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Chlorine Transfer from Chloramine to Amines in Aqueous Medium. 1. Reaction between Chloramine and Methylamine

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The kinetics and the equilibrium constant for the chlorine-transfer reaction from chloramine to monomethylamine are determined in aqueous solution. The reaction is investigated by spectrophotometry in NH_3/NH_4Cl and $NaOH/NaHCO_3$ buffer solutions from pH 8 to 13. The reaction is first order in total amine and chloramine. At 25 °C, under the considered experimental conditions, the rate constant is shown to depend on the nature and concentration of the buffer. For a 1 M NH_3/NH_4Cl buffer solution, the rate constant increases from pH 8.5 up to an approximate pH value close to 10; then, it decreases and becomes practically constant at pH > 12.8. Such a behavior is interpreted in terms of buffer-assisted reactions. These results are complementary to the observations of previous authors. The enthalpy and entropy of activation are calculated from kinetic results obtained between 8 and 42 °C in the two pH ranges for which k is practically pH and buffer independent.

Introduction

The preparation of hydrazine, N_2H_4, and substituted hydrazines, $RR'NNH_2$, by the Raschig process was investigated by several authors.[1-13] A kinetic model was derived for alkaline medium (pH > 11)[9,10,13] with three reactions taken into account: formation of hydrazines by reacting chloramine, NH_2Cl, with amines RR'NH; spontaneous decomposition of chloramine; oxidation of hydrazines by chloramine. The side reactions lead to secondary products and decrease the yield in hydrazine.

At the same time, Snyder and Margerum[14,15] and, later, Isaac and Morris[16,17] observed, between pH 4 and 10, a reversible transfer reaction for chlorine between chloramine and amines:

$$RR'NH + NH_2Cl \rightleftarrows RR'NCl + NH_3$$

We investigated this reaction in more alkaline medium (8 < pH < 13) in order to check if it must be taken into account in the kinetic model and also to get a better understanding of chloramine reactivity in aqueous solutions.

The reaction between methylamine and chloramine is the subject of this paper.

Experimental Section

Reagents. Methylamine and ammonia solutions were prepared by diluting pure reagent-grade products from Merck.

Sodium hydroxide, ammonium chloride, and sodium bicarbonate used for this study were Merck or Carlo Erba reagent-grade products.

Sodium hypochlorite required to prepare chloramine and methylchloramine was obtained by sparging pure chlorine gas into a 1 M sodium hydroxide solution until the pH reached 12.5.

In order to determine their molar absorptivities in the ultraviolet range, chloramine and methylchloramine were prepared by reacting sodium hypochlorite and aqueous ammonia or methylamine in the presence of diethyl ether as previously described.[18] For kinetic measurements, chloramine was prepared in situ.

Apparatus. The apparatus consisted of a 400-cm^3 thermostated spherical reactor fitted with adaptors for temperature and pH measurements and with inlet or outlet tubes for sampling or addition of reagent, for nitrogen bubbling, and for circulation toward the measurement cell of a spectrophotometer. In order to prevent any oxidation of solutions, a PTFE pump and piping were used.[19] The temperature in the reactor was defined at ±0.1 °C.

Procedure. A 250-cm^3 amount of a determined ammonium chloride solution and 40 cm^3 of a calculated sodium hydroxide solution or, depending on the experiments, 250 cm^3 of a determined ammonia solution and 40 cm^3 of a calculated $NaOH/NaHCO_3$ solution were poured into the reactor.

The concentrations of the NaOH and $NaOH/NaHCO_3$ solutions were calculated to obtain a buffered medium at the desired pH.

The thermal equilibrium being reached, chloramine was then prepared in situ by addition of 5 cm^3 of a standardized hypochlorite solution. The initial ratio of reactants $([NH_3]_0 + [NH_4^+]_0)/[ClO^-]_0$ was located between 5 for the more alkaline media and 200 when the pH was near 7. Under such conditions, the formation of chloramine was instantaneous and quantitative and the obtained chloramine did not undergo any spontaneous decomposition in the studied pH range.[19]

Finally, 5 cm^3 of a titrated methylamine solution was poured quickly into the reactor and the ultraviolet spectrum of the mixture was recorded between 300 and 200 nm at equal periods of time.

Quartz cells with a 1.00 cm path length and a Kontron Uvikon 860 double-beam spectrophotometer were used for absorbance measurements. In order to protect mixtures from oxidation, experiments were performed with a nitrogen cover.

A glass electrode (Tacussel TB/HS model) and a KCl saturated calomel reference electrode were used for pH measurements after suitable standardization. The pH was defined within 0.05 pH unit.

Analysis of Mixtures. The concentrations of chloramine and methylchloramine were determined from the measured absorbance A of the mixture at 244 and 252 nm by solving the simultaneous equations

$$A^{244} = 458.0[NH_2Cl] + 337.0[CH_3NHCl]$$

$$A^{252} = 408.5[NH_2Cl] + 372.0[CH_3NHCl]$$

The molar absorptivities at the maximum absorption wavelengths, 458.0 M^{-1} cm^{-1} at 244 nm for NH_2Cl and 372.0 M^{-1} cm^{-1} at 252 nm for CH_3NHCl, are given in the literature.[19,20] The others, 408.5 M^{-1} cm^{-1} at 252 nm for NH_2Cl and 337.0 M^{-1} cm^{-1} at 244 nm for CH_3NHCl, were calculated from the ultraviolet spectra of solutions obtained by diluting a stock solution (iodometrically standardized in acetic acid medium).

