The Chemistry of Nitroso-compounds. Part 14.[1] Nitrosation of Amines in Aqueous Solution by Dissolved Gaseous NOCl

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Quantitative results are reported for the interaction of several primary arylamines and secondary alkylamines in either 0.1M-NaOH or phosphate buffer (pH 6.85) at 25 °C with gaseous NOCl. These reactions, which are complete in a few seconds, yield substantial amounts of diazonium ion or *N*-nitrosamine products in addition to NO_2^- from competing hydrolysis. With an excess of amine, however, the conversion of NOCl into *N*-nitrosation products is quantitative.

The dependence of product yields on initial reactant concentrations suggest that *N*-nitrosamine and diazonium ion formation follows Rate = k_2^{Am}[Amine][NOCl]. The reactivity of amines more basic than *N*-methyl-4-nitroaniline (pK_A 1.49) towards NOCl is largely independent of their basicity and most react *ca.* 600—2 000 times faster than H_2O. The reactivity of less basic amines is proportional to their basicity, and no reaction is observed for 2,4-dinitroaniline (pK_A −4.53). For the competitive hydrolysis reaction, HO^- reacts only 94 times faster than H_2O itself.

The results are interpreted as evidence that NOCl reacts with the more basic amines (pK_A >1.49) on encounter, with substrate reactivity being kinetically important only for less basic compounds. This conclusion is supported by a comparison of independent rate measurements for the interaction of aniline and H_2O with NOCl in dilute acid.

WE have shown recently[2] that gaseous N_2O_3 and N_2O_4 are effective reagents for the *N*-nitrosation of both primary and secondary amines dissolved in either neutral or alkaline aqueous solutions. These reactions [equations (1) and (2)] were rapid and yields of *N*-nitrosamine or diazotate ion varied only slightly over a broad range of amine basicities (pK_A 11.12 to −1.0): no reaction was detected, however, for weakly basic amines such as 2,4-dinitroaniline or for amine cations.[2a] The ability to effect the nitrosation of amines in this way implied that competitive hydrolysis of N_2O_3 and N_2O_4 was relatively slow and rate ratios for *N*-nitrosopiperidine formation relative to hydrolysis in 0.1M-NaOH were *ca.* 3 300 for N_2O_3 and *ca.* 2 000 for N_2O_4.[2b] Other evidence suggested that the hydrolysis of both nitrogen oxides was not strongly catalysed by HO^-.[2]

$$R_2NH + N_2O_3(N_2O_4) \xrightarrow{HO^-} R_2NNO + H_2O + NO_2^-(NO_3^-) \quad (1)$$

$$PhNH_2 + N_2O_3(N_2O_4) \xrightarrow{2HO^-} PhN_2O^- + 2H_2O + NO_2^-(NO_3^-) \quad (2)$$

These reactions with N_2O_3 and N_2O_4 were complicated by extensive dissociation of both reagents in the gaseous phase. Further, the results[2b] for the nitrosation of piperidine, in particular, suggested that their constituent nitrogen oxide radicals recombined in the aqueous solution to form more reactive metastable species (ON–ONO and O_2N–ONO, respectively) in contrast to the less reactive thermodynamically stable isomers (O_2N–NO and O_2N–NO_2) formed in the gaseous phase. It seems probable that these metastable N_2O_3 and N_2O_4 isomers react with most amine substrates on encounter so that their formation from radical components is rate-limiting. This would explain the negligible effect of amine basicity on the reaction rates.

In retrospect, the interaction of nitrous gases with amino-compounds in solution is more easily examined using NOCl, as this reagent is much less dissociated than either N_2O_3 or N_2O_4 in the gas phase[3] and it may exist only as a single molecular isomer. Nitrosation by gaseous NOCl in organic solvents is an established, synthetically useful, practice.[4] To our knowledge, reactions of gaseous NOCl with organic substrates in neutral and alkaline aqueous solutions have not previously been reported other than in the patent literature.[5] Reactions in acidic aqueous solutions, however, are well known,[6] where the NOCl is usually generated *in situ* by the addition of HCl to nitrite [equation (3)]. Further, there is good evidence that under these conditions NOCl reacts with several aromatic amines on encounter.[7]

$$HNO_2 + HCl \rightleftharpoons H_2ONO^+ + Cl^- \rightleftharpoons NOCl + H_2O \quad (3)$$

