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The Chemistry of Combined

Residual Chlorination

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INTRODUCTION

The decay of the combined chlorine residual was investigated in this work. Recent concerns about the formation of undesirable compounds such as chloroform with free residual chlorination have focused attention on the alternative use of combined residual chlorination. This work investigates the applicability of reactions proposed to describe the transformations and decay of the combined residual with time. The reactions presently accepted proved in some instances to be inadequate to explain the results observed, with modifications being proposed.

PROCEDURES

Sodium hypochlorite was added to buffered solutions of ammonia with the chlorine residual being monitored over periods extending up to 10 days. The reaction was studied at four initial concentrations of hypochlorite of 100, 50, 25 and 10 mg/L as Cl_2 with molar application ratios of chlorine to ammonia, defined herein as M ratios, of 0.90, 0.50, 0.25 and 0.05 at each hypochlorite dose. Sixty-eight experiments were conducted at the pH of 6.6 and 7.2.

The NaOCl solution was prepared by sparging research grade chlorine gas into a dilute NaOH solution. Phosphate salts were used for buffering and $KClO_4$ for maintenance of the ionic strength at $\mu = 0.05$. After the addition in batch with vigorous mixing of hypochlorite to the solution containing all other components, the test volumes were decanted into 200 mL glass stoppered flasks and stored in the dark at 25 ± 1^0C. Factors accounting for changes in pH with time were used in the kinetic constants described later.

The combined chlorine residuals were monitored with the DPD Titrimetric procedure, with some of the results checked with UV scans for reaction times up to 72

hours. The molar absorptivities used for the wavelengths of 231 and 295 nm were in agreement with published data[1-2-3]. Free chlorine and nitrogen trichloride were never detected at any time with either method of analysis, and the total oxidant contained in the first sample collected always equaled (±3%) the total oxidant added to the experiments.

The presence of contaminants, specially bromine, were considered because the reactions studied are very slow. Such bromine effects were believed to be minor because approximate calculations based on available information[4-5] indicate that a rather severe bromine contamination is necessary to affect the results significantly.

The DPD and the UV scan results for monochloramine and dichloramine were nearly identical at a pH of 6.6. The UV scans did give higher concentrations of monochloramine after several hours at the pH of 7.2 with the disagreement increasing with reaction time. The nature of this difference has not yet been ascertained but it could be caused by the oxidation of a small fraction of the NH_3-N to either NO_2^- or NO_3^-.

RESULTS AND DISCUSSION

The continuous decay of monochloramine together with the establishment of a rather flat peak followed by a decay in dichloramine were observed in all of the experiments at the pH of 6.6. See Fig.1.

The occurrence of several important simultaneous reactions precluded the use of conventional methods of analysis such as the initial rate method. However, at low M ratios monochloramine disappearance could be described well with a second-order reaction. This overall second-order rate decreased with larger ammonia concentrations, especially at the pH of 7.2. Finally, it was commonly observed that the concentration of dichloramine beyond the peak was more or less independent of the ammonia

concentration as shown in Fig.2.

Reaction Modeling

The general approach used was first to propose a logical reaction scheme and then to integrate numerically the resulting simultaneous differential equations. The rate constants were subsequently adjusted and the reaction scheme modified. The concentration of NH_3-N was obtained by computation based on the assumption that N_2 was the only end product of the ammonia nitrogen oxidation. This is supported by results of separate experiments not discussed herein[6] which indicate that the N_2 end product fits the observed stoichiometry of the Cl_2/NH_3 redox system.

The well studied rate constants for reactions 1 through 4 listed below could not be checked using batch procedures. The rate expressions proposed by Gray *et. al.*[3] at 25°C were used first in the numerical integration, with the equilibrium acid dissociation constants for HOCl, NH_4^+ and NH_3Cl^+ at 25°C being

$$K_A = 10^{-7.44}, \; K_B = 10^{-9.39}, \text{ and } K_C = 28, \text{ respectively.}$$

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \quad k_1 = 10^{10} \; \frac{L}{mole \; hr} \tag{1}$$

$$NH_2Cl + H_2O \rightarrow NH_3 + HOCl \quad k_2 = 0.070 \; hr^{-1} \tag{2}$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \quad k_3 = 5.5\times10^5 \; \frac{L}{mole \; hr} \tag{3}$$

$$NHCl_2 + H_2O \rightarrow NH_2Cl + HOCl \quad k_4 = 0.002 \; hr^{-1} \tag{4}$$

It appears that all of these reactions can become significant in combined residual chlorination at neutral pH values.