Results

When NH_2Cl is added to a methylamine solution, simultaneous reactions can be observed in accord with the equations

$$CH_3NH_2 + NH_2Cl + OH^- \rightarrow CH_3NHNH_2 + Cl^- + H_2O \quad (1)$$

$$CH_3NH_2 + NH_2Cl \rightleftarrows CH_3NHCl + NH_3 \quad (2)$$

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Table I. Equilibrium Constant at 25 °C for the Chlorine-Transfer Reaction between NH_2Cl and CH_3NH_2

pH	I, M	$[NH_3]_T$, M	$10^3[CH_3NH_2]_T$, M	$10^3[NH_2Cl]_0$, M	10^3a, M	10^3b, s^{-1}	K
8.27	0.50 ± 0.03	0.499	30.0	1.11	0.633	6.05	22 ± 3
8.55	0.51 ± 0.03	0.498	30.0	1.52	0.897	5.84	24 ± 4
9.27	1.05 ± 0.05	1.010	30.0	0.64	0.298	8.13	29 ± 4
9.28	0.79 ± 0.04	0.742	30.0	1.51	0.833	6.66	30 ± 5
9.29	0.53 ± 0.03	0.494	30.0	1.53	1.022	5.59	34 ± 5
9.85	1.05 ± 0.05	1.000	30.0	1.52	0.940	6.41	54 ± 8
10.12	0.98 ± 0.05	0.998	30.0	1.46	1.062	6.14	90 ± 13
10.29	1.05 ± 0.05	1.960	30.0	3.01	1.842	8.46	103 ± 15

We investigated the kinetics of methylchloramine formation from pH 8 to 13 and determined the equilibrium constant at 25 °C by direct measurement of actual concentrations of NH_2Cl and CH_3NHCl. The rate constant was obtained from the slope of the curves giving the concentration of CH_3NHCl vs time at zero time. Consequently, the results are valid even if NH_2Cl is involved in other reactions such as the formation or degradation of CH_3NHNH_2.

Reaction 2 was found to be first order with respect to each reactant as previously noticed by Snyder and Margerum[14,15] and Isaac and Morris.[16,17]

Equilibrium Constant. The equilibrium (2) can be observed if ammonia is present in large excess and if pH < 10.5.[14,15]

The apparent constant K was determined at 25 °C with concentrations of total ammonia between 0.5 and 2 M and concentrations of chloramine between 0.5×10^{-3} and 3×10^{-3} M. The concentration of methylamine was 30×10^{-3} M.

Under such experimental conditions, we verified that the mass balance

$$[NH_2Cl]_0 = [NH_2Cl] + [CH_3NHCl] \qquad (3)$$

was recovered within 5% of experimental error all along the concerned experiments, indicating that the NH_2Cl/CH_3NHNH_2 reaction and the formation of hydrazines from reaction 1 and from the CH_3NHCl/CH_3NH_2 and CH_3NHCl or NH_2Cl/NH_3 reactions were negligible.

Since ammonia and methylamine are present in large excess compared with chloramine, their concentrations can be considered constant during each run and equal to $[NH_3]_T$ and $[CH_3NH_2]_T$. Then

$$\frac{d[CH_3NHCl]}{dt} = k[CH_3NH_2]_T[NH_2Cl] - k'[NH_3]_T[CH_3NHCl]$$

where k and k' are the rate constants for the direct and reverse reactions.

According to (3)

$$\frac{d[CH_3NHCl]}{dt} = k[CH_3NH_2]_T[NH_2Cl]_0 - (k'[NH_3]_T + k[CH_3NH_2]_T)[CH_3NHCl]$$

After integration

$$[CH_3NHCl] = a(1 - \exp(-bt)) \qquad (4)$$

with

$$a = \frac{k[CH_3NH_2]_T[NH_2Cl]_0}{k'[NH_3]_T + k[CH_3NH_2]_T}$$

$$b = k'[NH_3]_T + k[CH_3NH_2]_T$$

a and b were determined by fitting the experimental concentration vs time data to relation 4 by the least-squares method, and the apparent equilibrium constant K was calculated according to

$$K = \frac{k}{k'} = \frac{[CH_3NHCl]_e[NH_3]_T}{[NH_2Cl]_e[CH_3NH_2]_T}$$

The results are presented in Table I. K is slightly dependent on ionic strength as shown by the values obtained at pH 9.28 for $0.50 \le I \le 1.05$ M (I calculated as $I = 0.5\sum C_i z_i^2$). Then, although the ionic strength was not kept constant from one experiment to another, the results are consistent.

