[Contribution from the U. S. Naval Ordnance Test Station]

A Kinetic Study of the Reaction between Nitromethane and Hydroxide Ion to Form Methazonate Ion

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The reaction between nitromethane and hydroxide ion in water solution proceeds *via* formation of *aci*-nitromethane, followed by formation of methazonate ion. Kinetic data presented in this paper support the mechanism $CH_3NO_2 + OH^- \rightleftarrows CH_2NO_2^- + H_2O$, $2CH_2NO_2^- \rightarrow C_2H_3N_2O_3^- + OH^-$. The value of ΔH_1 for the first reaction is −7.3 kcal.; the activation energy for the second is 15.8 kcal.

Introduction

Although it has been known for many years that an alkaline solution of nitromethane in water spontaneously forms methazonate salts, the mechanism of the reaction has not been satisfactorily elucidated. Hantzsch and Voigt[1] observed the slow development of an absorption band with maximum at 298 mμ when a water solution of nitromethane was made alkaline. This behavior was attributed without additional evidence to formation of methazonate ion.

If the Hantzsch suggestion is correct, it seems reasonable to suppose that formation of methazonate ion proceeds *via*

$$CH_3NO_2 + OH^- \rightleftarrows CH_2NO_2^- + H_2O \quad (A)$$

$$2CH_2NO_2^- \longrightarrow C_2H_3N_2O_3^- + OH^- \quad (B)$$

Since equilibrium A is reasonably well understood,[2] the proposed mechanism of methazonate ion formation may be tested by the very severe restrictions imposed by variation of the concentrations of nitromethane, hydroxide ion, ionic strength and of temperature. In this research the effect of variation of each of these parameters was studied. The kinetic data so obtained are consistent with the Hantzsch mechanism.

The effect of dielectric strength also was tested, but the complexities in this system do not permit any simple interpretation.

Experimental

1. Preparation of Materials.—Eastman Kodak Co. nitromethane was purified by first saturating the liquid with anhydrous gaseous ammonia at room temperature. A white precipitate formed which was removed by filtration; the excess ammonia was removed by distillation from sodium carbonate at reduced pressure. The resulting material was purified by fractionation.[2]

Standard sodium hydroxide solutions were prepared free of CO_2 and stored in polyethylene containers. The sodium hydroxide used in the preparation of these solutions gave a test for carbonate of less than 0.1% according to a standard procedure.[3]

Preparation of the sodium salt of the *aci* form of nitromethane has been described by Victor Meyer[4] and by Zelinsky.[5] When this preparation was attempted, a mixture of two compounds was observed. One of the products is the true *aci* salt, and the other is sodium methazonate.

The preparation of ammonium methazonate was considerably improved over the original method outlined by Dunstan and Goulding.[6] About 10 ml. of concentrated NH_4OH was added to 30 ml. of chilled, purified nitromethane and anhydrous ammonia was continuously passed through the mixture immersed in a bath at −8°. A very light straw-colored product crystallized out; it was filtered from the solution and washed with absolute ether. This material was then dried in a vacuum desiccator and stored at 5°. The compound gave a combustion analysis corresponding to the ammonium salt of methazonic acid. Accurate melting point determinations could not be made because of the decomposition of the compound during melting; the melting point is ≌ 128°. This material was used to determine the extinction coefficient of the methazonate ion at 298 mμ.

Upon acidifying a solution of ammonium methazonate, the strong absorption at 298 mμ disappeared, but reappeared when the solution was made alkaline. Thus the absorption at 298 mμ is attributable to the methazonate ion. According to Meister[7] the formula for methazonate ion is $O_2NCH_2CH{:}NO^-$.