Reaction 5 shown below was first proposed by Granstrom[1] in a slightly different form. An assumed equilibrium expression $\{[NH_2Cl]^2/[NHCl_2][NH_3]\}$ was the basis of the proposed existence of reaction 6, with the rate constants shown being those reported by Gray and co–workers[3]

$$NH_3Cl^+ + NH_2Cl \rightarrow NHCl_2 + NH_4^+ \quad k_5=3.5\times10^6 \frac{L}{mole\ hr} \tag{5}$$

$$NH_4^+ + NHCl_2 \rightarrow NH_2Cl + NH_3Cl^+ \quad k_6=23.0 \frac{L}{mole\ hr} \tag{6}$$

The redox reactions employed in the first reaction scheme are numbered 7, 8 and 9 below. They are based on the work of Wei[7], with I standing for an intermediate species and P for the sum of the end products (N_2,HCl,H_2O). The rate constant shown for reaction 7 was based on the work of Morris *et. al.*[8] with the constant being pH dependent in accord with their observations. The value of k_7 has been modified somewhat to account for our results. The rate constants for reactions 8 and 9 were set arbitrarily to maintain a very small concentration of I at all times[7–9], and to yield the proper ratio of monochloramine to dichloramine after long contact times.

$$NHCl_2 \rightarrow I \quad (slow) \quad k_7 = [\,5.5\times10^{-9}\,]/[\,H^+\,] \quad hr^{-1} \tag{7}$$

$$I + NH_2Cl \rightarrow P \quad (very\ fast) \tag{8}$$

$$I + NHCl_2 \rightarrow P + HOCl \quad (very\ fast) \tag{9}$$

The results of the reaction scheme above compared poorly with the experimental data. The rate of reaction 6 was obviously much too large. At the low M ratios in particular, the model was unable to predict the time and magnitude of the peak

dichloramine concentration. In addition, the numerical calculations at such conditions demonstrated that the concentrations of NH_2Cl generally would be governed by an equilibrium expression of the type $\{[NH_2Cl]^2/[NHCl_2][NH_3]\}$ past the peak in dichloramine. Commonly, no such relationship was evidenced with the results of this study. Finally, the computer simulations at pH values of 3.5 to 5.0 and M ratios larger than 0.50 indicated that the distribution of NH_2Cl and $NHCl_2$ was essentially unaffected by the inclusion of reaction 6.

The model results without reaction 6 were substantially better, especially when the peak dichloramine concentration was less than approximately 2 to 3×10^{-5} molar as shown in Fig.3. The predicted peak in dichloramine was generally too great, however, for peak concentrations in excess of approximately 4×10^{-4} molar as illustrated in Fig.4. This discrepancy was the most pronounced at the lower pH of 6.6, but it was also noticeable in some of the results obtained at a pH of 7.2. Finally, the discrepancy appeared to be independent of ammonia concentration. Reaction 6 was then eliminated from the model and further adjustments made in the reaction scheme.

Adjustment of Rate Constants for Reactions 2, 4 and 5

Increased rates for reaction 4 caused unacceptable discrepancies in the monochloramine results, and a considerably smaller k_5 failed to describe the observed disappearance of NH_2Cl. Likewise, very large rates for k_2 caused too much dependence on the ammonia concentration. It was concluded that the rate constants reported by Gray *et. al.*[3] were applicable to this work with minor modifications except for reaction 6, and that at least one more reaction was responsible for the consumption of NH_2Cl and probably $NHCl_2$ in the peak dichloramine region.

Adjustment of Redox Reactions

A second-order reaction in dichloramine was considered as an additional redox pathway analogous to the one proposed by Cromer *et. al.*[10] for dibromamine decay. Numerical results of the reaction scheme were improved with this addition but some differences in peak $NHCl_2$ concentrations still persisted. The observed stability of the residual at very low pH values and the difficulty in having a mechanism for the necessary pH dependency of a 2nd order $NHCl_2$ reaction prompted the search for another redox pathway.

The alternate path finally adopted was the empirical reaction[2]

$$NH_2Cl + NHCl_2 \rightarrow P \quad k_{10} = 35 \frac{L}{mole\ hr} \tag{10}$$

with the value for k_{10} being determined by numerical trial-and-error simulations. This reaction becomes significant in the neighborhood of the peak $NHCl_2$ concentration, with reaction 7 remaining the most important redox path elsewhere. At low oxidant levels, below 1.5×10^{-4}M, the rate of reaction 10 is considerably smaller than that of reaction 7 at all times. For the contact times and concentration ranges used in this work, the model results with the inclusion of reaction 10 are still consistent with the observation of Morris and co–workers[8] of the independence of the rate of disappearance of $NHCl_2$ from NH_2Cl. Also, reaction 10 has the desired pH dependency, becoming very small at low and high pH values. The model with reaction 10 yielded better results than with the assumed second-order reaction in dichloramine alone but some discrepancy still existed at the highest chlorine doses and lowest pH investigated. This is illustrated in Fig.5 which represents the poorest correlation between predicted and observed concentrations in NH_2Cl and $NHCl_2$. A more typical fit is shown in Fig.6.

