

azide **6**, 84.1%; mass balance, 100.3%. Photolyses to higher conversions gave similar product ratios.

Photolysis of Azide 7. The azide (106.6 mg, 0.478 mmol) and nonadecane (34.5 mg, 0.129 mmol) as internal standard were dissolved in dry degassed cyclohexane (2 mL) and irradiated in apparatus A at 22 °C for 0.25 h. GLC analysis on column C (temperature program, 165–200 °C at 2°/min) using the flame ionization detector gave the following yields: imine **7A**, 3.6%; imine **7B** (\equiv **7C**), 1.4%; azide **7**, 94.1%; mass balance 99.0%. Similar runs with conversions from 1 to 40% gave product ratios **7A** to **7B** (\equiv **7C**) in the range of 2.4 to 2.8.

Irradiation of Imines 7A and 7B (\equiv **7C**). Imines **7A** (50.0 mg, 0.256 mmol), **7B** (\equiv **7C**) (49.3 mg, 0.253 mmol), and nonadecane (33.3 mg, 0.124 mmol) were irradiated in apparatus A in pentane (5 mL) at 22 °C for 1.25 h. GLC analysis as described for azide **7** gave the following yields: **7A**, 100%; **7B**, 99.0%.

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- (11) It has been reported that the Ph/Me migratory ratio for **7** ranged from 1.87 to 2.45,^{10a} but more recently^{10b} this has been modified to unity. The latter figure was arrived at by a low (11%) conversion experiment. It was reported by these workers¹⁰ that the Ph/Me migratory ratio increased from 0.94 \pm 0.10 at 11% conversion to 1.44 ± 0.07 at 30% conversion. We have carried out photolyses of **7** to conversions as low as 1% and still find the ratio to be 1.3. In addition, the ratio did not appear to be dependent upon conversion up to 40%. Control experiments showed that both product imines are photostable (at least in the absence of **7**) for the lengths of times that azide **7** is photolyzed. We are unable to explain this discrepancy in observations, particularly since the method of analysis in the latter study^{10b} was direct analysis by GLC of the photolysate, apparently very similar to our method.
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- (26) The UV spectra of **6**, **10**, and **11** (in cyclohexane solution, this work) are all very similar and correspond closely with that of **3** in hexane solution given in Figure 1 of ref 2h. We are at a loss to explain why azide **1** in ref 2h [Ph(Me)EtCN₃] and **8** [Ph(Me)₂CN₃] differ so significantly in their UV spectra.
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Kinetics and Mechanism of Nitromethane Chlorination. A New Rate Expression

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Abstract: A kinetic study of the chlorination of nitromethane to trichloronitromethane (chloropicrin) was made. The rate of production of chloropicrin in the pH 6–8 range is first order in both nitromethane and hypochlorite anion. The kinetic dependence on halogenating reagent is a new observation and involves hypochlorite anion acting as a general base. Around pH 12 and above, the mechanism changes to a rate-controlling step of reaction between nitromethane anion or a chlorinated nitromethane anion and hypochlorous acid.

Introduction

The state of halogenation chemistry of nitroalkanes has been briefly summarized by Nielsen.¹ Previous reports have shown that the reaction is both acid and base catalyzed with the im-

portant observation that in acid media the reaction is zero order in halogenating species.^{2a,b} The reaction is subject to general base catalysis^{2a} which has defined the rate-limiting step as proton removal followed by rapid reaction of the nitronate

anion with halogenating species. In solutions of high pH, however, the reaction follows a different kinetic form, as Lii and Miller³ have shown for nitroethane:

$$\text{rate} = k[\text{CH}_3\text{CH}_2\text{NO}_2][\text{OCl}^-][\text{OH}^-]^{-1} \quad (1)$$

Formation of nitronate anion at pH > 11 is rapid and complete ($pK = 8.5$ for $\text{C}_2\text{H}_5\text{NO}_2$) and it appears that reaction of the nitronate anion with hypochlorous acid is then rate limiting. Thus, the term $[\text{CH}_3\text{CH}_2\text{NO}_2]_{\text{stoich}}[\text{OCl}^-][\text{OH}^-]^{-1}$ is equivalent to $[\text{CH}_3\text{CHNO}_2^-][\text{HOCl}]$ at high pH.⁴

This work reports a new rate expression which describes the behavior of the reaction in the intermediate pH range and, in addition, a similar observation of an inverse kinetic dependence on hydroxide ion in the chlorination of nitromethane at high pH.