The apparent constant K depends on pH. When the pH is low enough, the limit of K is K_{TR} corresponding to the equilibrium

$$CH_3NH_3^+ + NH_2Cl \rightleftarrows CH_3NHCl + NH_4^+$$

with

$$K_{TR} = \frac{[CH_3NHCl]_e[NH_4^+]_0}{[NH_2Cl]_e[CH_3NH_3^+]_0}$$

as $CH_3NH_3^+$ and NH_4^+ are present in large excess.

if $K^0_{NH_4^+}$ and $K^0_{CH_3NH_3^+}$ are the acidity constants of NH_4^+ and $CH_3NH_3^+$ at zero ionic strength, if f_i is the activity coefficient of the species i, and if a_i is its activity ($a_i = f_i[i]$), we can write

$$[CH_3NH_3^+] = \frac{a_{H^+}[CH_3NH_2]_T}{a_{H^+} + \frac{f_{CH_3NH_3^+}}{f_{CH_3NH_2}}K^0_{CH_3NH_3^+}}$$

$$[NH_4^+] = \frac{a_{H^+}[NH_3]_T}{a_{H^+} + \frac{f_{NH_4^+}}{f_{NH_3}}K^0_{NH_4^+}}$$

Then

$$K = K_{TR}\frac{a_{H^+} + \frac{f_{NH_4^+}}{f_{NH_3}}K^0_{NH_4^+}}{a_{H^+} + \frac{f_{CH_3NH_3^+}}{f_{CH_3NH_2}}K^0_{CH_3NH_3^+}}$$

The fitted curve by the least-squares method according to the previous relation for the experimental data is shown in Figure 1.

The fit gives

$$K_{TR} = 23 \pm 3$$

The value obtained for $K^0_{NH_4^+}f_{NH_4^+}/f_{NH_3}$, 1.91×10^{-10} M, is a fitted one and should be considered as a "mean" taking in account changes in ionic strength from 0.50 to 1.05 M and in medium composition (ionic environment) with pH, which affects the activity coefficients for such ionic strengths. It is consistent with the results of the literature about $K_{NH_4^+}$ and activity coefficients at high ionic strengths.[21,22] On the other hand, the calculation indicates that the value of $K^0_{CH_3NH_3^+}f_{CH_3NH_3^+}/f_{CH_3NH_2}$ can be neglected toward a_{H^+} in the studied pH range.

This result is confirmed by fitting the experimental data according to

$$K = K_{TR} + (f_{NH_4^+}/f_{NH_3})K^0_{NH_4^+}K_{TR}/a_{H^+}$$

which gives $K_{TR} = 23$ and $K^0_{NH_4^+}f_{NH_4^+}/f_{NH_3} = 1.93 \times 10^{-10}$ M, results consistent with the above ones.

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Table II. pH Dependence of the Rate Constant at 25 °C for the Chlorine-Transfer Reaction between NH_2Cl and CH_3NH_2

pH	I, M^a	$[NH_3]_T$, M	$10^3[CH_3NH_2]_T$, M	$10^3[NH_2Cl]_0$, M	10^2k, $M^{-1}\ s^{-1}$
8.28	1.00 ± 0.05	1.00	30.0	1.50	11.6 ± 0.6
9.28	1.05 ± 0.05	1.01	30.0	0.64	12.5 ± 0.6
9.85	1.05 ± 0.05	1.00	30.0	1.52	13.3 ± 0.6
10.12	0.98 ± 0.05	1.00	30.0	1.46	14.2 ± 0.7
10.29	1.02 ± 0.05	1.00	30.0	1.56	12.9 ± 0.6
10.47	1.00 ± 0.05	0.97	29.2	2.88	12.2 ± 0.6
10.74	1.02 ± 0.05	1.00	30.0	1.52	9.5 ± 0.5
11.14	1.02 ± 0.05	1.00	30.0	1.52	4.5 ± 0.3
11.80	1.02 ± 0.05	1.00	30.0	3.07	1.14 ± 0.05
12.90	1.09 ± 0.05	1.00	30.0	3.00	0.20 ± 0.02
10.29	1.05 ± 0.05	1.96	30.0	3.00	16.9 ± 0.8

^{a}Average ionic strength 1.03 ± 0.05 M.

Table III. Influence of Temperature on the Chlorine-Transfer Reaction between NH_2Cl and CH_3NH_2

T, °C	$[NH_3]_T$, M	$10^3[CH_3NH_2]_T$, M	$10^3[NH_2Cl]_0$, M	[NaOH], M	10^2k, $M^{-1}\ s^{-1}$
8	1.00	30.0	1.59	0	2.7 ± 0.2
15	1.00	30.0	1.59	0	4.9 ± 0.3
25	1.00	30.0	1.57	0	11.4 ± 0.6
35	1.00	30.0	1.56	0	24.6 ± 1.2
8.2	1.00	30.0	5.08	0.1	0.076 ± 0.004
25	1.00	30.0	3.00	0.1	0.23 ± 0.01
25	0.012	30.0	3.00	0.1	0.20 ± 0.01
35	0.012	30.0	2.96	0.1	0.61 ± 0.03
42	0.012	30.0	2.96	0.1	1.12 ± 0.06

