II), it is concluded that the carbonium ion mechanism may account for *ca.* 12% (high estimate) of the solvolysis rate of benzyl chloride while it is negligible (1.6% or less) in the solvolysis of *m*-chlorobenzyl chloride.[25] It is obvious that there is an appreciable contribution of the carbonium ion mechanism in the solvolysis of *p*-methylbenzyl chloride.

In order to estimate the contributions of the carbonium ion mechanism to the reactions with CN^-, calculated values of k_I are compared with experimental values of $k_2(B_0 - A_0)$. According to these comparisons, the carbonium ion pathway may account for an appreciable fraction of the reaction rate of benzyl chloride with CN^-, but it is negligible (*ca.* 1% or less) in the reaction of *m*-chlorobenzyl chloride with CN^-.

Conclusions

The first goal of this study was the determination of α-deuterium isotope effects in S_N2 reactions of a benzyl chloride. The data obtained for the reaction of *m*-chlorobenzyl chloride with CN^- and the solvolysis of *m*-chlorobenzyl chloride refer to practically pure S_N2 reactions. Results of k_H/k_D per α-D are a little higher than in the reaction of methyl iodide with CN^- ($k_H/k_D = 0.97$ per α-D)[3] or in the solvolysis of methyl iodide ($k_H/k_D = 0.955$ per α-D).[18] This corresponds to findings for other S_N2 processes in which isotope effects in reactions of methyl iodide and methyl chloride with the same nucleophile are compared.[20]

It is planned to carry out sample calculations of isotope effects from force constants at a later date. It will be necessary to consider solvation of the entering and leaving groups in the transition state model.[5]

The observed increases of k_H/k_D when going from the *m*-chloro to the unsubstituted compound must be due to an increased contribution of the parallel reaction *via* the carbonium ion pathway. It is very difficult to arrive at reliable quantitative estimates of the contributions of the carbonium ion mechanism. It even may be possible that decreasing electron-withdrawing power of the ring substituent would cause *decreases* of the values of k_H/k_D in the S_N2 reactions.

In order to obtain reliable information about the substituent effect on the isotope effects in the S_N2 reactions, it will be necessary to study the reactions of benzyl chlorides containing stronger electron-withdrawing substituents, such as *p*-CN, *m*-NO_2, and *p*-NO_2.

An unexpected side result is the occurrence of the carbonium ion mechanism in the reaction of *p*-methylbenzyl chloride with CN^-. It may be worthwhile to carry out a detailed study of this reaction in which $[Cl^-]$ and $[CN^-]$ are varied while the ionic strength is kept constant.

Registry No.—Cyanide ion, 57-12-5; benzyl chloride, 100-44-7; *m*-chlorobenzyl chloride, 620-20-2; *p*-methylbenzyl chloride, 104-82-5; benzyl-α,α-d_2 chloride, 33712-34-4; *m*-chlorobenzyl-α,α-d_2 chloride, 33712-35-5; *p*-methylbenzyl-α,α-d_2 chloride, 33712-36-6.

Acknowledgment.—The authors are pleased to acknowledge financial support of this work by the U. S. Atomic Energy Commission through Contract No. AT(30-1)-3796. Furthermore, they wish to thank Dr. C. M. Won for writing the computer program for the calculation of rate constants in parallel first- and second-order reactions and Dr. Norman D. Weiner for reading the manuscript prior to submission.

[25] A reviewer inquired about the possibility of α elimination as a side reaction.

It may be desirable to confirm experimentally the absence of α-elimination products in the reactions studied in this work. However, evidence for the insignificance of *base-promoted α elimination* was supplied by Bunnett and Reinheimer[26] for the reaction of *o*-chlorobenzyl chloride with LiOMe in MeOH. The present study is concerned with benzyl chlorides carrying groups with comparable or weaker electron-withdrawing power. It can be concluded that base-promoted α elimination is even less likely under the action of a weak base such as CN^-.

Furthermore, it is completely nonessential for the kinetics if some benzyl cyanide (instead of alcohol) is formed also on the S_N1 pathway, since it concerns the product-forming rather than the rate-determining step. Determination of the benzyl cyanide product ratio merely would supply a high limit of the relative contribution of the S_N2 reaction with CN^-.