It is believed that the discrepancies of the type shown in Fig.5 stem from two sources:

inaccuracies in the rate constants not experimentally verified and additional reactions not included in the model such as a conversion of NH_3 and $NHCl_2$ into NH_2Cl with a rate or mechanism different from that reported by Gray and co–workers[3] as well as possibly some nitrite and nitrate production. The formation of small amounts of an intermediate between NH_2Cl and $NHCl_2$ in reaction 5 is also kinetically feasible, based primarily on the work of Gray *et. al.*[3] concerning the rate limiting step in the disproportionation of monochlorinated amines with different basicities.

CONCLUSIONS

1- In the absence of free chlorine, the concentration of NH_3 does not seem to affect the rate of disappearance of the residual other than through the formation of $NHCl_2$ by NH_2Cl hydrolysis.

2- The reaction between $NHCl_2$ and NH_4^+ to form NH_2Cl is either much slower than reported by Gray *et. al.*[3] or the mechanism is different with a rate limiting step not involving NH_3 or NH_4^+.

3- A redox reaction in addition to the first-order decomposition of $NHCl_2$ appears necessary. Model simulation results indicated that a reaction of the type

$$NH_2Cl + NHCl_2 \rightarrow P$$

added to the first-order $NHCl_2$ decomposition can explain the results observed except at the higher chlorine doses.

ACKNOWLEDGEMENTS

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Figure Caption Sheet

Figure 1 Typical Experimental Results. Chlorine Dose = 100 mg/L; M ratio = 0.90

Figure 2 Effect of Initial NH_3 on $NHCl_2$ Concentration. Chlorine Dose = 100 mg/L; Initial pH = 6.64; M ratio = 0.90(curves 1 and 2); M ratio = 0.05(curves 3 and 4)

Figure 3 Experiment versus Model Results. Reactions 1-9 with 6 ignored; Chlorine Dose = 25 mg/L; M ratio = 0.25; Initial pH = 6.64

Figure 4 Experiment versus Model Results. Reactions 1-9 with 6 ignored; Chlorine Dose = 100mg/L; M ratio = 0.90; Initial pH = 6.64

Figure 5 Experiment versus Model Results. Reactions 1-10 with 6 ignored; Chlorine Dose = 100 mg/L; M ratio = 0.90; Initial pH = 6.64

Figure 6 Experiment versus Model Results. Reactions 1-10 with 6 ignored; Chlorine Dose = 25 mg/L; M ratio = 0.25; Initial pH = 6.64