Experimental Section

Kinetic Method. The kinetic method developed for studying the chlorination of nitromethane to chloropicrin was based on the water solubility of nitromethane and the water insolubility of the product chloropicrin. When a homogeneous solution of nitromethane is subjected to chlorination, a cloudiness sharply develops as soon as the solubility limit of chloropicrin is reached. As long as the initial concentration of nitromethane is kept significantly higher than the solubility of chloropicrin, then the reciprocal of the cloud point time multiplied by the solubility of chloropicrin (0.0031 M at 20 °C, below) will represent the velocity of the formation of chloropicrin in units of $\text{mol L}^{-1} \text{s}^{-1}$.

It was shown⁵ that there is no measurable buildup of mono- or dichloronitromethane during the measured portion of the reaction. Therefore the rate of appearance of chloropicrin can be equated to the rate of disappearance of nitromethane:

$$\text{vel} = \frac{[\text{CCl}_3\text{NO}_2]_{\text{sat}}}{\text{cloud point, s}} = \frac{d[\text{CCl}_3\text{NO}_2]}{dt} = \frac{-d[\text{CH}_3\text{NO}_2]}{dt} \quad (2)$$

Then

$$k_{\text{obsd}} = \text{vel}/[\text{CH}_3\text{NO}_2]_0, \text{ s}^{-1} \quad (3)$$

At 20 °C the solubility of chloropicrin in the 15.0% sodium chloride reaction mixture was determined by GLC on (a) the clear aqueous phase of a completed reaction; (b) the carbon tetrachloride extract of same; (c) the carbon tetrachloride extract of a quenched sample of reacting solution which had just reached the cloud point. The results, expressed in terms of chloropicrin weight percent in the aqueous brine phase, gave respective values of (a) 0.045; (b) 0.044; (c) 0.047%. An average value of 0.046% was used. This is equivalent to 0.0031 M (density of 15.0% brine = 1.104). Figure 1 summarizes the data from runs made at different nitromethane concentrations at constant pH (7.5) and hypochlorite concentration from 0.19 to 0.22. The linearity of the log-log plot from 0.0142 to 0.0460 M validates the kinetic method in this range and establishes a reaction order of 1.0 in nitromethane.⁶ The amount of nitromethane reacted at the cloud point represents 7% reaction at $[\text{CH}_3\text{NO}_2] = 0.0460$ and 22% reaction at $[\text{CH}_3\text{NO}_2] = 0.0142$ M.

Procedure. For kinetic runs the following solutions were made up: 15.0 wt % sodium chloride (ca. 2.83 M); 12.5 wt % sodium hydroxide; 5.80% nitromethane in 15.0% sodium chloride (contains 0.060 g of $\text{CH}_3\text{NO}_2/\text{mL}$). The reactions were always run in a 15% sodium chloride solution since use of 12.5% sodium hydroxide and chlorine to make bleach results in a "background" concentration of sodium chloride byproduct of 15%.