[26] J. F. Bunnett and J. D. Reinheimer, *J. Amer. Chem. Soc.*, **84**, 3287 (1962).

Kinetic Study of the Oxidation of *p*-Nitrosophenol by Nitric and Nitrous Acids

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Received September 24, 1971

The acid-catalyzed oxidation of *p*-nitrosophenol by nitric and nitrous acid in aqueous sulfuric acid solution has been studied kinetically in the acidity region of $-1 > H_0 > -6$ by means of polarographic and iodometric analysis. The experimental rate law is first order with respect to *p*-nitrosophenol, nitric acid, and nitrous acid. At low initial nitrous acid concentrations, autocatalysis is observed. The acidity profile of the rate constant has a maximum at $H_0 = -4.5$. The uv absorption of *p*-nitrosophenol is acidity dependent, which is in accordance with a protolytic equilibrium between *p*-nitrosophenol and its conjugate acid. The acidity at which half-protonation occurs is $H_0 = -3.7$. A possible reaction mechanism is discussed which assumes a rate-limiting attack of dinitrogen tetroxide on *p*-nitrosophenol in the low acidity region. At high acidities deprotonation of a reaction intermediate may become rate limiting.

The nitric acid oxidation of *p*-nitrosophenol was first studied by Veibel.[1] He reported a pseudo-first-order rate law with respect to *p*-nitrosophenol, the rate constant being strongly enhanced by an increase of the nitric acid concentration. The reaction was found to occur only if a small amount of nitrous acid was initially present. More recently, Ogata and coworkers have investigated the nitric acid oxidation of various aromatic nitroso compounds with aqueous dioxane as a solvent. In the case of nitrosobenzene,

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[1] S. Veibel, *Z. Phys. Chem., Abt. B.*, **10**, 22 (1930).

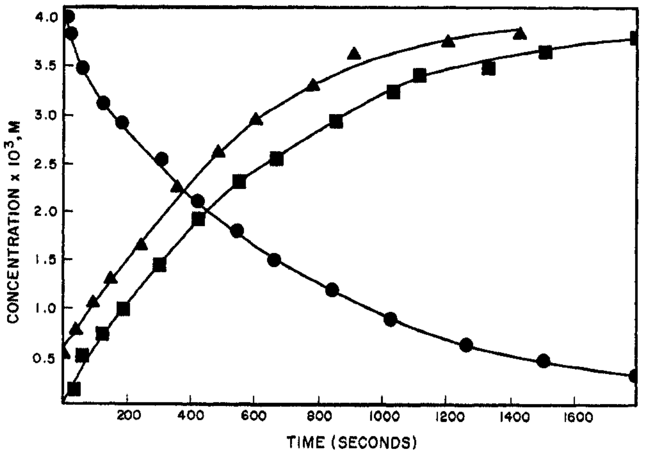

Figure 1.—Concentration-time curves for the oxidation of *p*-nitrosophenol by nitric and nitrous acid: ●, HOC_6H_4NO; ■, $HOC_6H_4NO_2$; ▲, HNO_2. Conditions: $[HOC_6H_4NO]_0 = 4 \times 10^{-3}$ *M*; $[HNO_2]_0 = 7 \times 10^{-4}$ *M*; $[NO_3^-] = 5 \times 10^{-2}$ *M*; $[H_2SO_4] = 5.5$ *M*; $T = 10°$.

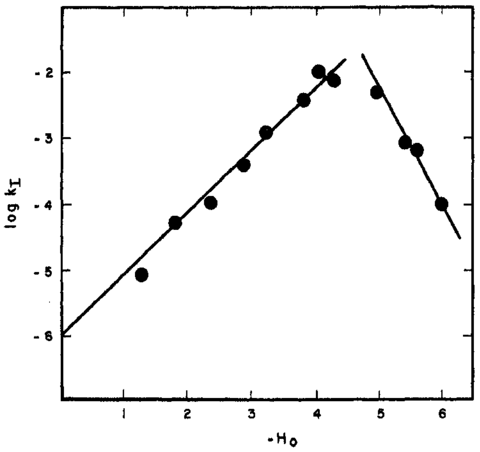

Figure 2.—Plot of the log of the pseudo-first-order rate constant' k_I, *vs.* the acidity function, H_0. Conditions: $[HOC_6H_4NO]_0 = 2 \times 10^{-3}$ *M*; $[HNO_2]_0 = 5 \times 10^{-4}$ *M*; $[NO_3^-] = 2.5 \times 10^{-2}$; $T = +3°$.