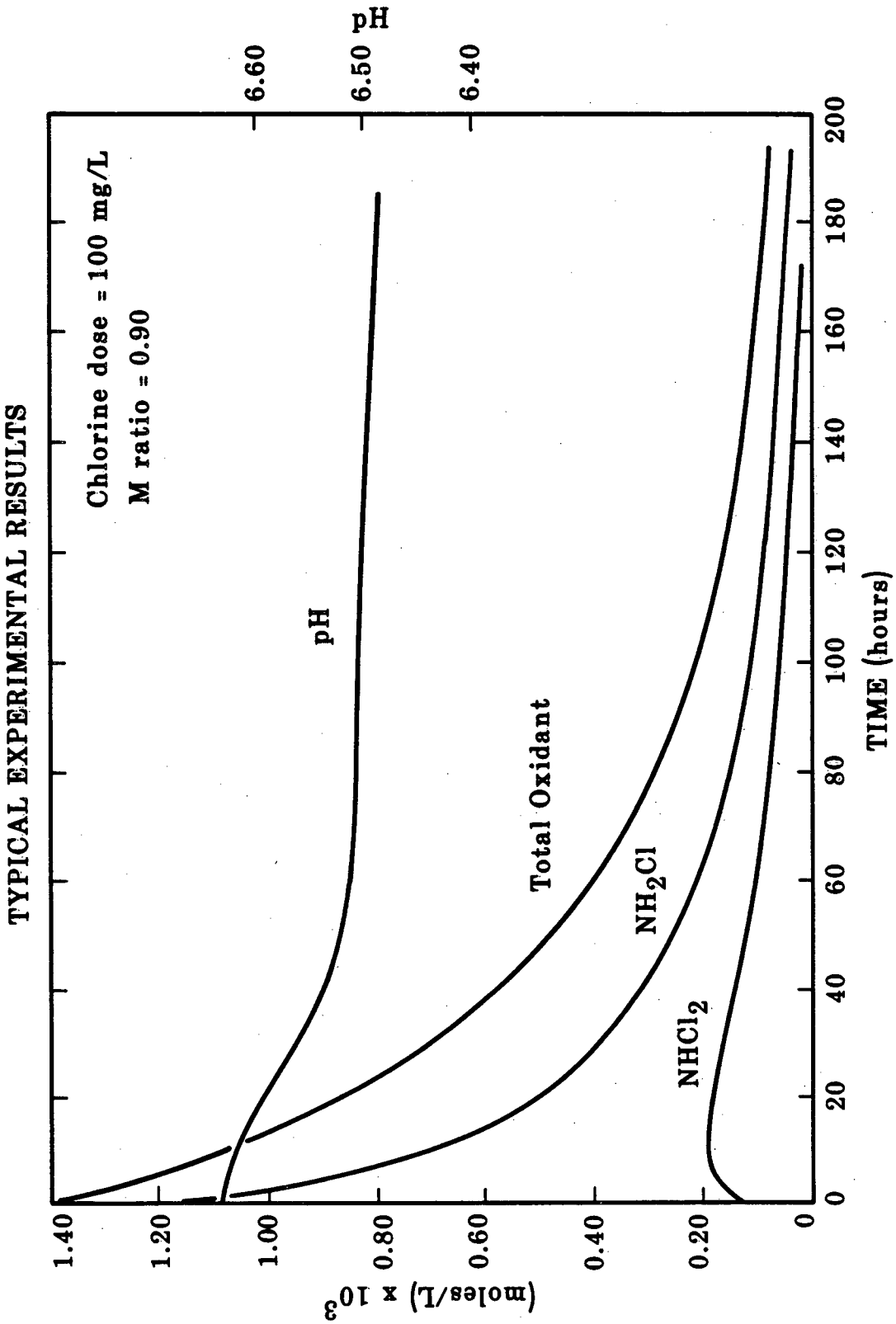

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Figure 1. Typical Experimental Results. Chlorine Dose = 100 mg/L; M ratio = 0.90