EXPERIMENTAL

Reagents, Substrates, and Products.—NOCl Gas (Matheson 99%) was used without further purification. Piperidine, morpholine, *N*-methylpiperazine, and aniline were dried over solid KOH and then distilled. 4-Nitroaniline, 3,5-dinitroaniline, 2-nitroaniline, and 4-chloro-2-nitroaniline were recrystallised from aqueous ethanol. *N*-Methyl-4-nitroaniline and 4-chloro-*N*-methyl-2-nitroaniline were prepared by methylation of the corresponding trifluoroacetanilide followed by hydrolysis.[8] Authentic *N*-nitrosoamine and diazonium ion products were prepared by standard methods.

Reaction Method.—The aqueous reaction solution (5 ml) of amine (if non-volatile) in either dilute NaOH or phosphate buffer was placed in a 50-ml conical flask and then purged with oxygen-free nitrogen for *ca.* 30 min. Volatile amines were added to the reaction solution after purging. The flask was closed with a Subaseal stopper and brought to 25 °C by immersion in a water-bath. With a syringe, 0.5—10 ml quantities of gaseous NOCl (measured at 1 atm and 25 °C) were injected into the flask through the Subaseal stopper. After the flask had been shaken for 3 min, small aliquots of the aqueous solution were withdrawn for immediate analysis. Independent tests established that the amount of reaction products did not change with time over *ca.* 2 h and that reaction was complete in much less than the usual 3 min shaking period. The dead volume above the reaction solution was *ca.* 60 ml, so the partial pressure of NOCl in the reaction flask prior to mixing varied from 0.167 to 0.008 atm.

Analytical Procedure.—*N*-Nitrosopiperidine, *N*-nitroso-*N*-methylpiperazine, *N*-nitrosomorpholine, and aniline were assayed by g.l.c. against standard solutions of authentic materials prepared in the same solvent as that under investigation. Typically, 0.5—1 μl of the reaction solution was injected directly onto the column (8% Carbowax 20M plus 2% KOH on Chromosorb W, 80—100 mesh at 190 °C) of a Perkin-Elmer F 33 Gas Chromatograph with P–N specific FID using N_2 carrier gas. Concentrations were linearly related to peak heights, which were reproducible for any given sample to better than ±3%.

Concentrations of diazonium ions produced from primary aromatic amines were determined by coupling an aliquot (usually 0.2—2 ml) of the reaction solution with 0.06M-R-salt (2-hydroxynaphthalene-3,6-disulphonic acid, Na salt) in borate buffer at pH or 7.5 (5—10 ml) and measuring the absorbance of the azo dye produced at its $\lambda_{max.}$. The $\lambda_{max.}$ and ε for each azo dye were determined by exhaustive diazotisation of a standard solution of the aromatic amine with an excess of HNO_2 at 0 °C followed by coupling as above. To minimise errors arising from relatively rapid decomposition of the diazonium ions in alkaline solution, these reactions were carried out in phosphate buffers at pH 6.85. Diazonium ion concentrations were then reproducible to better than ∓5%.

The extent of reaction with *N*-methyl-4-nitroaniline [$\lambda_{max.}$ (0.1M-NaOH–2% dioxan) 406 nm log ε 4.14] and 4-chloro-*N*-methyl-2-nitroaniline [$\lambda_{max.}$ (0.1M-NaOH–2% dioxan) 458 nm log ε 3.65] was determined by spectrophotometric assay of the reaction solutions for the reduction in the concentration of starting material. These measurements were reproducible to better than ∓5%.

The concentration of NO_2^- formed by concurrent hydrolysis was determined by the modified Shinn's procedure.[9] Independent checks established that decomposition of the *N*-nitrosoamine products (to release HNO_2) was insignificant during the NO_2^- assay (⩽0.5%).