Hydrazine methazonate was prepared by allowing a heterogeneous mixture of anhydrous hydrazine and nitromethane to stand in contact about 24 hours. A slow reaction occurred with very slight gas evolution. The color of the solution deepened to a dark red. At the end of about 24 hours the resultant homogeneous solution was poured into absolute ethanol and allowed to stand overnight at −5°. The pale yellow elongated crystals produced were separated and washed with ether and vacuum dried. This compound gave a combustion analysis corresponding to the hydrazine salt of methazonic acid. Again, an accurate melting point could not be obtained because of decomposition, but it appears to be in the range 96–102°. This material would ignite and burn rapidly without explosion, and was insensitive to hammer blows. Its absorption spectrum was identical to that of the other methazonate salts.

If the preparation of ammonium methazonate were attempted at temperatures below −10°, a white crystalline product formed very rapidly in the solution upon passage of ammonia into the nitromethane. This compound was quite unstable at room temperature, decomposing spontaneously with evolution of ammonia and leaving a liquid residue which appeared to be nitromethane. The compound would not ignite or explode with a hammer blow. It is assumed to be the ammonium salt of *aci*-nitromethane.

2. Absorption Characteristics of Basic Nitromethane Solutions.—Aqueous solutions of nitromethane are almost transparent in the region 280–400 mμ. Since the 298 mμ peak develops very slowly after the nitromethane has been converted to the *aci* ion by addition to NaOH, the methazonate ion must be responsible for this absorption. This was verified by spectral data on three methazonate compounds prepared and identified by chemical analysis. All these compounds exhibited only one very pronounced absorption peak in the ultraviolet region with maximum at 298 mμ.

It was subsequently found that absorption of methazonate ion at 298 mμ obeys Beer's law if the solutions are of *p*H 10.5 or higher. Extent of absorption depends on *p*H of the solution at lower *p*H. If such solutions were made quite acid, they immediately became quite transparent at 298 mμ, and if made basic again without delay, substantially all the absorption was re-established as soon as the solutions were completely mixed. If the solution remained acid for some time before being made alkaline again, the original absorption peak at 298 mμ was diminished. This result is probably caused by hydrolytic decomposition of methazonic acid.

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[1] A. Hantzsch and K. Voigt, *Ber.*, **45**, 85 (1912); *cf.* G. Kortüm, *Z. physik. Chem.*, **B43**, 271 (1939), who repeated the experiment.

[2] D. Turnbull and S. H. Maron, This Journal, **65**, 212 (1943).

[3] W. D. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 489.

[4] Victor Meyer, *Ber.*, **27**, 1601 (1894).

[5] N. Zelinsky, *ibid.*, **27**, 3406 (1894).

[6] W. R. Dunstan and E. Goulding, *J. Chem. Soc. Trans.*, **77**, 1262 (1900).

[7] W. Meister, *Ber.*, **40**, 3435 (1907).

The *p*H of the solution controls the absorption according to

$$\mathrm{HM} \rightleftarrows \mathrm{M}^- + \mathrm{H}^+;\ K_1 = \frac{[\mathrm{M}^-][\mathrm{H}^+]}{[\mathrm{HM}]} \qquad (1)$$

where M represents the methazonate radical. Figure 1 illustrates the quantitative effect of *p*H upon the maximum absorption of sodium methazonate at 298 mμ. It can be seen from this curve that the solutions must have a *p*H >10.5 for full establishment of the 298 mμ absorption peak.

3. **Extinction Coefficient of Ammonium Methazonate.**—Pure ammonium methazonate was dissolved in dilute NaOH solution of *p*H 11–11.5; the absorption at 298 mμ was measured in the temperature range 0–45°. No measurable temperature effect on the absorption was observed. The value of ϵ, the extinction coefficient in the expression $D = \log I_0/I = \epsilon cl$, was found to be 17,840 liters mole^{-1} cm.$^{-1}$. When a basic solution of nitromethane was allowed to react completely, the observed resultant peak height was a little more than 95% of that expected on the basis of this value.

4. **Preparation of Reaction Mixtures.**—Reaction mixtures were prepared by two techniques. The first method was adopted to study the effect on the over-all rate of nitromethane concentration at constant hydroxide ion concentration. The second method was designed to study the effect of hydroxide ion concentration at constant nitromethane concentration.