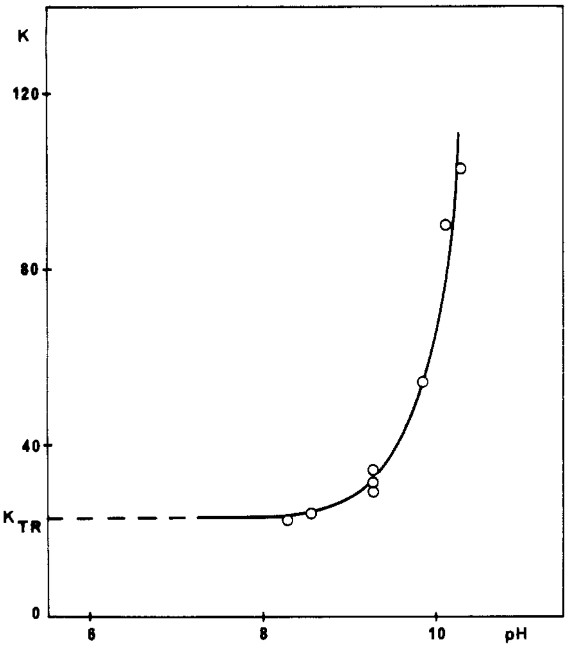

Figure 1. Experimental pH dependence of the equilibrium constant at 25 °C for the chlorine-transfer reaction between NH_2Cl and CH_3NH_2: (○) experimental data. The curve was calculated with $K = K_{TR} + (f_{NH_4^+}/f_{NH_3})K^0_{NH_4^+}K_{TR}/a_{H^+}$.

Kinetics. For pH < 10.5, the rate constant was calculated from the expressions of a and b already given. For pH > 10.5, the formation of methylhydrazine and its reaction with chloramine are not negligible. In this case, the mass balance (3) is not verified and eq 4 cannot be used in a strict sense. However, we found that a fitting of the experimental data according to the similar relation

$$[CH_3NHCl] = a'(1 - \exp(-b't))$$

allowed us to calculate the slope at zero time and, therefore, the rate constant according to

$$k = a'b'/([NH_2Cl]_0[CH_3NH_2]_0)$$

a' and b' are only fitting parameters allowing an accurate calculation, which give better results than a graphical determination or use of a polynomial expression only applicable in the first times of the reaction.

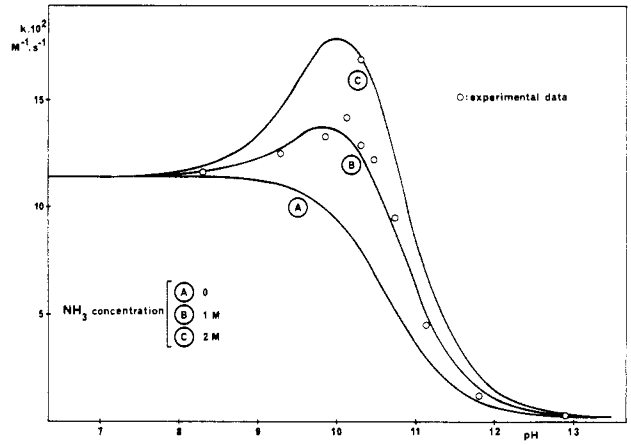

Figure 2. Experimental and calculated pH dependence of the rate constant for several ammonia concentrations at 25 °C (from eq 5 with $\lambda_0 = 8.3 \times 10^{-4}\ M^{-1}\ s^{-1}$, $\lambda_1 = 5.7 \times 10^9\ M^{-2}\ s^{-1}$, and $\lambda_2 = 0.74\ M^{-2}\ s^{-1}$) for the chlorine-transfer reaction between NH_2Cl and CH_3NH_2.

The results obtained in a 1 M NH_3/NH_4Cl buffer solution are presented in Table II. The procedure used for preparing solutions allowed the ionic strength (calculated as $I = 0.5\sum C_iz_i^2$) to be located between 0.98 ± 0.05 and 1.09 ± 0.05 M and to be considered as practically constant with an average value of 1.02 ± 0.05 M.

Figure 2 shows the plot of the experimental data (k, pH). The rate constant k becomes practically pH independent below pH 8 and above pH 12.8 and reaches a maximum value when the pH is located between the pK_a of NH_4^+ and that of $CH_3NH_3^+$. In this range, the rate constant increases with the concentration of total ammonia as shown for pH 10.29.

These phenomena can be attributed to the influence of buffer on the kinetics.

Effect of Temperature. The rate constant was determined between 8 and 42 °C with a concentration of methylamine equal to 0.03 M in the two pH ranges for which k is practically pH and ammonia concentration independent.

The experimental data are summarized in Table III.

The values of the energy of activation E and of the preexponential factor A can be derived from the evolution of k with

Table IV. $[HCO_3^-]$ Dependence of the Rate Constant at 25 °C for the Chlorine-Transfer Reaction between NH_2Cl and CH_3NH_2

$10^2[HCO_3^-]_T$, M	$10^3[NH_3]_T$, M	$10^3[CH_3NH_2]_T$, M	$10^3[NH_2Cl]_0$, M	pH	10^3k, M^{-1} s^{-1}
1.25	12.0	15.0	2.98	11.11	45.0 ± 2.2
	12.0	30.0	3.05	11.31	31.8 ± 1.6
	12.0	30.0	3.04	11.50	23.0 ± 1.2
2.50	12.0	30.0	3.02	11.06	54.7 ± 2.7
	12.1	30.0	2.89	11.34	33.0 ± 1.7
	12.0	30.0	3.00	11.52	23.2 ± 1.2
3.75	11.9	30.0	3.12	10.93	75.0 ± 3.8
	12.0	30.0	2.98	11.23	43.5 ± 2.2
	12.0	30.0	2.98	11.45	28.0 ± 1.4

temperature, which is consistent with Arrhenius' law.