In a typical run, a weight of 200 g of 15% sodium chloride was added to the reactor; sodium hydroxide was metered in via a Sage pump over a measured time interval while chlorine was metered in through a flow meter to the desired pH.⁷ Standardizations of pH were made with Van Waters and Rogers concentrated pH 7.0 buffer solution. The concentrated buffer was used because of the concentrated salt environment and the quicker response of the electrode between reaction mixture and buffer. With the dilute buffer the response was very slow. The temperature was brought under control (usually to 20.0 °C) and a sample of bleach solution removed and quenched in excess aqueous sodium iodide-acetic acid mixture. As soon as possible after quenching the bleach analysis sample, the pH was recorded, and the desired

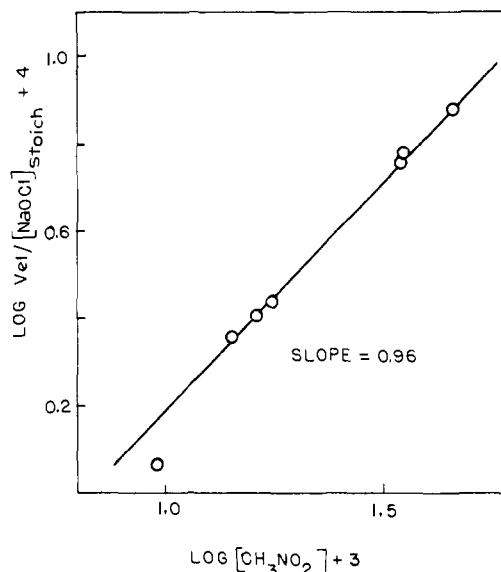


Figure 1. Reaction order in nitromethane, 20 °C, pH 7.6.

volume of nitromethane stock solution (usually 4.0 mL) was added by syringe. A stopwatch was manually started halfway through the addition and stopped when the cloud point was visible (usually quite sharp). The pH at the cloud point was also observed so that an average value during the run could be used. Generally, the two pH values did not vary by more than 0.1–0.2 pH units.

Analysis. Product analyses were made by gas chromatograph using a 6 ft \times $\frac{1}{8}$ in. stainless steel column packed with a bonded phase Carbowax 400 on Porosil S. Analyses were made isothermal at 100 °C, 20 mL/min helium, detector at 200 °C.

Hypochlorite analyses were made by quenching a 2.0-mL (2.20 g) sample in a diluted solution of 10 mL of 10% aqueous sodium iodide and a few milliliters of glacial acetic acid, mixed just prior to sampling. The iodine formed was titrated with 0.10 N sodium thiosulfate.

Results

The nature of the kinetic method required relatively high concentrations of substrate compared to, say, a spectrophotometric method. Since hydroxide undergoes an overall increase during the reaction, this resulted in an inability to maintain constant pH in the region of about $8.5 < \text{pH} < 11.5$. The rates were then investigated in (1) an intermediate region of pH 6–8 where the buffer effect of OCl^-/HOCl kept pH constant and (2) a high region of pH 12–13 where excess hydroxide kept pH constant. The kinetics were also investigated in a carbonate buffer system.

pH 6–8 Region. Effect of Hypochlorite Concentration. The hypochlorite concentration was varied from approximately 0.1 to approximately 0.4 M, while maintaining both the nitromethane concentration and pH constant. The slope of the log plot of 1.02 shows that the reaction is directly dependent on hypochlorite concentration. The general term "hypochlorite" is used for the total amount of titratable material expressed in terms of the molecular weight of NaOCl and designated as $[\text{NaOCl}]_{\text{stoich}}$.

Effect of pH. The pK_a of hypochlorous acid in 15% sodium chloride at 20 °C was determined to be 7.3 by pH-metric titration. The pH range studied encompassed the extreme forms of hypochlorite from hypochlorous acid to hypochlorite anion. A plot of k_{obsd} against pH is shown in Figure 2. The form of this curve is S-shaped with an inflection point at pH 7.3, which is the pK_a of hypochlorous acid. Thus, the response to pH is actually a response to the concentration of hypochlorite anion. This is shown to be true by the pH data recalculated and plotted in Figure 3. The response of $\log k_{\text{obsd}}$ to $\log [\text{OCl}^-]_{\text{actual}}$ is linear with slope of 1.0. The second-order rate