4.1 **Method 1.**—Approximately 100 ml. of standard aqueous solutions of purified nitromethane were transferred into a flask immersed in a constant temperature bath. When the temperature arrived within one degree of the bath temperature, the *p*H electrodes were immediately standardized against a temperature-calibrated reference buffer held in a similar flask at bath temperature, and then the electrodes were quickly transferred to the test solution. The test sample was then adjusted to the desired *p*H level by titrating a standard solution of sodium hydroxide into it while stirring with a stream of nitrogen gas. The nitrogen was first saturated with water at bath temperature in order to avoid changes in the concentration of the solution by evaporation. The addition did not change the temperature of the mixture by more than 1–2°. When the desired *p*H was attained, the electrodes were again checked against the reference buffer. If the buffer readings prior and subsequent to the *p*H measurement agreed within 0.02 *p*H unit, a 4-ml. sample of the reaction mixture was quickly transferred with a Pyrex vacuum jacketed pipet to a quartz absorption cell in the spectrophotometer cell compartment at the temperature of the reaction mixture. During the course of the absorption measurements, the *p*H of the remaining test liquid was again verified.

4.2 **Method 2.**—It was rather difficult to arrive at exactly the *p*H desired because the pseudo acid behavior of nitromethane resulted in rather slow neutralization. After it was clearly demonstrated by method 1 that the reaction with respect to the nitromethane concentration was always second order, it was necessary to vary only the OH ion concentration to establish its order. In experiments in which nitromethane concentration varied (usually the value was nearly 0.008 *M*), corrections for small concentration variations were made by applying the previously determined second-order law.

After brief mixing a sample could be quickly transferred to the spectrophotometer, and the exact *p*H value of the remaining test solution could then be measured at leisure. This procedure allowed rapid preparation of samples having high reaction rates and introduction to the spectrophotometer in sufficiently short time to permit significant rate measurements starting near zero time. In view of the stoichiometry of reactions 1 and 2, it was surprising to find that the *p*H of the mixtures remained constant to within 0.05 *p*H unit during the measurements, which in some cases required as long as four hours. In fact, very little change in *p*H occurred in typical mixtures over a period of seventy-two hours, perhaps because the system of weak acids (nitromethane, *aci*-nitromethane, methazonic acid) and sodium hydroxide acts as a buffer solution.

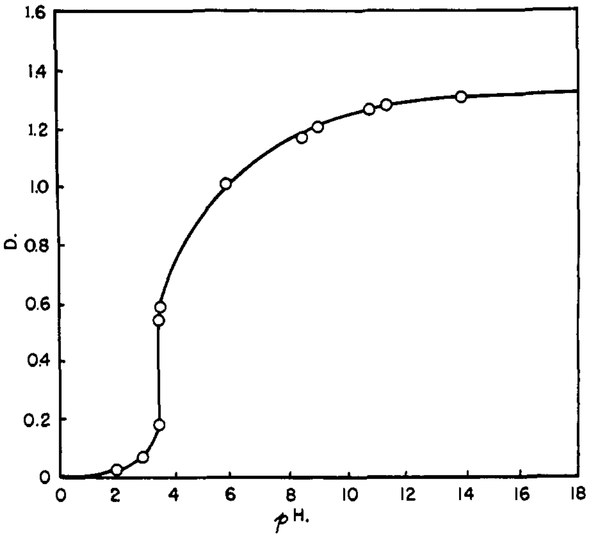


Fig. 1.—Effect of *p*H on the light absorption of 8 × 10^{-5} molar aqueous solution of sodium methazonate at 298 mμ.

5. **Rate Measurements.**—Initial rate determinations were made by measuring absorption at 298 mμ with a Beckman Model DU spectrophotometer. The instrument had its cell compartment surrounded by aluminum blocks constructed so that the temperature of the absorption cells could be controlled by circulating fluid through the blocks from a thermostated bath. It was desirable that the cell compartment be maintained at the bath temperature ±0.2°. For such adjustment at temperatures above 25° it was necessary to offset the heat losses in the circulating system by passing the bath fluid through a manually variable heat reservoir prior to its entry into the instrument. For studies at 0° a refrigerated fluid was used and a separate ice-bath for preparing the mixtures prior to introduction into the spectrophotometer.