RESULTS AND DISCUSSION

As for N_2O_3 and N_2O_4 examined previously,[2] our experiments involved the manual mixing of *ca.* 60 ml of a dilute gaseous mixture of NOCl in nitrogen at atmospheric pressure with 5 ml of aqueous amine solution at 25 °C. The solution also contained either dilute NaOH or 0.5M-phosphate buffer (pH 6.85) to prevent any reaction by the usual acid-catalysed nitrosation pathways following hydrolysis of the NOCl. Both the hydrolysis [equation (4)] and nitrosation [equation (5)] reactions appeared to be complete within a few seconds of mixing the gaseous and aqueous phases. We believe the bulk of the amine nitrosation reaction occurs in the aqueous phase following absorption of the gaseous NOCl because it is possible to inhibit the formation of *N*-nitrosamine by

$$NOCl + 2HO^- \longrightarrow NO_2^- + Cl^- + H_2O \qquad (4)$$

$$R_2NH + NOCl \xrightarrow{HO^-} R_2NNO + Cl^- + H_2O \qquad (5)$$

the addition of 0.5M-NaN_3 to the aqueous solution. Details of this effect will be reported later.

Gaseous NOCl appears to be only slightly dissociated [equation (6)] at room temperature. Extrapolation of

$$2NOCl \rightleftharpoons 2NO + Cl_2 \qquad (6)$$

Beeson and Yost's [3] data (from measurements at 100—220 °C) gives a value of $K_p = 7.4 \times 10^{-8}$ atm. for equation (6) at 25 °C. Thus, even at the low partial pressures (0.167—0.008 atm) employed for our experiments, the dissociation is probably less than 1%. Further, dissociation of nitrogen oxide gases in solution is usually lower than in the gaseous phase.[10] We are, therefore, confident that our reactions primarily involve the interaction of molecular NOCl with the amine substrate. This greatly simplifies the interpretation of the results compared to N_2O_3 and N_2O_4, which are probably more dissociated than NOCl and may exist in two isomeric forms.[2]

Reaction of NOCl *with Piperidine.*—The formation of *N*-nitrosopiperidine by this reaction was examined in detail principally to determine the rate expression. Evidence summarised in Figure 1 shows that the yield of *N*-nitrosopiperidine from 2.02×10^{-3}M-piperidine in 0.1M-NaOH at 25 °C varies linearly with both the titratable nitrite concentration (TNC) and the yield of NO_2^- formed by concurrent hydrolysis of NOCl. The former quantity derived from the sum of NO_2^- plus *N*-nitrosamine found in the reaction solution after *ca.* 3 min should equal the amount of NOCl initially added. The related relationship between the yield of *N*-nitrosopiperidine and the initial [piperidine] for reaction with a constant 3×10^{-2}M-NOCl in 0.1M-NaOH at 25 °C is shown in Figure 2. A linear dependence applies only at low [piperidine], because the yield of *N*-nitrosopiperidine levels off to a maximum at [piperidine] ⩾ *ca.* 0.3M. Significantly, this maximum is approximately equal to the [NOCl]. These results imply that the nitrosation reaction, as expected, follows equation (7) and that

$$\text{Rate} = k_2^{Am}[\text{piperidine}][\text{NOCl}] \qquad (7)$$

virtually all the NOCl is trapped by the amine when [piperidine] ⩾ *ca.* 0.3M.

At lower [piperidine], hydrolysis of NOCl [equation (4)] clearly competes with the formation of *N*-nitrosamine [equation (5)]. The relative rates of these reaction can be deduced from the product yields by means of equation (8), where k_2^S refers to the gross rate of hydrolysis. The

$$\frac{k_2^{Am}[\text{piperidine}]}{k_2^S[H_2O]} = \frac{[N\text{-nitrosopiperidine}]}{[NO_2^-]} \qquad (8)$$

average value of the product ratio from Figure 1 is 0.064, whereby substitution in equation (8) assuming $[H_2O] = 55.5$M gives $k_2^{Am}/k_2^S = 1\,760$ for NOCl compared to values of 3 300 and 2 000 obtained earlier for N_2O_3 and N_2O_4, respectively.[2b] It is of interest to determine how much of the gross hydrolysis rate results from reaction by H_2O and HO^-, respectively, and with this in mind the influence of HO^- on the yield of *N*-nitrosopiperidine was also investigated. These results are summarised in Figure 3 for reaction of 2.02×10^{-3}M-