For a slightly alkaline medium (pH 8 at 25 °C, NH_2Cl and total ammonia concentrations respectively equal to 1.5×10^{-3} and 1 M), the calculation gives

$$E = 14.2 \pm 2.1 \text{ kcal mol}^{-1} \qquad A = 2.60 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

from which the apparent enthalpy and entropy of activation are

$$\Delta H_0^* = 13.6 \text{ kcal mol}^{-1} \qquad \Delta S_0^* = -17.6 \text{ cal mol}^{-1} \text{ s}^{-1}$$

For a very alkaline medium (pH 12.9 at 25 °C, 3×10^{-3} M in NH_2Cl, and concentration of ammonia between 12×10^{-3} and 1 M), the results are

$$E = 14.3 \pm 2.1 \text{ kcal mol}^{-1} \qquad A = 6.25 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

$$\Delta H_0^* = 13.7 \text{ kcal mol}^{-1} \qquad \Delta S_0^* = -25.0 \text{ cal mol}^{-1} \text{ s}^{-1}$$

Discussion

Kinetics. The results for the kinetics of the reaction of CH_3NHCl formation can be interpreted in terms of buffer-assisted reactions by stating the scheme

$$CH_3NH_2 + NH_2Cl \xrightarrow{\lambda_0} CH_3NHCl + NH_3$$

$$H^+ + CH_3NH_2 + NH_2Cl \xrightarrow{\lambda_1} CH_3NHCl + NH_3 + H^+$$

$$NH_4^+ + CH_3NH_2 + NH_2Cl \xrightarrow{\lambda_2} CH_3NHCl + NH_3 + NH_4^+$$

Then, we can write

$$\frac{d[CH_3NHCl]}{dt} = \lambda_0[NH_2Cl][CH_3NH_2] + \lambda_1[H^+][NH_2Cl] \times [CH_3NH_2] + \lambda_2[NH_4^+][NH_2Cl][CH_3NH_2]$$

If we assume that

$$[CH_3NH_2]_T = [CH_3NH_2] + [CH_3NH_3^+]$$

$$[NH_3]_T = [NH_3] + [NH_4^+]$$

we obtain

$$[CH_3NH_2] = \frac{\dfrac{f_{CH_3NH_3^+}}{f_{CH_3NH_2}} K^0_{CH_3NH_3^+}[CH_3NH_2]_T}{a_{H^+} + \dfrac{f_{CH_3NH_3^+}}{f_{CH_3NH_2}} K^0_{CH_3NH_3^+}}$$

$$[CH_3NH_3^+] = \frac{a_{H^+}[CH_3NH_2]_T}{a_{H^+} + \dfrac{f_{CH_3NH_3^+}}{f_{CH_3NH_2}} K^0_{CH_3NH_3^+}}$$

$$[NH_4^+] = \frac{a_{H^+}[NH_3]_T}{a_{H^+} + \dfrac{f_{NH_4^+}}{f_{NH_3}} K^0_{NH_4^+}}$$

f_i is the activity coefficient of the species i, a_i is its activity defined as $a_i = f_i[i]$, and K_i^0 is its acidity constant at zero ionic strength.

Then, at zero time

$$\left(\frac{d[CH_3NHCl]}{dt}\right)_0 = k[NH_2Cl]_0[CH_3NH_2]_T$$

with

$$k = \left[\lambda_0 + \lambda_1 a_{H^+} + \frac{\lambda_2 a_{H^+}[NH_3]_T}{a_{H^+} + \dfrac{f_{NH_4^+}}{f_{NH_3}} K^0_{NH_4^+}}\right] \times \frac{\dfrac{f_{CH_3NH_3^+}}{f_{CH_3NH_2}} K^0_{CH_3NH_3^+}}{a_{H^+} + \dfrac{f_{CH_3NH_3^+}}{f_{CH_3NH_2}} K^0_{CH_3NH_3^+}} \qquad (5)$$

Under our experimental conditions, the ionic strength is practically constant and equal to 1.03 M. However, for high ionic strengths, the activity coefficients and acidity constants are affected by changes in ionic environment.[21] In our study, it varies with pH and, then, the activity coefficients of NH_4^+, $CH_3NH_3^+$, CH_3NH_2, and NH_3 cannot be strictly defined and only "mean" values can be obtained. To fit the experimental data to relation 5 and to calculate the λ_i constants, we first assumed that all f_i values were equal to unity. After the data were fitted by the least-squares method, the values of k were recalculated from the obtained set of λ_i constants at each studied pH and compared with the experimental values. Then, the values of $f_{CH_3NH_3^+}/f_{CH_3NH_2}$ and $f_{NH_4^+}/f_{NH_3}$ were modified and the previous procedure was repeated until the calculated rate constant agreed with the experimental data within an error of 10%. This method gives fitted "mean" values for $K^0_{NH_4^+}f_{NH_4^+}/f_{NH_3}$ and $K^0_{CH_3NH_3^+}f_{CH_3NH_3^+}/f_{CH_3NH_2}$ that take in account changes in medium composition.