The *p*H of the reaction mixture was measured with a Beckman Research Model G *p*H meter, with external type electrodes. The calomel reference electrode was a Beckman type 1170, while the glass electrode was a Beckman Type E 1190-75. All measurements were referred to Beckman *p*H 10 buffer, assuming temperature calibration of the buffer supplied by Beckman to be correct. For readings at temperatures 0, 35 and 45° the method described by Beckman Bulletin 95-B was utilized.

Concentrations and times were so adjusted that in no case did the reaction in the measured range proceed beyond 1% of the total expected sodium methazonate formation. The observed initial rates were expressed in increase in absorption (optical density relative to water) per minute, and these rates were constant over the time observed. The effect of the ionic strength on the reaction rate was not large enough to justify any correction except in the cases where sodium chloride was added to the reaction mixtures.

6. **Primary Salt Effect.**—The ionic strength of the reaction mixtures was changed in some studies by direct addition of weighed amounts of C.P. sodium chloride to the reaction mixtures prior to the final addition of sodium hydroxide.

Results and Discussion

1. **Kinetics.**—Rate of formation of methazonate ion was determined from rate of increase in the height of its absorption peak.

Although the value ϵ 17,830 is somewhat uncertain because the purity of the ammonium methazonate is uncertain, it is nevertheless true that *D*, the optical density, is proportional to the concentration of methazonate ion. The rates summarized in Table I are expressed as *D*/min.

By use of the technique outlined in 4.1, the order with respect to nitromethane was determined at 3 *p*H values over the temperature range 0–45°. Typical data (for 25°) are presented in Table II. The constancy of $k = (\mathrm{d}D/\mathrm{d}t)/N_0^2$, where N_0 represents the initial concentration of nitromethane at a given *p*H, shows that the reaction is second order in nitromethane over the range studied.

Table I

Summary of Experimental Results[a]

Temp., °C.	pH	$1/\left(\frac{dD}{dt}\right)^{1/2}$	$1/[OH^-]$	$-\log (dD/dt)$
0.0	10.84	46.90	1,431	
.0	11.07	37.42	848	
.0	12.49	23.34	32	
25.6	10.00	25.17	10,000	
25.6	10.00	25.52	10,000	2.81
25.6	10.00	25.13	10,000	
25.6	11.00	8.944	1,000	
25.6	11.00	8.449	1,000	1.86
25.6	11.00	8.452	1,000	
25.6	11.65	7.003	224	
25.6	11.65	7.538	224	1.72
25.6	12.00	7.071	100	
25.6	12.00	6.572	100	1.67
25.6	12.00	7.156	100	
25.6	12.50	6.419	32	1.60
25.6	12.50	6.201	32	
35.0	9.81	19.01	7,828	
35.0	9.97	14.62	5,404	
35.0	10.06	11.69	4,389	
35.0	10.29	9.02	2,591	
35.0	10.62	7.790	1,212	
35.0	10.77	6.24	859	
35.0	11.32	4.972	241	
45.0	10.00	6.833	2,500	1.67
45.0	10.00	6.947	2,500	1.68
45.0	11.00	3.658	250	1.13
45.0	11.00	3.732	250	1.14
45.0	11.96	2.840	27.5	0.91
45.0	11.96	2.849	27.5	0.91
45.0	12.53	2.510	7.38	0.80
45.0	12.53	2.622	7.38	0.84

[a] The square roots of the reciprocal rates given in the third column are calculated for a single value of nitromethane concentration = 0.008 M. The actual values of nitromethane concentration employed (range 0.0002–0.05 M) were determined by the requirements of OH^- concentration and temperature and were fixed for convenience of rate measurement.