the rate law is first order in nitrosobenzene while the order with respect to both nitric and nitrous acids is one-half. The proposed reaction mechanism involves an attack by nitrogen dioxide and its conjugate acid as the rate-limiting step.[2] With identical reaction conditions *p*-nitrosophenol was found to be oxidized much faster than other nitrosobenzenes. Furthermore, in this case, no dependence of the rate on the initial nitrous acid concentration was observed, and the order with respect to nitric acid was unity. The authors account for this fact by assuming that the rate-limiting step is no longer the attack by nitrogen dioxide but rather the decomposition of a reaction intermediate.[3]

We have studied the nitric acid oxidation of *p*-nitrosophenol with aqueous sulfuric acid as a solvent, allowing the reaction to be studied over a wide range of acidities. By selecting suitable reaction conditions it was possible to establish quantitatively the effect of nitrous acid on the reaction. The kinetic data indicate a reaction mechanism which is different from the one that has been suggested by Ogata for the dioxane-water system.

Experimental Section

Materials Used.—Technical *p*-nitrosophenol (American Cyanamid Co.) was purified by recrystallization from ethanol. The pure substance had mp 132–133°. Potassium nitrate (J. T. Baker Chemical Co.), sodium nitrite (Matheson Coleman and Bell), and sulfuric acid (J. T. Baker Chemical Co.) were reagent grade.

Kinetic Procedures.—The kinetic runs were carried out in a thermostat with a temperature constancy of ±0.1°. In a standard run 180 ml of a solution of *p*-nitrosophenol in aqueous sulfuric acid of known acidity were mixed with 20 ml of a solution of sodium nitrite and potassium nitrate in sulfuric acid. To minimize heat effects during mixing, both solutions always had identical acidities. Suitable aliquots (10 ml) of the reaction mixture were quenched in aqueous ammonia (30 ml) at 0°.

Analytical Methods.—The decay of *p*-nitrosophenol concentrations as well as the formation of *p*-nitrophenol was monitored by means of polarographic analysis. The quenched samples had pH 9.8 ± 0.1 and were directly suitable for analysis. Since a sufficiently high concentration of ammonium sulfate was always present, no additional buffer was added. In the concentration range from 5×10^{-8} to 1×10^{-5} *M*, a linear dependence of the wave heights on the concentration was observed. Under our experimental conditions, the half-wave potentials, measured against the saturated calomel electrode were −0.38 ± 0.1 V for *p*-nitrosophenol and −0.73 ± 0.2 V for *p*-nitrophenol. The polarographic measurements were carried out with a Leeds & Northrup Electrochemograph at 25°.

The analysis of nitrous acid could not be achieved by the usual spectrophotometric methods because of the strong optical absorption of the reaction mixture. Therefore, nitrous acid was determined by iodometric titration in which nitrous acid is reduced to nitrogen monoxide. Since reoxidation by air readily occurs, the titration was carried out in an argon atmosphere, but to avoid evaporation of nitrous acid, the solution was initially kept alkaline while the purified argon was passed through. After 5 min the flow rate of argon was reduced. The solution was then acidified with the deoxygenated sulfuric acid and some potassium iodide was added. The titration was carried out with 0.01 *N* sodium thiosulfate solution which had been prepared by diluting a 1 *N* solution with oxygen-free distilled water. With these precautions taken, reproducible results were obtained.

Usually, the reaction was monitored by measuring the decay of *p*-nitrosophenol. However, if initial reaction rates were to be determined, it was more practical to monitor the nitrous acid.

The uv spectra of nitrosophenol and its conjugate acid were measured on a Cary 15 recording spectrophotometer. The ionization ratio was calculated according to a reported method.[4]

Results

Stoichiometry and Empirical Rate Law.—The stoichiometry of the oxidation of *p*-nitrosophenol as given by eq 1 is known from previous work.[1] As in many

$$HOC_6H_4NO + HNO_3 \longrightarrow HOC_6H_4NO_2 + HNO_2 \quad (1)$$

other cases of nitric acid oxidations, the reaction is autocatalyzed by nitrous acid. Consequently, no reaction is observed if a nitrous acid scavenger such as sulfamic acid is added to the reaction mixture. At low initial nitrous acid concentrations an induction period is observed.