The fitted values of λ_i are

$$\lambda_0 = (8.3 \pm 1.5) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

$$\lambda_1 = (5.7 \pm 1.1) \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$$

$$\lambda_2 = 0.74 \pm 0.20 \text{ M}^{-2} \text{ s}^{-1}$$

They were obtained with $K^0_{CH_3NH_3^+}f_{CH_3NH_3^+}/f_{CH_3NH_2} = 2.0 \times 10^{-11}$ M and $K^0_{NH_4^+}f_{NH_4^+}/f_{NH_3} = 2.1 \times 10^{-10}$ M, consistent with literature data.[21,22]

Figure 2 gives the calculated curves $k = f(\text{pH})$ for different ammonia concentrations. The figure shows the quality of fit for the assigned rate constants. For pH < 8, the rate constant stabilizes at 0.114 M^{-1} s^{-1} and becomes pH and ammonia concentration independent.

In order to verify the generality of the buffer effect, runs with different $NaOH/NaHCO_3$ buffered solutions were conducted. The ionic strength was located between 0.03 and 0.1 M. It was not constant, but in this range, the activity coefficient of a univalent ion is between 0.85 and 0.79[25] and for a divalent ion is between 0.53 and 0.38.[25]

Then, to a first approximation, it is possible to neglect the variations of the activity coefficients around the average values

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[25] Sun, M. S.; Harriss, D. K.; Magnuson, V. R. *Can. J. Chem.* **1980**, *58*, 1253.

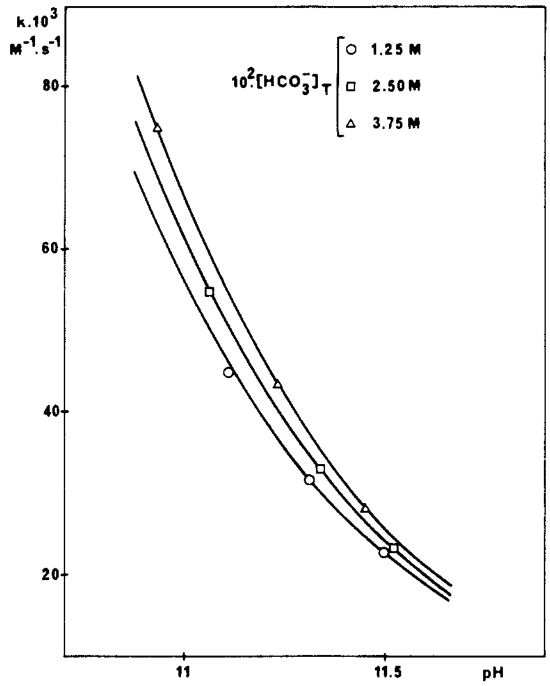

Figure 3. Experimental [HCO$_3^-$] dependence of the rate constant at 25 °C for the chlorine-transfer reaction between NH_2Cl and CH_3NH_2 (curves calculated with the fitted values of p and k^0).

of 0.82 and 0.45 corresponding to an average ionic strength of 0.06 M.

The results are given in Table IV and Figure 3. Each value of k is the mean of two determinations (maximum deviation 5%).

For each pH value between 11 and 11.7, the rate constant k increases linearly as a function of the total HCO_3^- concentration:

$$k = k^0 + p[\mathrm{HCO_3^-}]_T \qquad (6)$$

The intercept k^0 is the rate constant for the studied pH but without bicarbonate.

Table V gives the values of k^0 and p calculated from our experiments. In the studied pH range $a_{H^+} \ll K^0_{NH_4^+}f_{NH_4^+}/f_{NH_3}$ and in the presence of HCO_3^-, according to the previous reaction scheme, the expression of the rate constant is

$$k = \left[\lambda_0 + \left(\lambda_1 + \frac{\lambda_2 f_{NH_3}[NH_3]_T}{f_{NH_4^+}K^0_{NH_4^+}}\right)a_{H^+} + \frac{\lambda_3 a_{H^+}[HCO_3^-]_T}{a_{H^+} + \dfrac{f_{HCO_3^-}}{f_{CO_3^{2-}}}K^0_{HCO_3^-}}\right]\frac{\dfrac{f_{CH_3NH_3^+}}{f_{CH_3NH_2}}K^0_{CH_3NH_3^+}}{a_{H^+} + \dfrac{f_{CH_3NH_3^+}}{f_{CH_3NH_2}}K^0_{CH_3NH_3^+}}$$

The comparison with relation 6 gives

$$k^0 = \left[\lambda_0 + \left(\lambda_1 + \frac{\lambda_2 f_{NH_3}[NH_3]_T}{f_{NH_4^+}K^0_{NH_4^+}}\right)a_{H^+}\right]\frac{\dfrac{f_{CH_3NH_3^+}}{f_{CH_3NH_2}}K^0_{CH_3NH_3^+}}{a_{H^+} + \dfrac{f_{CH_3NH_3^+}}{f_{CH_3NH_2}}K^0_{CH_3NH_3^+}}$$

$$p = \frac{\lambda_3 a_{H^+}}{a_{H^+} + \dfrac{f_{HCO_3^-}}{f_{CO_3^{2-}}}K^0_{HCO_3^-}}\;\frac{\dfrac{f_{CH_3NH_3^+}}{f_{CH_3NH_2}}K^0_{CH_3NH_3^+}}{a_{H^+} + \dfrac{f_{CH_3NH_3^+}}{f_{CH_3NH_2}}K^0_{CH_3NH_3^+}}$$

The fit of k^0 and p experimental data (Table V) to the previous relations by the least-squares method can be achieved on the basis of an average ionic strength of 0.06 M as previously discussed and by assuming that activity coefficients for molecules are equal to unity for such an ionic strength.