Table II

Kinetics with Respect to Nitromethane at 25°

pH	$N_0 \times 10^3$	(dD/dt)	k
10.00	19.19	0.0087	23.7
10.00	31.13	.0223	23.0
10.00	8.92	.0019	23.8
11.00	8.64	*.0160*	220
11.00	18.06	.0700	215
12.00	7.96	.0197	311
12.00	13.91	.0698	361
12.00	4.42	.0059	304

If the reaction is simply Nth order in OH^- ion, log dD/dt *vs.* pH should be linear with slope N. That this is not the case is evident from an inspection of Table I. The order in OH^- varies over the whole range of pH studied approaching zero at high values of pH and 2 at low pH. This suggests a relation of the form

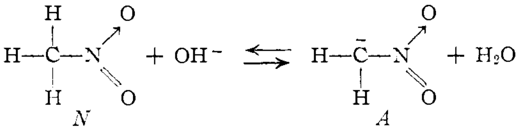
$$\frac{d[M]}{dt} = k\frac{X^2[OH^-]^2}{(Y + Z[OH^-])^2} \qquad (2)$$

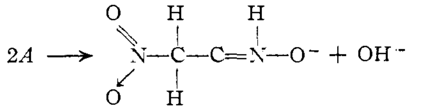
where Y is of the same order of magnitude as $Z[OH^-]$ in the middle pH range, d[M]/dt is the observed rate of formation of methazonate ion, X is the concentration of nitromethane, and k is a constant.

In setting up a mechanism to produce an expression of the form shown in (2), it soon became apparent that the rate-determining step must involve two negative ions. This postulate was tested by studying the effect of ionic strength of the solution on the reaction rate. The results of this study, which are reported in the last section of this paper, show that the rate-determining step involves two singly charged species of like sign.

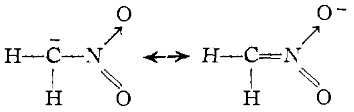
Since the *aci*-nitromethane is formed in basic solutions of nitromethane, it seems reasonable that the reaction of two *aci*-nitromethane ions is the slow step.

The reaction to form methazonate ion from nitromethane may be written


(a)


(b)

Two points should be mentioned: (1) it does not seem possible at this time to state in detail how the resonating *aci*-nitromethane ions



form the methazonate ion.

2. If a hydrogen atom in nitromethane is replaced by an alkyl or aryl group, the analogous reaction to form methazonate ion does not occur. Since it is difficult to conceive that all three hydrogen atoms on the methyl group are involved in the mechanism, steric hindrance may be involved.

Using the modified Hantzsch–Voigt[1] mechanism (a), (b), the following kinetic equations may be expected. Equilibrium a is rapid compared to the rate of reaction b and, since the water concentration is relatively high, we write

$$K_1 = \frac{A}{N[OH]} \qquad (3)$$

where A represents the total concentration of the resonating *aci* ions and N is the concentration of nitromethane. It follows that

$$\frac{dD}{dt} = \frac{60\epsilon k_2 K_1{}^2 N_0{}^2[OH^-]^2}{(1 + K_1[OH^-])^2} \text{ moles l.}^{-} \text{ min.}^{-1} \qquad (4)$$

Equation 4 is of the required form, as shown in equation 2. Since K_1 is approximately[2] 10^3 and $[OH^-]$ varies in the range $10^{-1.5}$–10^{-4}, the order in $[OH^-]$ varies from nearly zero to two as shown in Table II.

Inverting equation 4 and taking square roots

$$\frac{1}{(dD/dt)^{1/2}} = \frac{1}{(60\epsilon)^{1/2}k_2{}^{1/2}K_1N_0[OH^-]} + \frac{1}{(60\epsilon)^{1/2}k_2{}^{1/2}N_0} \qquad (5)$$

For each temperature, values for $1/(dD/dt)^{1/2}$

taken from Table I are plotted as a function of $1/[OH^-]$; K_1 is the intercept (at $1/[OH^-] = 0$) divided by the slope, and k_2 is evaluated from the intercept.