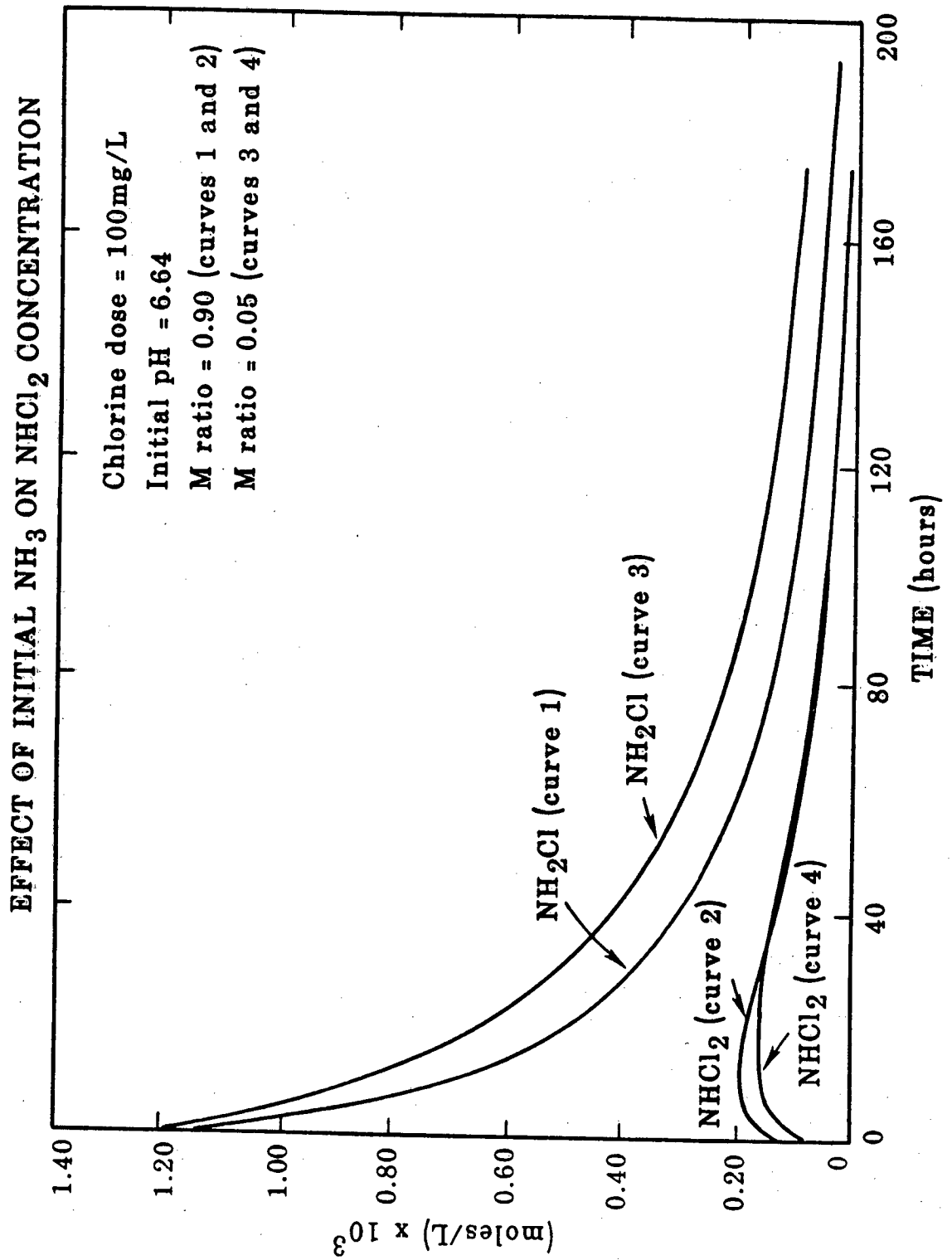

Figure 2. Effect of Initial NH_3 on $NHCl_2$ Concentration. Chlorine Dose = 100 mg/L; Initial pH = 6.64; M ratio = 0.90 (curves 1 and 2); M ratio = 0.05 (curves 3 and 4)

