or of a solid solution of silver bromate and sodium bromate from aqueous solutions of the salts came to be suspected from certain difficulties encountered in attempts to determine bromate ion in the presence of sodium ion, using silver nitrate as precipitant. Estimated gravimetrically the precipitate was always too light. Volumetric determination of the excess of silver ion in the filtrate by the Volhard method revealed the same error, in that too much silver ion was found unprecipitated. These analytical errors appeared regularly and despite care in the original precipitation of the bromate ion with silver nitrate.

The equilibrium relations at room temperature in the ternary system consisting of silver bromate, sodium bromate and water were therefore investigated. The isotherm at 25° shows the formation of a 1:1 double salt capable of forming continuous solid solutions with silver bromate. The salts actually form two solid solutions: sodium bromate containing up to about 3% of silver bromate, and silver bromate containing up to 39.0%, a limit corresponding to the compound $AgBrO_3 \cdot NaBrO_3$.

The consequent contamination (which is of an equilibrium nature and therefore unavoidable) of silver bromate with sodium bromate whenever the silver salt is precipitated from solution containing sodium ion, and especially in the presence also of excess of bromate ion, not only explains the above-mentioned analytical difficulties in the attempted determination of bromate by precipitation as silver bromate, but also accounts, presumably, for the difficulty experienced in the preparation of pure silver bromate.[1-4] This difficulty is obvious from the great variation in the values of the aqueous solubility of the salt reported in the literature. In fact, even the C. P. grade of silver bromate used in the present experiments was found to contain about 1.8% of sodium bromate.

Such behavior on the part of silver bromate appears important not only in connection with possible applications of silver bromate in analytical procedures, but also because of its frequent use in experimental tests of theoretical principles involving solutions of electrolytes.[1-7]

Experimental Procedure

The solubility measurements were made by methods already described for similar determinations. The ternary complexes were made up by weight, using distilled water, C. P. sodium bromate and C. P. silver bromate. The sodium bromate was found to be of satisfactory purity (100.0 ± 0.1%) by iodometric titration using standard thiosulfate. The silver bromate was analyzed in several ways: (1) after reduction with sodium nitrite in the presence of nitric acid and of a small excess of sodium bromide, the precipitate of silver bromide was weighed and was found to correspond to 98.4% silver bromate. (2) After reduction with sulfur dioxide in the presence of nitric and hydrochloric acids, thus precipitating all the silver as silver bromide and chloride, the filtrate was evaporated, finally with sulfuric acid, and weighed, after recrystallization, as sodium sulfate; the sodium was evident in this residue, from ordinary flame tests. The result showed about 1.8% sodium bromate. (3) After reduction with sodium nitrite in the presence of nitric acid and of a small excess of silver nitrate, the precipitate of silver bromide was weighed, and, on the assumption that the original sample consisted of silver and sodium bromates, a purity of 98.0% silver bromate was calculated. These analyses were all done in duplicate and with blank corrections for reagents and apparatus. A value of 98.2% silver bromate and 1.8% sodium bromate was therefore assumed in calculating the compositions of ternary complexes prepared from the C. P. silver bromate.

It must be pointed out that these quantitative analyses of the silver bromate, with consequent correction of the compositions of the synthetic ternary complexes, were performed after a preliminary study of the ternary isotherm had indicated first of all the extensive formation of solid solution between the two salts, and, second, from certain consistent deviations of the tie-lines from the stoichiometric composition of the 1:1 compound, the probability of the presence of a definite amount of sodium bromate in the supposedly C. P. silver bromate.

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(1) Hill, THIS JOURNAL, **39**, 220 (1917).

(2) Reedy, *ibid.*, **43**, 1443 (1921).

(3) Dalton, Pomeroy and Weymouth, *ibid.*, **46**, 61 (1924).

(4) Vosburgh and McClure, *ibid.*, **66**, 1062 (1943).

(5) Noyes, *Z. physik. Chem.*, **6**, 246 (1890).

(6) Owen, THIS JOURNAL, **55**, 1922 (1933).

(7) Neuman, *ibid.*, **56**, 28 (1934).