Table V. Experimental Values of k^0 and p at 25 °C for the Chlorine-Transfer Reaction between NH_2Cl and CH_3NH_2

pH	10^3k^0, M^{-1} s^{-1}	p, M^{-2} s^{-1}
11.0	52.3	0.320
11.1	44.0	0.264
11.2	35.1	0.256
11.3	30.0	0.192
11.4	24.9	0.172
11.5	21.0	0.152
11.6	18.5	0.116
11.7	16.1	0.100

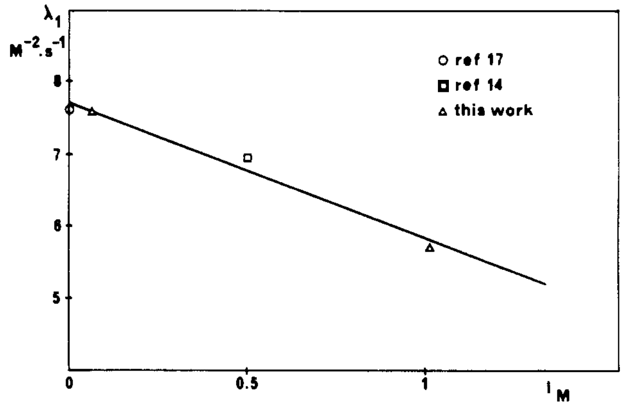

Figure 4. Ionic strength dependence of λ_1 at 25 °C for the chlorine-transfer reaction between NH_2Cl and CH_3NH_2.

Then, $K^0_{HCO_3^-}f_{HCO_3^-}/f_{CO_3^{2-}} = 1.03 \times 10^{-10}$ M and $K^0_{CH_3NH_3^+}f_{CH_3NH_3^+}/f_{CH_3NH_2} = 1.97 \times 10^{-11}$ M and the estimated λ_1 constants are (λ_1 calculated by noting that for $[NH_3]_T = 12 \times 10^{-3}$ M, $\lambda_2[NH_3]_T f_{NH_3}/(f_{NH_4^+}K^0_{NH_4^+})$ is negligible toward λ_1 and that $\lambda_0 \ll \lambda_1 a_{H^+}$)

$$\lambda_1 = (7.6 \pm 1.5) \times 10^9 \text{ M}^{-2}\text{ s}^{-1} \qquad \lambda_3 = 5.47 \pm 1.60 \text{ M}^{-2}\text{ s}^{-1}$$

The mechanism of the observed buffer catalysis cannot be determined from our results and requires a deeper study.

The influence of ionic strength on λ_1 is shown in Figure 4, where the values of λ_1 are plotted against ionic strength I from the results of Isaac and Morris[17] given for $I = 0$, from those of Snyder and Margerum[14] obtained for $I = 0.5$ M, and from ours, which are established for $I = 1.02$ M.

We have also considered the results obtained in HCO_3^-/CO_3^{2-} buffered solutions, although the ionic strength was not constant for these experiments. Nevertheless, Figure 5 shows that the value of λ_1 obtained in this case is consistent with the others and that our approximation is justified.

Within a 10% error for λ_1, the plot gives a straight-line graph with an intercept of 7.70×10^9 M^{-2} s^{-1} and a slope of -1.87×10^9 M^{-1} s^{-1} (correlation coefficient equal to −0.9913).

A similar relation is obtained by Laidler[26] to describe the influence of ionic strength for reactions between a molecule and an ion

$$k = k_0(1 + 2.303bI)$$

where k_0 is the rate constant for $I = 0$ and b a semiempirical parameter.

Applying the above relation to λ_1 gives

$$\lambda_1 = \lambda_{10}(1 + 2.303bI)$$

with

$$\lambda_{10} = 7.70 \times 10^9 \text{ M}^{-2}\text{ s}^{-1} \qquad b = -0.102 \text{ M}^{-1}\text{ s}^{-1}$$

The linear dependence of λ_1 on I and the resulting value of b confirm that the pathway involving this rate constant is a molecule/ion interaction.

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(26) Laidler, K. J. *Chemical Kinetics*, 2nd ed.; McGraw-Hill: New York, 1965.

Inorg. Chem. **1989**, *28*, 3813–3819

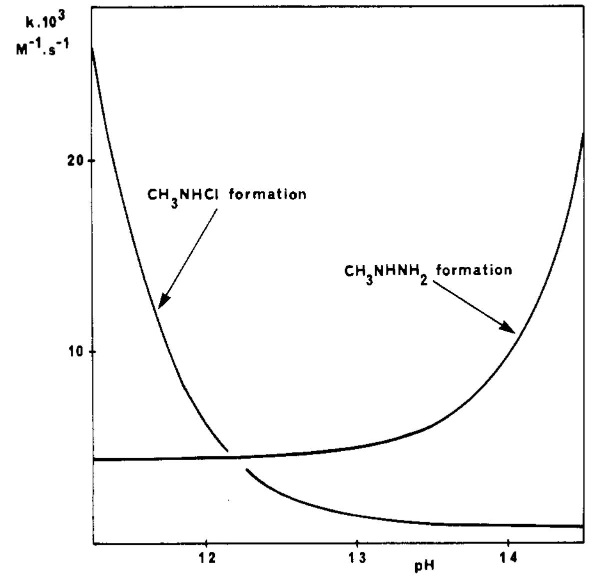

Figure 5. Comparison of the rate constants of formation of CH_3NHCl and CH_3NHNH_2 at 25 °C.