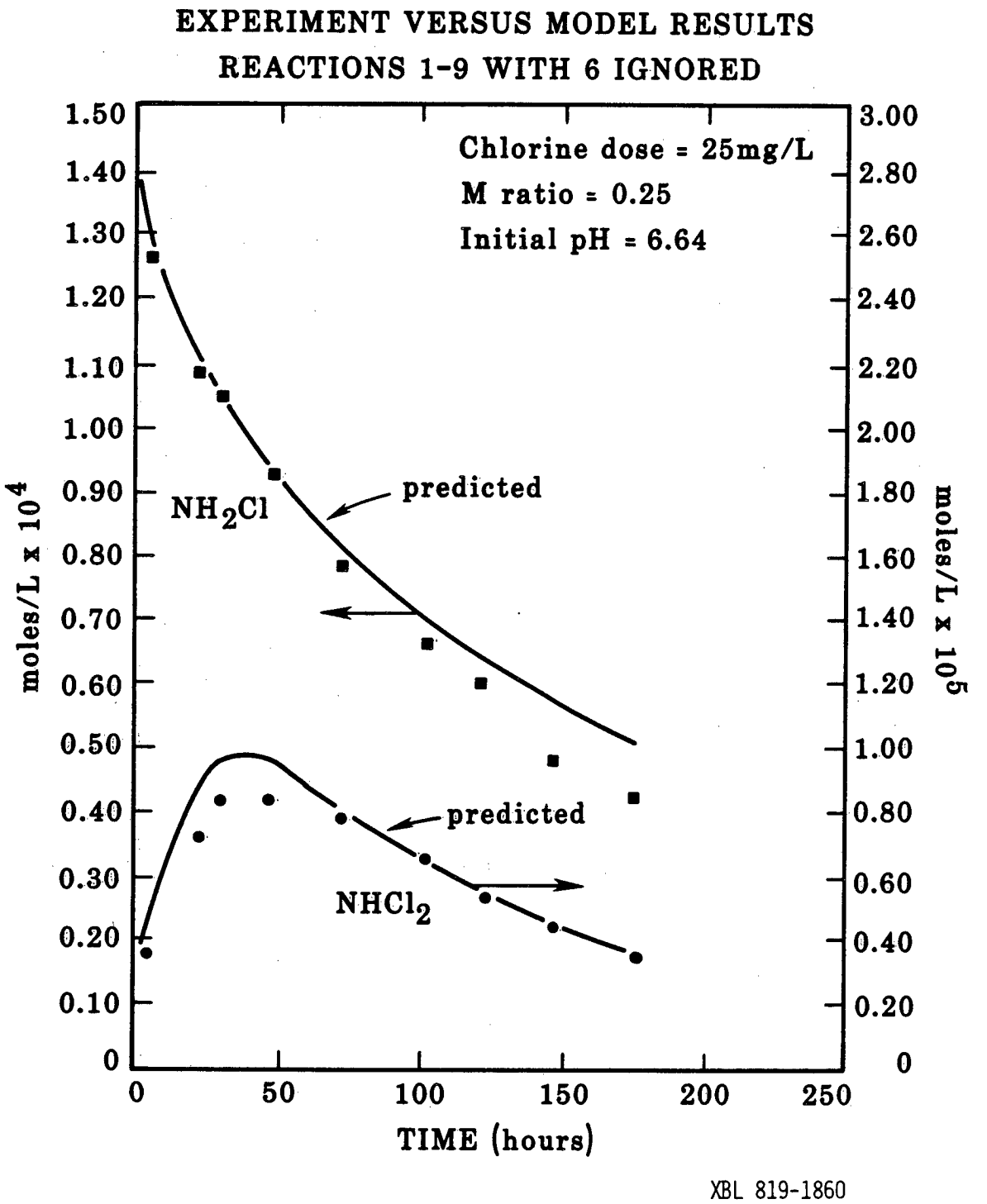

Figure 3. Experiment versus Model Results. Reactions 1-9 with 6 ignored; Chlorine Dose = 25 mg/L; M ratio = 0.25; Initial pH = 6.64