To reduce the overall reaction order, all experiments are run with $[H^+] \gg [NO_3^-] \gg [HOC_6H_4NO]$, the acidity being established by sulfuric acid and the nitrate ion being added as potassium nitrate. If a sufficient amount of nitrous acid, added in the form of sodium nitrite, is initially present, the induction period disappears and the reaction obeys pseudo-first-order kinetics with respect to *p*-nitrosophenol.

By simultaneous monitoring of the concentrations of

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(2) Y. Ogata and H. Tezuka, *J. Amer. Chem. Soc.*, **89**, 5428 (1967).

(3) Y. Ogata and H. Tezuka, *J. Org. Chem.*, **33**, 3179 (1968).

(4) V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2102 (1951).

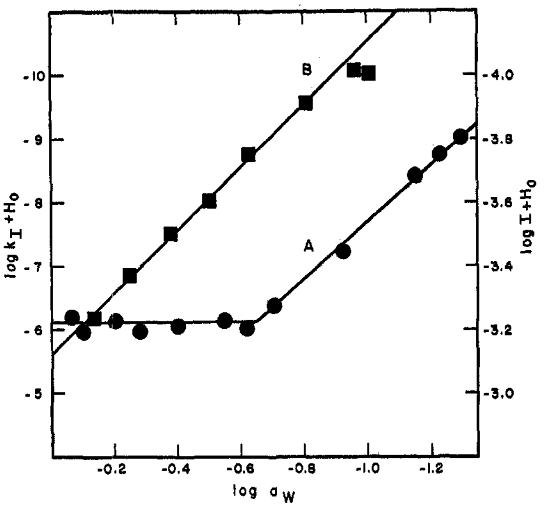

Figure 3.—Bunnett plots: curve A, left scale, data of Figure 2; curve B, right scale, data of Figure 4.

p-nitrosophenol, *p*-nitrophenol, and nitrous acid as shown in Figure 1, the validity of the stoichiometric equation is confirmed. The pseudo-first-order rate coefficient, k_I (Roman numerals indicate experimentally observed rate constants), is constant if $5 \times 10^{-4}\ M <$ [HOC$_6$H$_4$NO] $< 5 \times 10^{-3}\ M$, indicating that the dimerization of *p*-nitrosophenol is kinetically unimportant in this concentration range. For $2 \times 10^{-2}\ M <$ [NO$_3^-$] $< 5 \times 10^{-1}\ M$, the relation $k_\mathrm{II} = k_\mathrm{I}/[\mathrm{NO_3^-}]$ was verified. Therefore, provided that the induction period is suppressed and the acidity remains constant, a simple second-order rate law is obtained (eq 2). For [H$_2$SO$_4$] = 4.5 *M*, [HOC$_6$H$_4$NO]$_0$, =

$$\text{rate} = k_\mathrm{II}[\mathrm{NO_3^-}][\mathrm{HOC_6H_4NO}] \qquad (2)$$

$4 \times 10^{-3}\ M$, [NaNO$_2$]$_0$, = $5 \times 10^{-4}\ M$; and [KNO$_3$] = 0.4 *M*, the pseudo-first-order rate constants amount to $k_\mathrm{I} = 9.6 \times 10^{-4}$ sec^{-1} (0°), $k_\mathrm{I} = 3.2 \times 10^{-3}$ sec^{-1} (10°), $k_\mathrm{I} = 8.7 \times 10^{-3}$ sec^{-1} (19.5°), $k_\mathrm{I} = 2.4 \times 10^{-2}$ sec^{-1} (30°), where the numbers in parentheses denote the reaction temperatures. Graphical evaluation of the Arrhenius equation leads to the temperature dependence given by eq 3.

$$k_\mathrm{I} = 7.2 \times 10^{10} \exp(-17{,}300/RT)\ \mathrm{sec^{-1}} \qquad (3)$$

The Effect of Acidity and the Protonation of *p*-Nitrosophenol.—The pseudo-first-order rate constant, k_I, measured with $5 \times 10^{-4}\ M$ nitrous acid initially present, is strongly affected by a variation of sulfuric acid concentration. Figure 2 depicts a plot of log k_I *vs.* the Hammett acidity function, H_0.[5] The resulting acidity profile has a maximum at $H_0 = -4.5$. which is defined by the intersection of two straight lines, the respective slopes being +0.9 and −2. The data also fit a Bunnett plot.[6] Again one obtains two straight lines which intersect at log $a_\mathrm{w} = -0.65$. The slopes of the low and high acidity parts are $w \simeq 0$ and $w \simeq +5$, respectively, as shown in Figure 3, curve A.