Influence of CH_3NHCl Formation on the Synthesis of CH_3NHNH_2. The comparison of the rate constants for the formation of CH_3NHCl and CH_3NHNH_2 by the reaction of CH_3NH_2 and NH_2Cl is shown in Figure 5.

From the plotted curves, it can be seen that below pH 11, CH_3NHCl is formed preferably to CH_3NHNH_2, while for pH > 14, CH_3NHCl is a minor product compared to CH_3NHNH_2.

In the pH range 11–14, CH_3NHNH_2 and CH_3NHCl are produced in comparable amounts. Then, if CH_3NHNH_2 is prepared at too low a pH, the amount of CH_3NHCl can be appreciable. For instance, at pH 14, the ratio of methylhydrazine to methylchloramine is equal to 11, while for pH 13 it is equal to 3.5. So, to prepare CH_3NHNH_2, a high pH value is required.

However, in practice, another reaction should be taken into account: oxidation of methylhydrazine by chloramine, which is acid- and base-catalyzed[27,28] and the influence of which leads us to adjust the pH near 13.8–14 to obtain the highest yields in CH_3NHNH_2.[28]

Conclusion

This study confirms the experimental results of Snyder and Margerum about the transfer of chlorine between chloramine and methylamine. It shows that the evolution of the rate constant with pH can be interpreted in terms of buffer-assisted reactions, involving molecule/molecule and ion/molecule interactions.

In order to analyze more closely the mechanism of the reaction, the influence of the nature of the amine has been studied at the present time.

Finally, the chlorine-transfer reaction must be taken into account in the kinetic model governing the synthesis of CH_3NHNH_2 by the Raschig process.

Registry No. NH_2Cl, 10599-90-3; CH_3NH_2, 74-89-5.

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Synthesis, Spectroscopy, and Structural Characterization of Five-Coordinate, Bis(aryldiazenido)technetium Complexes and Their Protonation Reactions. X-ray Structure of $[TcCl(PPh_3)_2(NNC_6H_4Br)_2]$

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The reaction of $[TcCl_4(PPh_3)_2]$ with arylhydrazines in methanol yields $[TcCl(PPh_3)_2(NNPh)_2]$ (**1**). Complex **1** displays trigonal-bipyramidal geometry with phosphine ligands occupying axial sites. The technetium–aryldiazenido moieties are nearly equivalent, with Tc–N–N bond angles of 166.2 (6) and 170.7 (7)° and multiple bonding throughout. The chloride ligand occupies the remaining equatorial coordination site. The addition of HCl(g) to complex **1** in methanol gives the neutral, six-coordinate "hydrazido(2–)" complex $[TcCl_2(PPh_3)_2(NNPh)(NNHPh)]$. The reaction of complex **1** with HBr(g) gives the doubly protonated, cationic species $[TcBr_2(PPh_3)_2(NNPh)(NHNHPh)](Br)$. The ^{99}Tc NMR spectra for these species are presented, which suggest that the metals exhibit considerable Tc(V) character and that the formal oxidation states of −1 and +1 are not accurate descriptions of the electron density on the technetium. The ^{1}H NMR, mass, and electronic spectroscopic data are also presented for the various species, along with the crystal structure of the five-coordinate bis(aryldiazenido) precursor. Crystal data for $C_{48}H_{38}N_4P_2ClBr_2Tc$: monoclinic space group $P2_1/n$, $a = 12.174$ (2) Å, $b = 19.008$ (3) Å, $c = 20.162$ (3) Å, $\beta = 106.39$ (1)°, $V = 4476$ (1) Å^3 to give $Z = 4$. Structure solution and refinement based on 4135 reflections converged at $R = 0.053$ and $R_w = 0.062$.

Introduction

The search for new technetium complexes for use in diagnostic nuclear medicine continues to be an active area of research. As the basic coordination chemistry of technetium rapidly unfolds, an increasing emphasis is being placed on complexes incorporating easily functionalized ligands.

Technetium nitrosyl chemistry has been studied with a variety of coligands.[2] However complexes that incorporate the organodiazenido ligand, a species isoelectronic with the nitrosyl ligand, have yet to be reported. Both species are geometrically versatile. However the organodiazenido ligand has the added capacity to be easily functionalized.

Aryldiazenido ligands, M—N=NR units with sp^2 hybridization on the β-nitrogen, may display a number of structural conformations (see Figure 1).[3] In the "singly bent" conformation (I), it can be considered either formally a neutral, 3-electron-donor ligand or a 2-electron-donating, monocationic ligand. The latter is the convention we have adopted throughout this work. In the "doubly bent" mode of coordination (II), it serves formally as a 2-electron-donating, monoanionic ligand.

Both the α- and β-nitrogens in the aryldiazenido moiety are basic and susceptible to protic attack. The products of the pro-

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