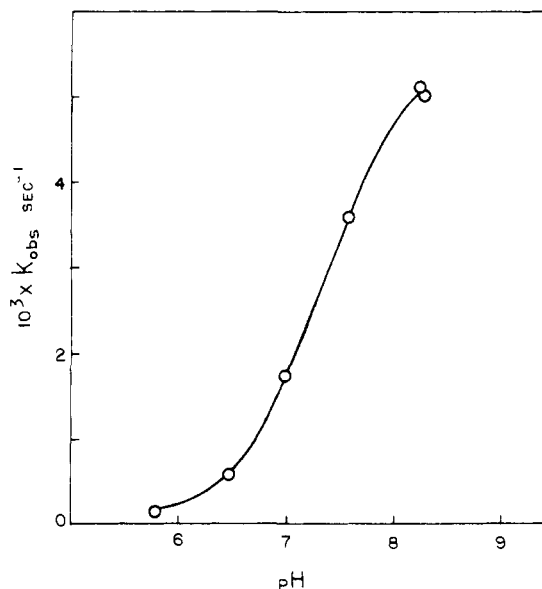


Figure 2. pH profile of observed first-order rate constant in intermediate pH range, 20 °C.

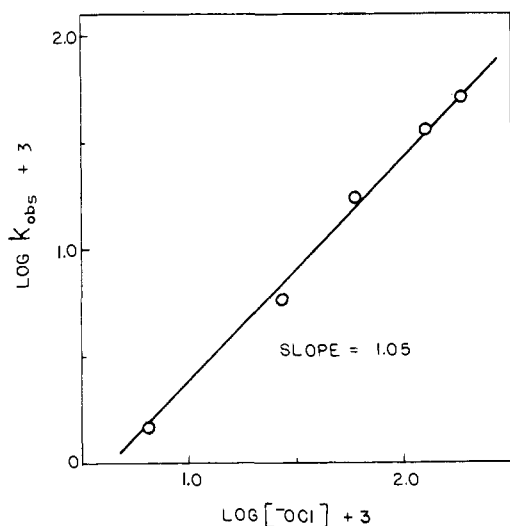


Figure 3. Reaction order in hypochlorite anion, 20 °C.

constant, $k_{\text{obsd}}[-\text{OCl}]_{\text{actual}}$, is also invariant over a 300-fold change in the concentration of hydroxide ion, showing that hydroxide ion catalysis in this pH region is insignificant.

Thermokinetic Parameters. The thermokinetic parameters were found to be $\Delta H^\ddagger = 16.1$ kcal/mol and $\Delta S^\ddagger = -11$ eu. It was necessary to estimate the solubility of chloropicrin in 15% brine from 10 to 30 °C. Using the base value determined in this work at 20 °C and assuming a similar trend with temperature as found by Thompson,⁹ the solubility of chloropicrin at each temperature of interest was calculated.

pH 12–13 Region. Effect of pH. The behavior of rate showed an *inverse* relationship to increasing pH. The data is listed in Table I. When this rate data is plotted vs. pH for those runs at constant (0.20 M) hypochlorite concentration, a linear relationship appears. This is fortuitous, however, since in theory the response should be curved concavely (see Figure 4) if eq 9 is the correct description of the reacting system. The discrepancy is explained by the fact that the rate of formation of nitronate anion is only about six times greater than the rate of reaction of nitronate anion with hypochlorous acid at pH 12, while at pH 13 the ratio is about 600.