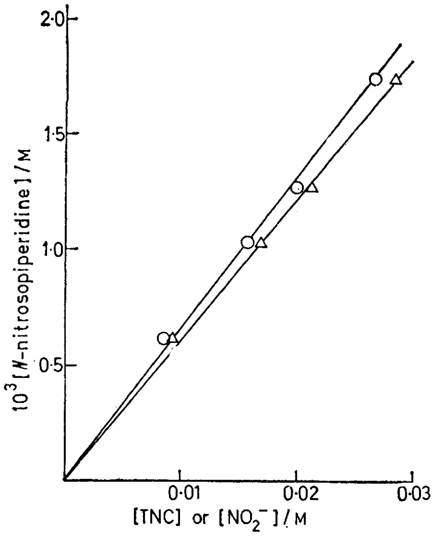

FIGURE 1 Variation in the yield of N-nitrosopiperidine with TNC (△) and NO_2^- (○) for reaction of 2.02 × 10^{-3}M piperidine with NOCl in 0.1M-NaOH at 25 °C

piperidine with 1.14 × 10^{-2}M-NOCl at 25 °C where the linear plot of [NO_2^-]/[N-nitrosopiperidine] *versus* [HO^-] shows that the yield of N-nitrosopiperidine decreases with increasing [HO^-]. To differentiate between hydrolysis by H_2O and HO^-, an extra term has to be included in the left-hand denominator of equation (8). This modified equation, on rearrangement gives equation (9),

$$\frac{[NO_2^-][\text{piperidine}]}{[N\text{-nitrosopiperidine}]} = \frac{k_2^{H_2O}[H_2O]}{k_2^{Am}} + \frac{k_2^{HO^-}[HO^-]}{k_2^{Am}} \quad (9)$$

where $k_2^{H_2O}$ and $k_2^{HO^-}$ refer to the second-order rates of hydrolysis of NOCl by H_2O and HO^-, respectively. From the intercept and slope of Figure 3, respectively, values of $k_2^{Am}/k_2^{H_2O} = 1\,980$ and $k_2^{Am}/k_2^{HO^-} = 21$ are obtained assuming [H_2O] = 55.5M. It follows that HO^- is only 94 times better than H_2O in hydrolysing NOCl (*i.e.* $k_2^{HO^-}/k_2^{H_2O} = 94$). The slope of Figure 1 (*i.e.* k_2^{Am}/k_2^{S}) provides an independent check of the $k_2^{Am}/k_2^{H_2O}$ ratio *via* equation (10) where an appropriate

$$k_2^{Am}/k_2^{S} = \frac{k_2^{Am}[H_2O]}{k_2^{H_2O}([H_2O] + 9.4)} \quad (10)$$

allowance (*i.e.* $k_2^{HO^-} = 9.4\ k_2^{H_2O}$) is made for the contribution to the gross hydrolysis rate by 0.1M-NaOH. Substitution in equation (10) and assuming [H_2O] = 55.5M gives $k_2^{Am}/k_2^{H_2O} = 2\,060$, which is in good agreement with that obtained from Figure 3. Further, the yield of N-nitrosopiperidine expected for a given [piperidine] in 0.1M-NaOH can be calculated from the k_2^{Am}/k_2^{S} ratio in conjunction with equation (8). Comparison with the experimental results in Figure 2 constitutes another independent check of the k_2^{Am}/k_2^{S} ratio and the self-consistency of the experimental results. For Figure 2, the calculated yields (solid line) from 3 × 10^{-2}M-NOCl assuming $k_2^{Am}/k_2^{S} = 1\,760$ are in good agreement with the experimental data (open circles). This confirms that the falling-off in Figure 2 arises from complete trapping of the NOCl by excess of piperidine.