The data in Table I have been so plotted using the method of least squares to establish the slope and intercept at each of the temperatures 0, 25.6, 35 and 45°. From (5)

$$k_2' = 60k_2 = \frac{1}{(N_0)^2\,(\text{Intercept})^2\epsilon}\ \text{moles}^{-1}\ \text{l. min.}^{-1} \qquad (6)$$

An Arrhenius plot of k'_2 values so obtained (see Fig. 2) gives

$$\log k_2 = 8.04 - \frac{15{,}800}{2.303RT} \qquad (7)$$

where the dimensions of k_2 are moles^{-1} l. sec.$^{-1}$. The term $10^{8.04}$ is the pre-exponential factor in the Arrhenius equation and the activation energy E_2 = 15.8 kcal.

2. **Energetics.**—Since the relation between K_1 and T was found to be

$$\log K_1 = \frac{-\Delta H_1}{4.576}(1000/T) - 1.82$$

the values of ΔH_1 were calculated and tabulated in the last column of Table III. It is evident that ΔH_1 = −7.3 kcal./mole. Turnbull and Maron[2] made a study of the equilibrium constant K_N, for the reaction

$$CH_3NO_2 \rightleftharpoons CH_2NO_2^- + H^+ \qquad (C)$$

$$K_N = A[H^+]/N \qquad (8)$$

Thus

$$\frac{K_N}{K_W} = \frac{A}{N[OH^-]} = K_1 \qquad (9)$$

where

$$K_W = [H^+][OH^-]$$

Table III compares the values of K_N calculated from K_1 values of this paper with those from the data of Turnbull and Maron, who used a different method. The latter are somewhat higher than the values reported in this work.

TABLE III

VALUE OF CONSTANTS CALCULATED FROM RATE DATA

Temp., °C.	$k_2'\epsilon$	K_1	$K_N = K_1K_W$	K_N[a] (lit.)	$-\Delta H_1$
0.0	29.80	11,607	1.4×10^{-11}	2.3×10^{-11}	7.34
25.6	333.01	3,675	3.7×10^{-11}	6.2×10^{-11}	7.37
35.0	716.41	2,584	5.1×10^{-11}	8.9×10^{-11}	7.37
45.0	1937.1	1,705	6.8×10^{-11}	12.4×10^{-11}	7.35

[a] Interpolated or extrapolated from the data of Turnbull and Maron.[2]

From (9) it is evident that

$$\Delta H_N = \Delta H_W + \Delta H_1 \qquad (10)$$

It has been shown that ΔH_1 is −7.3 kcal. The accepted value for ΔH_W = +13.780 kcal.[8] Thus

$$\Delta H_N = 6.4\ \text{kcal.}$$

in good agreement with the value reported by Turnbull and Maron.

3. **The Entropy Factor.**—The absence of an accurate value for the extinction coefficient, ϵ, of the methazonate ion, has little effect upon the entropy of activation if ϵ is known within 50%.

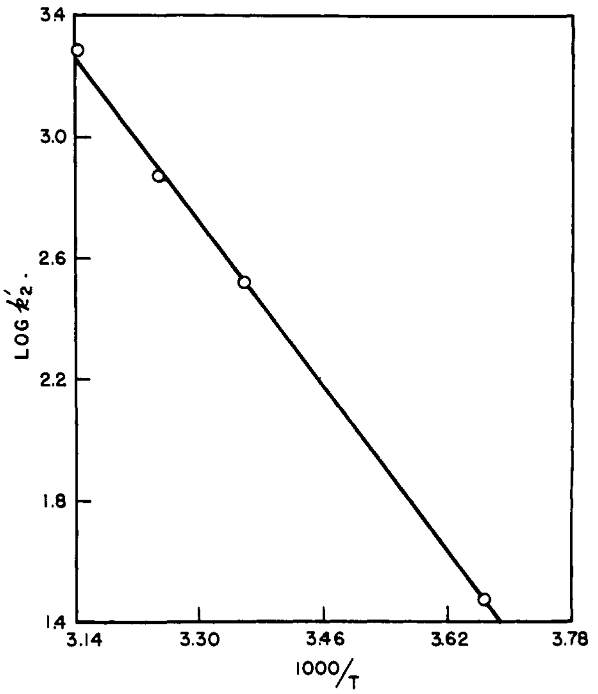


Fig. 2.—Arrhenius plot for reaction B.