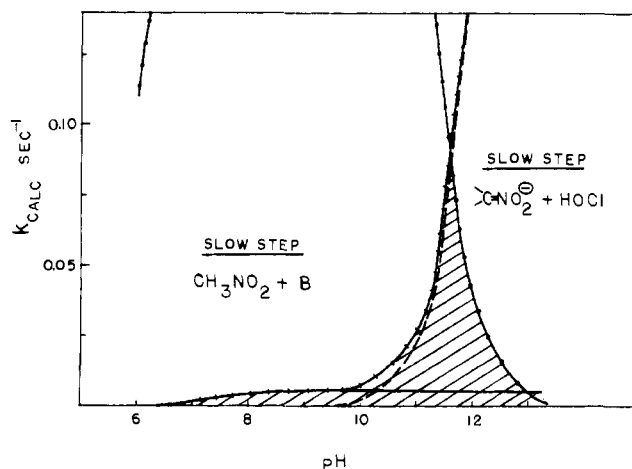


Figure 4. Calculated composite kinetic graph of nitromethane chlorination:

$k_2 \text{HOCl}([\text{>C}=\text{NO}_2^-]/[\text{CH}_3\text{NO}_2])/[\text{HOCl}]$, ————;
 $k_1^- \text{OCl}[-\text{OCl}]$, ————; $k_1^- \text{OCl}[-\text{OH}]$, - - - - -;
 $k_1^- \text{OH}[-\text{OH}] + k_1^- \text{OCl}[-\text{OCl}]$, + + + + +.

Table I. Observed First-Order Rate Constants as a Function of pH in the High pH Range

[NaOCl] _{st} , M	[CH ₃ NO ₂], M	pH	k_{obsd} , s ⁻¹
0.207	0.0185	12.1	16×10^{-3}
0.204	0.0185	12.3	12.2×10^{-3}
0.195	0.0186	12.6	9.0×10^{-3}
0.196	0.0181	13.0	3.8×10^{-3}

Table II. Observed First-Order Rate Constants as a Function of Carbonate Ion Concentration. Determination of Carbonate Catalytic Constant

[CO ₃ ²⁻]	[-OCl]	pH	k_{obsd} , s ⁻¹ × 10 ⁻³	$k_1 \text{CO}_3^{2-}$, M ⁻¹ s ⁻¹ ^a
0.0316	0.144	9.44	4.37	0.0180
0.059	0.138	9.25	5.28	0.0278
0.062	0.143	9.30	5.38	0.0258
0.111	0.134	9.20	6.58	0.0274
0.111	0.135	9.20	6.18	0.0236
0.134	0.141	9.20	6.67	0.0220
0.134	0.141	9.20	6.79	0.0229
				0.024 ± 0.003

^a $k_1 \text{CO}_3^{2-} = (k_{\text{obsd}} - k_1^- \text{OCl}[-\text{OCl}])/[-\text{CO}_3^{2-}]$, where $k_1^- \text{OCl} = 0.0254 \text{ M}^{-1} \text{ s}^{-1}$.

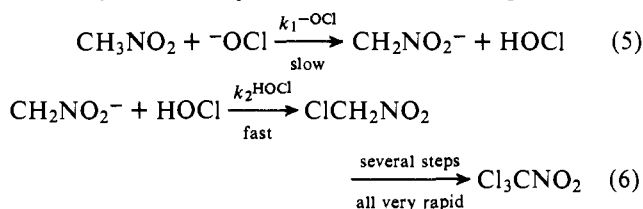
Catalysis by Carbonate. Several kinetic runs were made at different concentrations of sodium carbonate at constant hypochlorite and constant pH. Table II summarizes the rate results. A plot of k_{obsd} against carbonate ion concentration was also made (columns 1 and 4 of Table II). Neglecting the small differences in hypochlorite concentration, the least-squares slope of the plot gave a value for the carbonate catalytic constant ($k_1 \text{CO}_3^{2-}$) of $0.024 \text{ M}^{-1} \text{ s}^{-1}$, which is in good agreement with the average value $0.024 \text{ M}^{-1} \text{ s}^{-1}$ from Table II. The intercept of the same plot agrees extremely well with the value determined previously for $k_1^- \text{OCl}$. Therefore no catalysis by hydroxide ion was detected up to pH 9.8. The pK_a of HCO_3^- was determined to be 9.10 in 15% sodium chloride at 20 °C.