At even higher acidities the rate constant as monitored by the decay of the *p*-nitrosophenol concentration increases again. However, the reaction now apparently leads to polynitro compounds suggesting that, in this acidity region, nitration by attack of the nitronium ion, NO$_2^+$, becomes important.

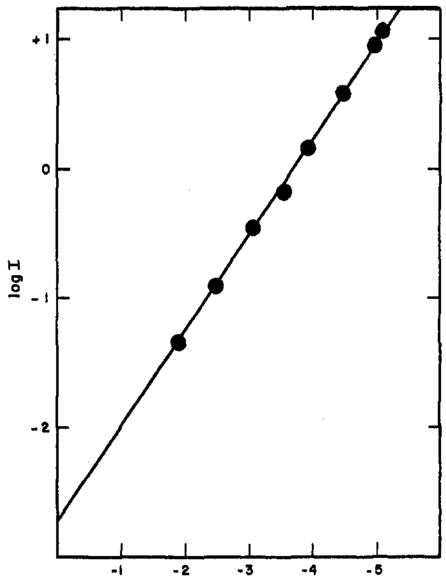

Figure 4.—Logarithmic plot of the ionization ratio, *I*, *vs.* the acidity function, H_0.

The uv spectrum of *p*-nitrosophenol in neutral aqueous solution shows an absorption maximum at 300 nm with an extinction coefficient of 1.8×10^4 M^{-1} cm^{-1}. If the acidity is increased, the absorption at 300 nm decreases. Simultaneously the appearance of a new absorption with a maximum at longer wavelengths is observed. At an acidity of $H_0 = -5.6$, this maximum is shifted to 390 nm with an extinction coefficient of 1.7×10^4 M^{-1} cm^{-1}. The latter value is probably not very accurate owing to the slow decomposition of *p*-nitrosophenol at high acidity.

The absorption at high acidities may be accounted for in terms of a protolytic equilibrium between *p*-nitrosophenol and its conjugate acid according to eq 4. If

$$\mathrm{HOC_6H_4NO} + \mathrm{H^+} \rightleftharpoons \mathrm{HOC_6H_4\overset{+}{N}OH} \qquad (4)$$

one calculates the ionization ratio, *I*, from the absorptivities at 300 nm and 390 nm,[4] a plot of log *I* *vs.* $-H_0$ is linear with a slope of +0.74. The point of half-protonation is at $H_0 = -3.7$ (Figure 4). A Bunnett plot is likewise linear, the slope being $w = 1.0$. Comparison of curves A and B in Figure 3 shows that the acidity function which governs the acidity dependence of the rate constant is definitely different from the one related to the protonation of *p*-nitrosophenol.

The acidity dependence of the ionization ratio also fits a Bunnett–Olson LFER plot[7] which yields a pK_A of −2.85 and a slope of +0.3. The p*K* obtained from the Bunnett–Olson plot is 0.85 log unit more positive than the H_0 value of half-protonation. This indicates that the H_0 scale differs by this amount from the true acidity function applicable to eq 4.

It should be noted that the neutral form of *p*-nitrosophenol is tautomeric with benzoquinone monoxime, the equilibrium being on the side of the oxime.[8,9] In basic aqueous solution, *p*-nitrosophenol dissociates

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[5] C. F. O'Connor, *J. Chem. Educ.*, **46**, 686 (1969).

[6] J. F. Bunnett, *J. Amer. Chem. Soc.*, **83**, 4956, 4968, 4973, 4978 (1961).

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[8] R. K. Norris and S. Sternhell, *Tetrahedron Lett.*, 97 (1967).

[9] H. Uffmann, *ibid.*, 4631 (1966).