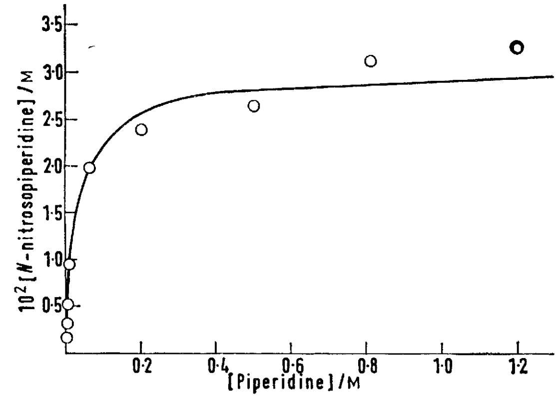

FIGURE 2 Variation in the yield of N-nitrosopiperidine with initial [piperidine] for reaction with *ca.* 3 × 10^{-2}M-NOCl in 0.1M-NaOH at 25 °C. Solid line is the calculated yield assuming $k_2^{Am}/k_2^{S} = 1\,760$ (see text)

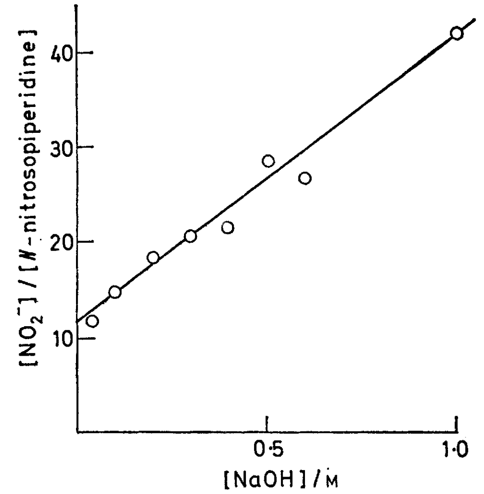

FIGURE 3 Effect of [NaOH] on the yield of N-nitrosopiperidine for the reaction of 2.02 × 10^{-3}M-piperidine with *ca.* 1.14 × 10^{-2}M-NOCl in 0.1M-NaOH at 25 °C

Reaction of NOCl *with Other Amines*.—The influence of substrate basicity on the reactivity of gaseous NOCl was examined with several other primary aromatic amines and secondary mixed or aliphatic amines. The pK_A of these compounds varied from 11.12 to —4.53. Measurements were made at 25 °C in either 0.1M-NaOH or 0.5M-phosphate buffer at pH 6.85. The phosphate buffer was beneficial for the primary aromatic amines [equation (11)] because diazonium ion stability is poor in alkaline

$$ArNH_2 + NOCl \longrightarrow ArN_2^+Cl^- + H_2O \quad (11)$$

media. For a fixed concentration of each amine (1.59 × 10^{-4} to 2.2 × 10^{-3}M depending on the analytical procedure) yields of both N-nitrosation (*i.e.* N-nitrosoamine or diazonium ion) and hydrolysis (*e.g.* NO_2^-) products were determined at several different initial [NOCl] over the range 0.50 × 10^{-2} t0 3.0 × 10^{-2}M. This enabled the construction of plots similar to Figure 1 for piperidine from which k_2^{Am}/k_2^S ratios [*cf.* equation (8)] could be determined. For all but one amine, these plots were linear and the values of k_2^{Am}/k_2^S so obtained are summarised in the Table. The exception was aniline, which gave a curved plot, Figure 4, for data from both the azo-coupling assay {using 2.2×10^{-3}M-aniline} and the g.l.c. determination of unchanged aniline (using 2.2×10^{-4}M-aniline). The cause of this curvature is not fully understood: the reaction solutions became coloured after the addition of NOCl due principally to the formation of *p*-nitrosophenol, but at a concentration too low to explain the curvature. Within experimental error, the two independent procedures for determining the extent of reaction are consistent and Figure 4 is reasonably linear for $[NO_2^-] \leqslant$ *ca.* 1.5×10^{-2}M so a value of $k_2^{Am}/k_2^S = 1\,640$ for aniline was taken from this section of the plot. No reaction with gaseous NOCl was observed for 2,4-dinitroaniline (pK_A —4.53), the weakest base examined, and an upper limit to k_2^{Am}/k_2^S is cited in the Table for 4-chloro-*N*-methyl-2-nitroaniline (pK_A —1.49) because the extent of its reaction was too low to be measured with the usual accuracy.