For this reason it is instructive to calculate $\Delta S^\ddagger$ for reaction 2. Following Eyring[9]

$$\Delta S^\ddagger = -23.7\ \text{e.u.}$$

An entropy of activation of this magnitude is in harmony with the postulated reaction 2 in which two negative ions must react in order to produce methazonate ion.[10] The result may also be expressed as

$$k_2 = \mathbf{A}e^{-E_2/RT}$$

where **A** is the "pre-exponential factor." In the present case

$$k_2 = 10^{8.04}\, e^{-15{,}800/RT}\ \text{l. mole}^{-1}\ \text{sec.}^{-1}$$

4. **Primary Salt Effect.**—For a given solvent at constant temperature, the rate constant k_2 is given by the Brönsted[11] relationship, which is valid for dilute solutions

$$\log k_2 = \log k_2^0 + AZ_1Z_2\sqrt{\mu}$$

where k_2^0 is the rate constant extrapolated to zero ionic strength, μ is the ionic strength, and Z_1 and Z_2 are the charges on the reacting species (1) and (2). At 25° the constant A is 1.02 for water solutions. Hence, a plot of log k_2 *vs.* $\sqrt{\mu}$ at 25° for dilute solutions of nitromethane and hydroxide ion should be linear, with a slope of 1.02.

TABLE IV

EFFECT OF CHANGING IONIC STRENGTH

pH	$N_0 \times 10^3$, moles/l.	NaCl $\times 10^2$, moles/l.	NaOH $\times 10^3$, moles/l.	$\frac{dD}{dT} \times 10^2$	$\frac{d \log k_2}{d\sqrt{\mu}}$
11.00	8.33	0.0	6.4	8.56	+0.6
11.00	8.33	4.43	6.4	10.50	

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(8) "International Critical Tables," Vol. 7, McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p. 232.

(9) *Cf.* S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," First Ed., McGraw-Hill Book Co., Inc., New York and London, 1941, p. 199.

(10) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 134.

(11) V. K. La Mer, *Chem. Revs.*, **10**, 179 (1932).

The nitromethane–sodium hydroxide solutions were made up at various ionic strengths with NaCl as indicated in paragraph 6, and the rate constants measured. Table IV gives the results. The slope is about 0.6 positive. A positive slope can result only if two ions of like charge are involved. The charge on the ions must be integral and, in this case, it must be concluded that two negative ions of unit charge are involved. As pointed out by La Mer,[11] in many other cases the deviations from the Brönsted equation are only as to magnitude, without effect on the sign of the slope. The data show that two negatively charged ions react to form methazonate ion and that each ion probably carries a unit charge.

Acknowledgment.—The authors wish to express their indebtedness to Professor Milton Burton for discussions of the results.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Photolysis of Ammonia in the Presence of Propane and Oxygen[1]

BY H. GESSER[2]

RECEIVED AUGUST 5, 1954

The photolysis of ammonia in systems with propane and oxygen both individually and combined was studied. Hydrogen atoms and NH_2 radicals from the primary dissociation of ammonia abstract hydrogen from propane at high propane pressures, high temperatures and at low intensity. The products, H_2, N_2, C_3H_6, isoproylamine, 2,3-dimethylbutane, do not give a material balance because of polymer and C_9 formation. Oxygen cleans up the primary hydrogen atoms and reacts with NH_2 radicals by a proposed reaction sequence to produce nitrogen. The three component system is complicated by the formation of acetone which subsequently competes with ammonia for part of the incident light. The photolysis of ammonia in a static system at −80° shows that hydrazine is probably not a product. Reactions are proposed to account for the experimental results.