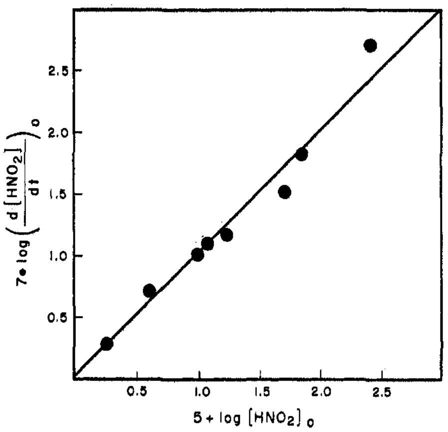

Figure 5.—Dilogarithmic plot of the initial reaction rate *vs.* the initial nitrous acid concentration. Conditions: $[HOC_6H_4NO]_0 = 4 \times 10^{-3}\,M$, $[NO_3]^- = 5 \times 10^{-2}\,M$; $[H_2SO_4] = 5.5\,M$; $T = 10°$.

with formation of a resonance stabilized anion which has an absorption maximum at 397 nm.[10]

The Induction Period and the Influence of Nitrous Acid.—Since nitrous acid is a reaction product and at the same time a reactant, its kinetic order can only be elucidated by determining the variation of the initial rate with the initial nitrous acid concentration, provided that $[HNO_2]_0 \ll [HOC_6H_4NO]_0 \ll [HNO_3]$. Figure 5 depicts a plot of log $(d[HNO_2]/dt)_0$ as determined by the tangent method *vs.* log $[HNO_2]_0$. For $1.5 \times 10^{-5}\,M < [HNO_2]_0 < 2.4 \times 10^{-3}\,M$, a straight line with unity slope is obtained. This implies a first-order dependence on nitrous acid concentration. Consequently, the complete rate law at constant acidity is given by eq 5. The rate constant k_{III} can be evaluated

$$\text{rate} = k_{III}[HNO_2][NO_3^-][HOC_6H_4NO] \qquad (5)$$

if the reaction is carried out in the presence of just enough nitrous acid to make the induction period disappear. For a typical experiment depicted in Figure 1, one obtains a half-life of 450 sec and a value of $k_{III} = 4.3 \times 10^1\,M^{-2}\,\text{sec}^{-1}$. The data of Figure 5 are represented by eq 6. The slope obviously represents

$$(d[HNO_2]/dt)_0 = 9 \times 10^{-3}[HNO_2]_0 + 8 \times 10^{-8}\,M\,\text{sec}^{-1} \qquad (6)$$

the pseudo-first-order rate constant with respect to nitrous acid. Therefore, one should expect that $k_{III} = \text{slope}/[\text{nitrosophenol}]_0 \times [NO_3^-]$. Inserting the concentrations of Figure 5, one obtains $k_{III} = 4.5 \times 10^1\,M^{-2}\,\text{sec}^{-1}$. This agrees with the value observed above for an induction period of zero. Therefore, the validity of the rate law, eq 5, is evidently not confined to the limiting condition of a zero induction period. The small positive intercept in eq 6, which represents the initial rate at $[HNO_2]_0 = 0$ can be accounted for either by spontaneous decomposition of nitric acid with formation of nitrous acid or by trace impurities of nitrite in the potassium nitrate used in our experiments. The direct oxidation by nitric acid alone can be ruled out because of the complete quenching of the reaction by sulfamic acid.

Discussion

In an acidic system containing nitrous and nitric acids, various species are present which are known to possess oxidizing properties.[11] Among these, however, only NO_2 and N_2O_4 require the presence of both nitric and nitrous acids for their formation. Since no significant reaction is observed if either of them is absent, the major reaction path has to involve an attack by either NO_2 or N_2O_4. For NO_2 as the oxidizing agent an order of one-half with respect to both nitric acid and nitrous acids has to be expected, provided that the equilibrium of eq 7 is shifted to the right side. A

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad (7)$$

kinetic dependence of this type has been found in the case of the oxidation of nitrosobenzene in dioxane–water[2] and also for the oxidation of 2,5-dimethylnitrosobenzene in carbon tetrachloride.[12] Contrary to these results, we have obtained an order of unity for both reactants. No deviation from a first-order dependence has been observed for concentrations of HNO_2 as low as $1.5 \times 10^{-5}\,M$, in spite of the fact that in this range the equilibrium concentration of NO_2 is already significant based on a dissociation constant of $1.53 \times 10^{-5}\,M$.[13] For NO_2 to be the oxidizing entity, this would necessarily require that the order for nitrous acid change from unity to one-half at low concentrations.