Values of k_2^{Am}/k_2^S for reaction of various amines with dissolved NOCl at 25 °C

	Amine	pK_A	k_2^{AM}/k_2^S
A	Piperidine	11.12	1 760 [a]
B	Morpholine	8.33	595 [a]
C	*N*-Methylpiperazine	9.8	628 [a]
D	*N*-Methylpiperazinium ion	5.11	1 253 [b]
E	Aniline	4.65	1 640 [b]
F	*N*-Methyl-4-nitroaniline	1.19	931 [a]
G	4-Nitroaniline	0.99	510 [b]
H	3,5-Dinitroaniline	0.35	294 [b]
I	2-Nitroaniline	—0.3	220 [b]
J	4-Chloro-2-nitroaniline	—1.02	113 [b]
K	4-Chloro-*N*-methyl-2-nitroaniline	—1.49	⩽10 [b]

[a] In 0.1M-NaOH. [b] In 0.5M-phosphate buffer (pH 6.85).

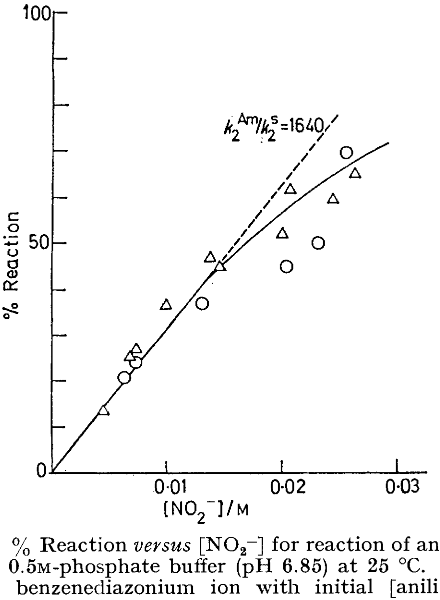

FIGURE 4 % Reaction *versus* [NO$_2^-$] for reaction of aniline with NOCl in 0.5M-phosphate buffer (pH 6.85) at 25 °C. ○ From yield of benzenediazonium ion with initial [aniline] = 2.2×10^{-3}M; △ From amount of unchanged substrate with initial [aniline] = 2.2×10^{-4}M

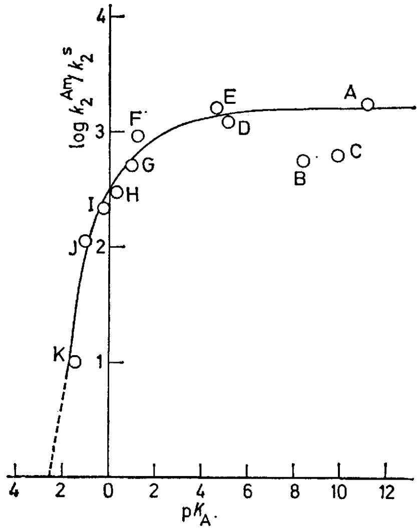

FIGURE 5 Variation of log k_2^{Am}/k_2^S with substrate pK_A for the nitrosation of amines by NOCl in aqueous solution at 25 °C (For definition of A—K see Table)