Introduction

The mechanism whereby ammonia decomposes photochemically, though the subject of many thorough investigations,[3] is not completely understood. The most recent studies[4] have not entirely eliminated doubt concerning the step by which nitrogen is formed.

It was hoped that by the addition of foreign gases (other than hydrazine) it would be possible to clarify certain steps in the mechanism and perhaps obtain information about reactions of the NH_2 radical. The systems chosen were ammonia and propane, ammonia and oxygen, and ammonia, oxygen and propane.

Experimental

The apparatus was of the conventional type used in this Laboratory and was constructed free of stopcocks (except for some preliminary work with ammonia and propane). The analytical units consisted of a furnace containing copper and copper oxide and maintained at 210° for the analysis of mixtures of hydrogen and nitrogen, and of oxygen and nitrogen; a copper oxide furnace of quartz maintained at 700° for the combustion of the isopropylamine and ammonia fraction; a platinum wire unit for the analysis of hydrogen in the presence of nitrogen and excess oxygen; a hydrogenator with a P_2O_5 absorber to remove the last traces of ammonia from the propane and propylene fraction prior to analysis of propylene in the hydrogenator.

It was difficult to separate isopropylamine[5] quantitatively from ammonia. A combustion method was developed to determine isopropylamine in the presence of ammonia. The propane fraction was distilled from the ammonia fraction at −150° by means of a Le Roy still.[6] The ammonia and isopropylamine were then distilled from the remaining C_6 fraction at −110° and oxidized in the copper oxide furnace at 700°. The nitrogen produced was pumped off through a trap immersed in liquid nitrogen. The water formed was used as a carrier by means of which the gases were cycled through the furnace several times. It was found necessary to heat the U-traps on either side of the furnace to prevent formation of any stable compound between the ammonia, carbon dioxide and water. The carbon dioxide was separated from the water, measured and corrected for the blank from the impurity in ammonia.

Ammonia was prepared by mixing J. T. Baker C.P. ammonium chloride and Merck Reagent Grade sodium hydroxide pellets and warming. The gas was dried by passage through a column of potassium hydroxide pellets, repeatedly degassed at −140°, and distilled into the storage bulb from −110°. The gas prepared in this manner proved to be of high purity and upon combustion was shown to contain 0.04% carbon.

Propane was Phillips Research Grade certified as 99.99% pure and was fractionated by bulb to bulb distillation. The middle third was retained and was shown within the limits of analysis to be free of unsaturated and higher hydrocarbons.

Oxygen was prepared by heating Merck Reagent Grade potassium permanganate and dried by passage through a trap immersed in liquid nitrogen. Analysis showed it to contain 0.03% nitrogen.

The light source was a Hanovia S-100 Alpine Burner. The beam was collimated by one quartz lens and a stop and passed over a droplet of mercury in a tube to reduce the photosensitized reaction. Negligible amounts of hydrogen were produced when propane alone was illuminated in this manner. The mercury lines observed below 2200 Å. were those at 1942, 1974 and 1995 Å. The ammonia bands lying closest to these lines are at 1974 and 1940 Å.[7] The de-

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[3] For review see (a) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941; (b) P. A. Leighton, "Exposés de Photochimie," Hermann et Cie, Paris, 1938.

[4] (a) C. E. Herrick, Jr., Ph.D. Thesis, University of Rochester (1943); (b) M. Vanpée, *Bull. soc. chim. Belg.*, **53**, 179 (1944); (c) C. C. McDonald, A. Kahn and H. E. Gunning, *J. Chem. Phys.*, **27**, 908 (1954).

[5] Isopropylamine and 2,3-dimethylbutane were identified by means of mass spectrographic analysis as products in the ammonia–propane system. Acetone was similarly identified in the ammonia–oxygen–propane system. Unpublished work done in this Laboratory by Dr. L. S. Forster.

[6] D. J. Le Roy, *Can. J. Res.*, **B29**, 492 (1950).

[7] A. B. F. Duncan, *Phys. Rev.*, **47**, 822 (1935).