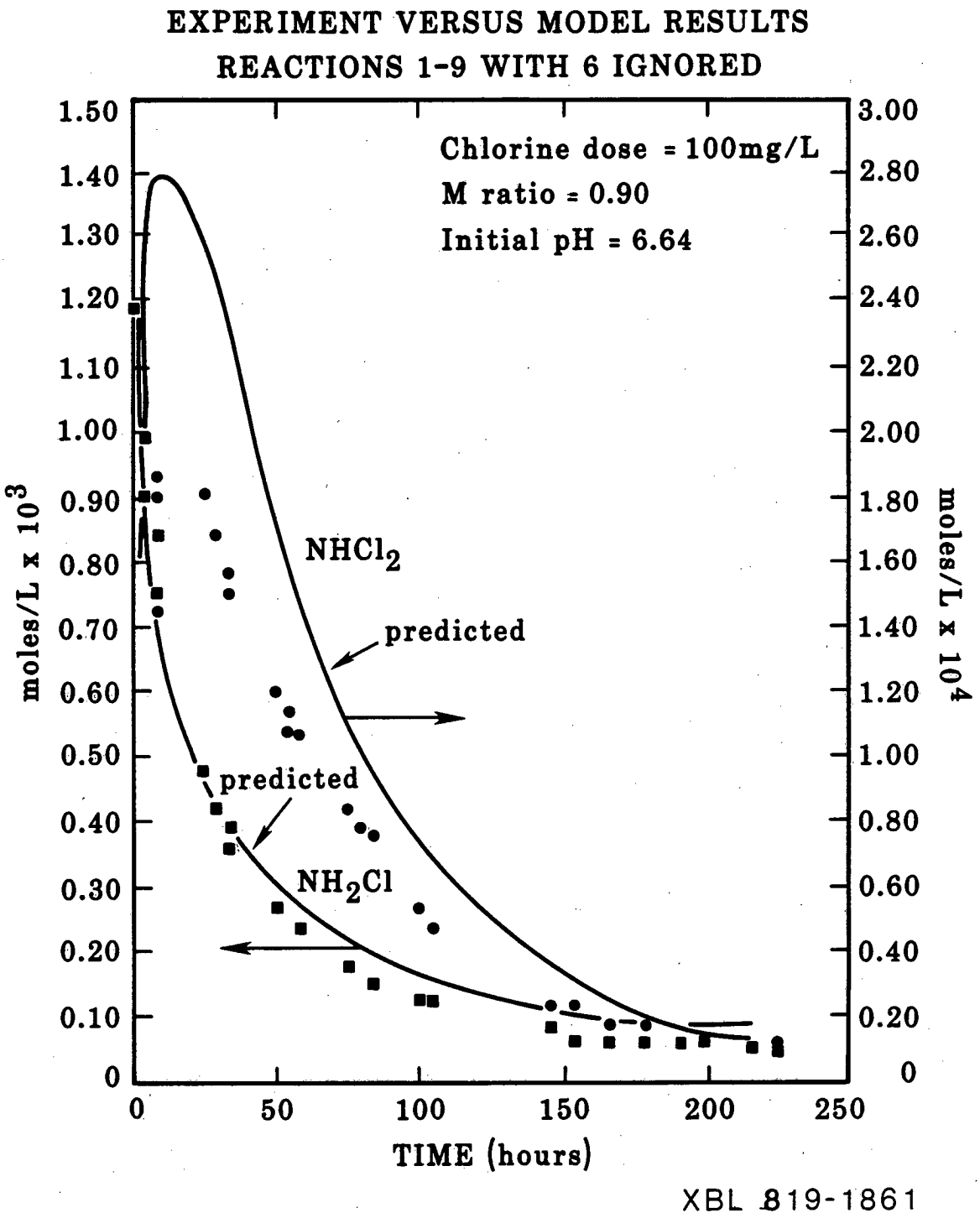

Figure 4. Experiment versus Model Results. Reactions 1-9 with 6 ignored; Chlorine Dose = 100 mg/L; M ratio = 0.90; Initial pH = 6.64

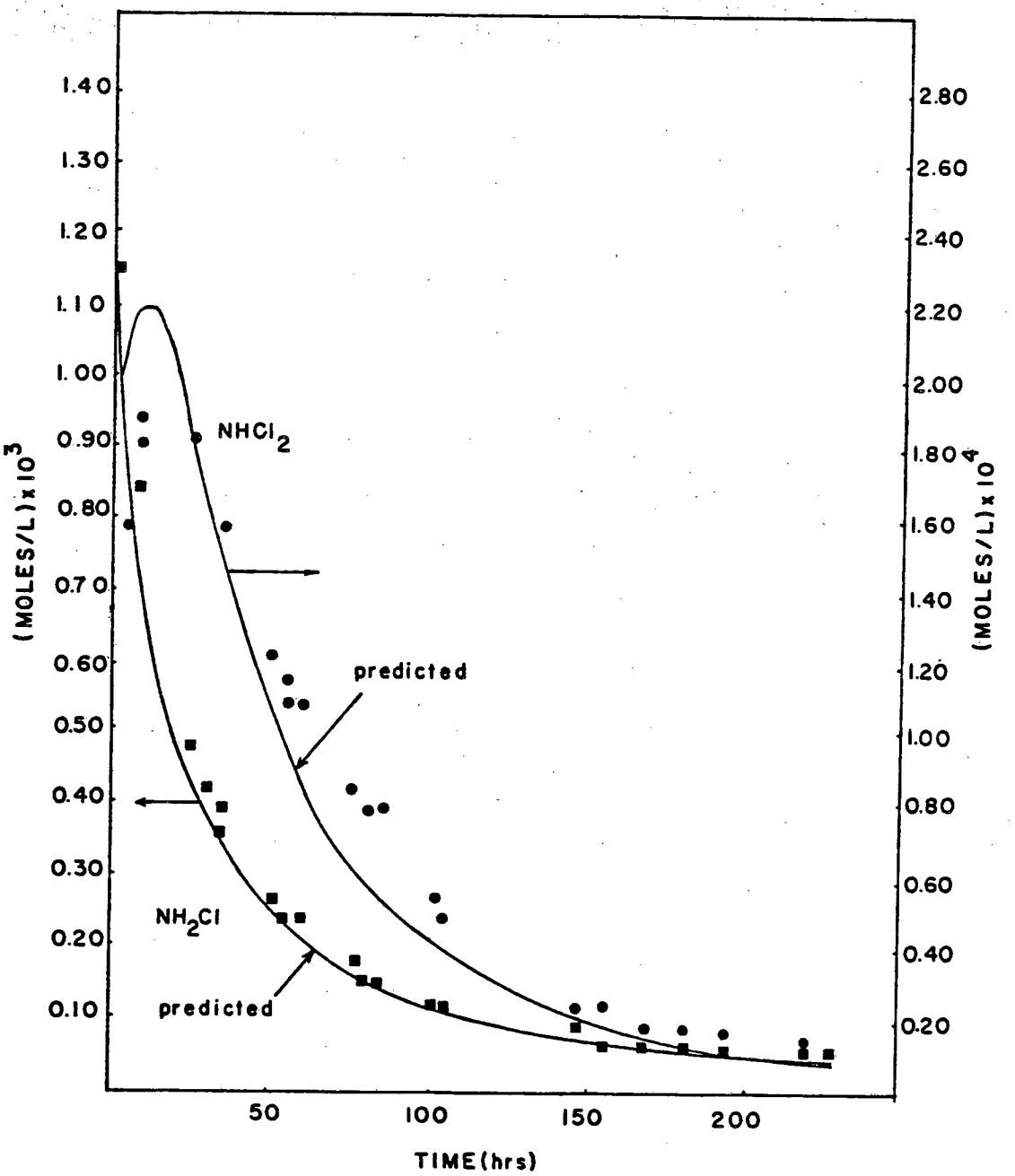

Figure 5. Experiment versus Model Results. Reactions 1-10 with 6 ignored; Chlorine Dose = 100 mg/L; M ratio = 0.90; Initial pH = 6.64