Reactivity of NOCl.—A significant feature of the k_2^{Am}/k_2^S ratios is their low variation from piperidine (pK_A 11.12) to *N*-methyl-4-nitroaniline (pK_A 1.49). Thus the reactivity of these compounds towards NOCl appears to be influenced by factors other than basicity and, in this context, it should be noted that the *N*-methylpiperazinium ion (in phosphate buffer) is *ca.* twice as reactive as neutral *N*-methylpiperazine (in 0.1M-NaOH). For compounds less basic than *N*-methyl-4-nitroaniline, however, the k_2^{Am}/k_2^S ratio decreases steadily with decreasing pK_A. The overall variation in substrate reactivity, best appreciated from the plot of log k_2^{Am}/k_2^S *versus* pK_A in Figure 5, suggests that either diffusion of NOCl into the aqueous solution is rate-limiting, or reaction of the more basic amines with NOCl is an encounter-controlled process. We cannot discount the former explanation completely,* but favour the latter because independent measurements for the diazotisation of anilines (pK_A 5.08—2.65) in dilute HCl [7] suggest that the interaction of these amines with NOCl proceeds at, or very near, the rate of encounter (*e.g.* Rate = 2.6×10^9 [PhNH$_2$][NOCl] l mol^{-1} s^{-1} for aniline at 25 °C). The sharp reduction in k_2^{Am}/k_2^S for amines below pK_A *ca.* 1.5 can then be related to the onset of reactivity control of the amine nitrosation with hydrolysis of NOCl competing more effectively as the reactivity of the amine decreases. The relatively slow rate of the competing hydrolysis requires further explanation. The rate for H_2O appears to be as expected because the k_2^{Am}/k_2^S ratio approaches unity in the region of pK_A —1.75, the usual basicity assumed for H_2O. The rate for HO^- (pK_A 15.75), however, is *ca.* 21 slower than the rate of nitrosation of piperidine despite

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* If diffusion of NOCl were rate-limiting, the higher reactivity of most amines over HO^- also requires that the amine concentration is higher at the interface than in the bulk of the aqueous solution. Further, the same qualification would have to apply to added 0.5M-NaN$_3$ which inhibits *N*-nitrosamine formation.

expectations that both reactions would proceed at a similar encounter rate. We have no proven explanation for this difference but observations that alkoxide ions react with NOCl at similar rates as piperidine suggest that enhanced solvation of HO^- is responsible.

As noted above, the rate at which aniline reacts with NOCl in dilute acid has been measured independently as $k_2^{\mathrm{Am}} = 2.6 \times 10^9$ l mol^{-1} s^{-1} at 25 °C.[7c] The rate of hydrolysis of NOCl under similar conditions, calculated by means of equation (12) from the equilibrium constants for the formation of both NOCl

$$k_2^{\mathrm{S}} = K^{\mathrm{NOCl}} \,.\, k^{\mathrm{NOCl}}/K^{\mathrm{NO^+}} \qquad (12)$$

$\left(K^{\mathrm{NOCl}} = \dfrac{[\mathrm{HCl}][\mathrm{HNO_2}]}{[\mathrm{NOCl}][\mathrm{H_2O}]} = 0.88 \times 10^3 \text{ at } 25\ ^\circ\mathrm{C}\right)$[11] and $\mathrm{NO^+}\left(K^{\mathrm{NO^+}} = \dfrac{[\mathrm{HCl}][\mathrm{HNO_2}]}{[\mathrm{NO^+}][\mathrm{Cl^-}]} = ca.\ 5 \times 10^6\right)$* assuming that the interaction of Cl^- with NO^+ to give NOCl occurs on encounter $\left(k^{\mathrm{NOCl}} = \dfrac{8RT}{3\eta} = 7.4 \times 10^9 \,\mathrm{l\,mol^{-1}\,s^{-1}} \text{ at } 25\ ^\circ\mathrm{C}\right)$ is $k_2^{\mathrm{S}} = 1.76 \times 10^6$ l mol^{-1} s^{-1}. This gives a calculated value of $k_2^{\mathrm{Am}}/k_2^{\mathrm{S}} = 1\,760$ for aniline, compared to our experimental value of 1 640. Bearing in mind both the approximations and the different conditions for each set of data, this very close agreement may be fortuitous. It does suggest, however, that our mechanistic interpretation of these reactions is correct.

Conclusion.—The findings for gaseous NOCl are very similar to those reported earlier [2] for gaseous N_2O_3 and N_2O_4, where yields of either *N*-nitrosamine or diazonium ion were also relatively insensitive to substrate basicity over the range pK_A 11.12—1.0, but thereafter diminished substantially. As for NOCl, no reaction was apparent with 2,4-dinitroaniline (pK_A —4.53). This supports our deduction that metastable N_2O_3 and N_2O_4 isomers must form from their radical components in the aqueous solution and react with the more basic amines at rates approaching the encounter control limit.[2b]

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* $K^{\mathrm{NO^+}}$ has not been measured in HCl. The value cited is estimated from data [12] for $HClO_4$ and H_2SO_4.

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