Based on these considerations N_2O_4 appears to be the most likely oxidizing species. This gives rise to a "true" rate law as given by eq 8. To obtain an estimate

$$\text{rate} = k_0[N_2O_4][HOC_6H_4NO] \qquad (8)$$

of k_0 one has to consider eq 9 for which $K = 3 \times 10^{-3}\,M^{-1}$ has been reported[14] (a_w = activity of water).

$$\frac{[N_2O_4]a_W}{[HNO_2][H^+][NO_3^-]} = K \qquad (9)$$

With $[NO_3^-] \gg [HNO_2]$ the N_2O_4 equilibrium concentration is given by eq 10. If one assumes $[H^+]$

$$[N_2O_4] = \frac{K[H^+][NO_3^-][HNO_2]_{\text{anal}}}{a_W + K[H^+][NO_3^-]} \qquad (10)$$

$= 3.5 \times 10^2\,M$ and $a_w = 0.53$ for the reaction at $[H_2SO_4] = 5.5\,M$ corresponding to Figure 5, the second term of the denominator of eq 10 becomes negligible provided that $[NO_3^-] < 5 \times 10^{-2}\,M$. Therefore, comparing eq 5 and eq 8 one obtains eq 11. This yields an estimated value of $k_0 = 2.4 \times 10^1\,M^{-1}\,\text{sec}^{-1}$.

$$k_0 = \left(\frac{k_{III}a_w}{[H^+]K}\right) M^{-1}\,\text{sec}^{-1} \qquad (11)$$

The kinetic results may be explained in terms of a mechanism described by the reaction sequence shown in eq 12a–d. At higher acidities where *p*-nitrosophenol

$$H_3O^+ + NO_3^- \rightleftharpoons HNO_3 + H_2O \qquad (12a)$$

$$HNO_3 + HNO_2 \rightleftharpoons N_2O_4 + H_2O \qquad (12b)$$

$$N_2O_4 + HOC_6H_4NO \longrightarrow HOC_6H_4NO_2 + N_2O_3 \qquad (12c)$$

$$N_2O_3 + H_2O \longrightarrow 2HNO_2 \qquad (12d)$$

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[10] E. Havinga and A. Schors, *Recl. Trav. Chim. Pays-Bas*, **69**, 457 (1950).

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[13] M. Graetzel, A. Henglein, J. Lilie, and G. Beck, *Ber. Bunsenges. Physik. Chem.*, **73**, 646 (1969).

[14] J. V. L. Longstaff and K. Singer, *J. Chem. Soc.*, 2610 (1954).

exists predominantly in its protonated form, a reaction path given by eq 12e and 12f which is parallel to 12c

$$N_2O_4 + HOC_6H_4N^+OH \longrightarrow HOC_6H_4\overset{+}{N}O_2H + N_2O_3 \quad (12e)$$

$$HOC_6H_4\overset{+}{N}O_2H + H_2O \longrightarrow HOC_6H_4NO_2 + H_3O^+ \quad (12f)$$

has to be assumed. The reactions which cause the autocatalysis are 12c and 12e at low and high acidities, respectively. Reaction 12d may be considered to be fast except at very low values of a_w.[15]

The true rate law, eq 8, was derived with the assumption that the preceding steps are fast. This is obviously true for the protolytic equilibrium, 12a. The rate constant for the reverse reaction of eq 12b, determined by pulse radiolytic measurements, is 1×10^3 sec^{-1} $\times a_w$.[13] With this value and the previously mentioned value of the equilibrium constant, the forward rate constant is calculated to be $1.9 \times 10^3\ M^{-1}$ sec^{-1}.

Since the initial concentration of *p*-nitrosophenol is of the order of $10^{-3}\ M$, the equilibrium approximation appears to be applicable. Consequently, it is justified to assume that eq 12c is the rate-limiting step as long as the relative concentration of protonated *p*-nitrosophenol is not significant. The positive slope of the acidity profile of the rate constant is due to the formation of undissociated nitric acid which is known to increase according to the H_0 acidity function.