Discussion

The rate results in the intermediate pH region uncover a kinetic form not previously found for halogenations of nitroalkanes:

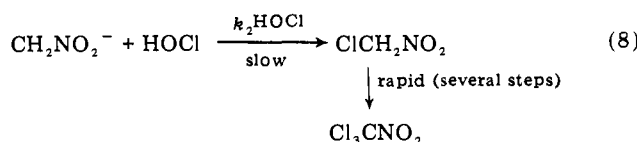
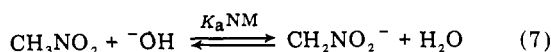
$$\text{velocity} = k_1[\text{CH}_3\text{NO}_2][-\text{OCl}] \quad (4)$$

If the results for the carbonate buffer are included, the validity of this rate expression spans the range from pH 6 to at least 9 in the particular case of nitromethane. The mechanism reflected by this rate expression is shown in the equations



Hypochlorite anion is acting as a general base in the rate-limiting step. The points for this mechanism are fourfold: (1) the reaction is first-order in hypochlorite anion (eq 4); (2) the finding of general base catalysis by carbonate ion (Table II); (3) the similarity to literature reports of general base catalysis for such halogenations in more acid solutions² (although for these the kinetic expression is zero order in halogen), and (4) the similarity of thermokinetic parameters found here ($\Delta H^\ddagger = 16$ kcal/mol, $\Delta S^\ddagger = -11$ eu) with those generally found for rate-controlling proton removals from other nitroalkanes ($\Delta H^\ddagger = 12-16$ kcal/mol, $\Delta S^\ddagger = -7$ to -16 eu).¹

The kinetic results alone are also consistent with another mechanism, i.e., a rapid, reversible proton removal by hydroxide followed by a slow attack of hypochlorous acid on the nitronate anion:



This alternative in the intermediate pH region is obviously ruled out by the finding of general base catalysis by carbonate ion (point 2). It is mentioned here because it does seem to be, in fact, the mechanism followed by the reaction at higher pH values, around 12 and above. At the higher base concentrations (Table I) conversion of nitromethane to nitronate anion ($\text{p}K_a^{\text{CH}_3\text{NO}_2} = 10.2$) is relatively rapid and the reaction whose rate is actually being measured is the much slower reaction 8. The rate expression describing this situation is

$$\begin{aligned} \text{velocity} &= k_2^{\text{HOCl}}[\text{CH}_2\text{NO}_2^-][\text{HOCl}] \\ &= k_2^{\text{HOCl}} \frac{K_a^{\text{HOCl}}}{K_w} [\text{CH}_3\text{NO}_2]_{\text{St}} [^- \text{OCl}] [^- \text{OH}]^{-1} \quad (9) \end{aligned}$$

This situation requires some comment at this point. The rate-controlling step has now shifted from proton abstraction to the subsequent halogenation step. In the former situation (intermediate pH range) we are quite confident based on literature data and our own results that there is no buildup of mono- and dichlorinated intermediates, i.e., the reactivity order

for proton abstraction is $\text{Cl}_2\text{CHNO}_2 \gg \text{ClCH}_2\text{NO}_2 \gg \text{CH}_3\text{NO}_2$. Thus the equality $d[\text{Cl}_3\text{CNO}_2]/dt = -d[\text{CH}_3\text{NO}_2]/dt$ can be made. Whether or not there is any buildup of less than fully chlorinated materials in the new situation depends upon the relative rates of their reaction with hypochlorous acid. The relative order $\text{Cl}_2\text{CNO}_2^- \gg \text{ClCHNO}_2^- \gg \text{CH}_2\text{NO}_2^-$ now is required in order to make the equality $d[\text{Cl}_3\text{CNO}_2]/dt = -d[\text{CH}_2\text{NO}_2^-]/dt$. This is important because we are measuring $d[\text{Cl}_3\text{CNO}_2]/dt$. No direct evaluation of this order is available from examination of literature data, and thus far the results of attempts at direct measurements in these laboratories have not been unequivocal. There is a suggestion from the relative rates of *protonation* of the anions of nitromethane and its monobromo derivative⁸ ($k_{\text{BrCHNO}_2^-}/K_{\text{CH}_2\text{NO}_2^-} = 4/1$) that there may be a moderate buildup of mono- and dichloro intermediates at high pH conditions if we assume a parallel behavior between chlorination and protonation. The rate constant for reaction 8 was found to be 9500 L/mol-s. This should be considered a *lower limit* for the reaction of nitronate anion with hypochlorous acid, while in the extreme reverse of the above anion reactivity ratios it would represent the rate constant for reaction of $\text{Cl}_2\text{CNO}_2^-$ with HOCl.