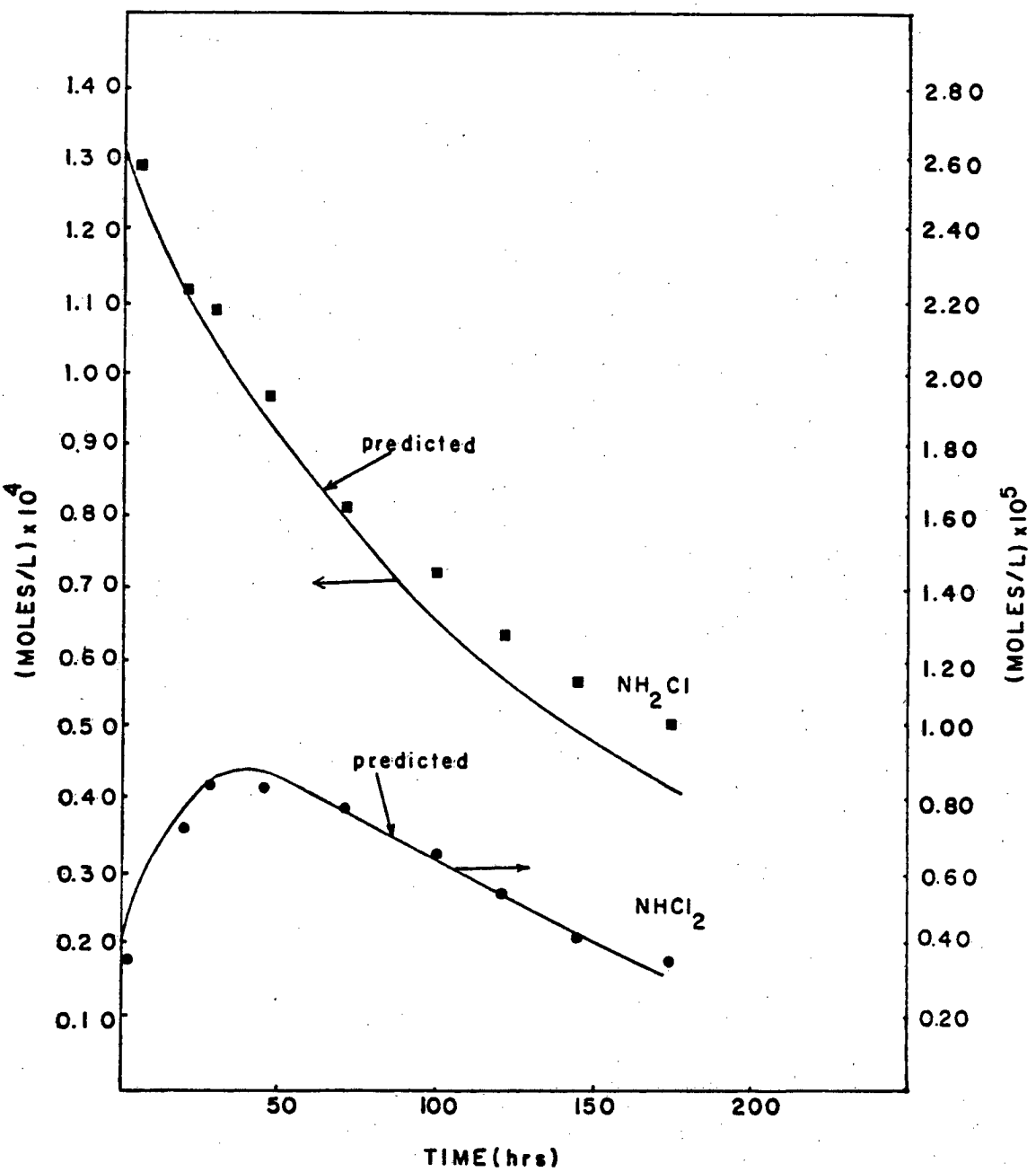

Figure 6. Experiment versus Model Results. Reactions 1-10 with 6 ignored; Chlorine Dose = 25 mg/L; M ratio = 0.25; Initial pH = 6.64

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