Since it is reported[16] that the nitrate ion is half-protonated at $H_0 = -2.8$, the rate constant should become acidity independent at $H_0 \simeq -4$. The experimental acidity profile, however, exhibits a maximum at $H_0 = -4.5$ and a decrease of the rate constant at higher acidities. This effect may be connected with a significant heterolytic dissociation of N_2O_4 at high acidity, which would reduce its equilibrium concention.[17,18] Alternatively, a protonated N_2O_4 species might be formed which could also account for the observed behavior, since its reaction with the equally charged protonated nitrosophenol is expected to be slow.

Most likely, however, a change in the rate-determining step from eq 12c to eq 12f is responsible for the rate decrease. This is supported by the slope of the Bunnett plot, Figure 3A, where the high acidity part with $w = 5$ is typical for a reaction whose rate is limited by a transfer of a proton to the solvent.[19]

Registry No.—*p*-Nitrosophenol, 104-91-6; nitric acid, 7697-37-2; nitrous acid, 7782-77-6.

Acknowledgment.—We wish to thank Professor N. C. Deno for helpful discussions and for written comments to improve the manuscript.

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Kinetics and Mechanism of the Hydrolysis of Guanosine and 7-Methylguanosine Nucleosides in Perchloric Acid

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Received September 7, 1971

Rates of hydrolysis of guanosine (Guo) and 7-methylguanosine (7-MeGuo) to ribose and guanine or 7-methylguanine were obtained spectrophotometrically and polarimetrically in 1–9 M $HClO_4$ at 30.0°. In 1–7 M $HClO_4$ the substrates are converted to their diprotonated forms to the extent of about 1–90%. Rate changes in this region are approximated by the expression $k_\psi = kh_0/(h_0 + K_a)$, where h_0 is the Hammett acidity function and k is the first-order rate constant for fragmentation of the nucleoside. For Guo k is $8.8 \pm 0.6 \times 10^{-4}$ sec^{-1} and for 7-MeGuo k is $1.2 \pm 0.1 \times 10^{-3}$ sec^{-1}. "Kinetic" (equilibrium) dissociation constants or pK_a values for Guo and 7-MeGuo are −2.42 (−2.42) and −2.48 (−2.61), respectively. In 7–9 M $HClO_4$ rates continue to increase slightly for Guo but decrease slightly for 7-MeGuo. A mechanism involving cleavage of a protonated ribose ring to give a Schiff-base intermediate is ruled out. Instead, a mechanism (A-1) involving reversible protonation of the purine ring to give a dication followed by rate-limiting cleavage of the heterocycle–sugar bond is advanced. This is similar to the mechanism of hydrolysis of the monocationic forms of these substrates in dilute acid.

Nucleosides, fragments of nucleic acids containing a heterocyclic base bonded to a sugar, are model compounds for the study of nucleic acid hydrolysis.[1] We have shown that the acid-catalyzed hydrolysis of some purine nucleosides takes place by the reaction of mono- as well as diprotonated forms.[2] Guanosine (Guo) and deoxyguanosine (dGuo) hydrolyze first by undergoing reversible protonation of the purine ring to give a monocation and then by rate-determining fragmentation to give a purine and a cyclic carboxonium ion form of the sugar. This cation on reaction with water gives the sugar, ribose or deoxyribose (Scheme I). This mechanism of hydrolysis of a monoprotonated species is supported, for example, by the fact that 1,7-dimethylguanosinium ion (1,7-diMeGuO$^+$) reacts at very nearly the same rate as monoprotonated Guo. The dimethyl cation, since it already bears a positive charge, need not protonate in order to react and hence it undergoes ready fragmentation.

In this paper we consider and eliminate the possibility that mono- and diprotonated purine nucleosides react by different mechanisms. We report the results of the hydrolysis of Guo and 7-methylguanosine (7-MeGuo) in perchloric acid. Our results allow a distinction to be made between two mechanistic possibil-

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[1] H. S. Loring in "The Nucleic Acids," E. Chargaff and J. N. Davidson, Ed., Academic Press, New York, N. Y., 1955, Chapter 5.

[2] J. A. Zoltewicz, D. F. Clark, T. W. Sharpless, and G. Grahe, *J. Amer. Chem. Soc.*, **92**, 1741 (1970). Additional references are included in this paper.