To obtain an overall picture of how the reaction behaves as a function of pH, a composite picture was made by superimposing lines calculated for (i) $k_1^{-\text{OCl}}[^- \text{OCl}]$, (ii) $k_1^{-\text{OH}}[^- \text{OH}]$, (iii) the sum of i and ii, and (iv) $k_2^{\text{HOCl}}[\text{CH}_2\text{NO}_2^-][\text{HOCl}]/[\text{CH}_3\text{NO}_2]_0^{-1}$ at pH values from 6 to 13. These are presented as Figure 4; all vertical coordinate values are in s^{-1} . The following values were used and their sources are indicated: $k_1^{-\text{OH}} = 22 \text{ M}^{-1} \text{ s}^{-1}$ and $\text{p}K_a(\text{CH}_3\text{NO}_2) = 10.2$;¹ $\text{p}K_a(\text{HOCl}) = 7.3$, $k^{-\text{OCl}} = 2.6 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ and $k_2^{\text{HOCl}} = 9500 \text{ M}^{-1} \text{ s}^{-1}$ (this work). The height of the shaded area represents the rate of reaction (in s^{-1}) as a function of pH at $[\text{CH}_3\text{NO}_2]_{\text{St}} = 0.020 \text{ M}$ and $[\text{NaOCl}]_{\text{St}} = 0.20 \text{ M}$.

According to Figure 4 the mechanistic crossover discussed earlier is indicated to come at around pH 11.5–12.0.

References and Notes

- (1) A. T. Nielsen in "The Chemistry of Nitro and Nitroso Groups", Part 1, S. Patai, Ed., Interscience, New York, 1969, pp 364–372.
- (2) (a) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **72**, 3574 (1950); (b) R. Junell, *Z. Phys. Chem., Abt. A*, **141**, 71 (1929); (c) K. J. Pedersen, *K. Dan. Vidensk. Selsk., Mat.-Fys. Medd.*, **12**, 3 (1932); *Chem. Abstr.*, **26**, 5825 (1932); (d) R. Junell, *Svensk. Kem. Tidskr.*, **46**, 125 (1934); (e) R. Junell, *Ark. Kemi, Mineral. Geol.*, **11B** 1 (1934).
- (3) R-R. Lil and S. I. Miller, *J. Chem. Soc. B*, 2271 (1971).
- (4) The authors of ref 3 also offer an alternative interpretation of their kinetic results: attack of $^- \text{OCl}$ on the nitronic acid.
- (5) When proton removal from the nitro compound is rate limiting the mono- and dihalogenated nitro compounds lose a proton much more rapidly than the parent nitromethane (see ref 1, pp 371, 2B). In addition, in the CCl_4 extract of a solution which had just reached cloud point and was quenched, the GLC showed no mono- or dichloronitromethane.
- (6) The ordinate of Figure 1 was $K_{\text{obsd}}/[\text{NaOCl}]$ because of the finding that the reaction was first order in hypochlorite.
- (7) Some runs were made using hypochlorite diluted from a stock solution of ordinary bleach. Standardizations then were also made immediately before reaction. This procedure made no difference in the results as long as the other conditions were identical.
- (8) Reference 1, p 366.
- (9) T. G. Thompson and J. H. Black, *Ind. Eng. Chem.*, **12**, 1067 (1920).