Hydrolysis Equilibrium of Dinitrogen Trioxide in Dilute Acid Solution

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Solutions of nitrous acid in dilute (0.1 M HCl) or more concentrated (~5 M HClO$_4$) acid exhibit a contribution to the ultraviolet absorbance that is quadratic in [HNO$_2$]. In dilute acid this excess absorbance is attributed to N$_2$O$_3$ formed through equilibrium 1, 2HNO$_2$ = N$_2$O$_3$ + H$_2$O. From the measured spectrum of $\epsilon_{N_2O_3}K_1$ vs. wavelength (245–260 nm) and by comparison with $\epsilon_{N_2O_3}$ obtained in pulse radiolysis by Grätzel et al., K_1 is determined as $(3.03 \pm 0.23) \times 10^{-3}$ M^{-1}, in agreement with the value calculated thermochemically. The coefficient of physical solubility of N$_2$O$_3$ in water is computed as 0.70 ± 0.05 M atm^{-1}. The extinction quadratic in [HNO$_2$] is independent of acid concentration in dilute acid but increases strongly in more concentrated acid, suggesting a possible second absorbing species of stoichiometry HN$_2$O$_3^+$.

Introduction

The aqueous phase equilibrium (eq 1) between nitrous acid

$$2HNO_2 = N_2O_3 + H_2O \qquad (1)$$
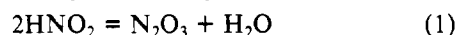
and its anhydride N$_2$O$_3$ is of current interest[1] as a link in the determination of the Henry law constants of NO$_2$, N$_2$O$_3$, and N$_2$O$_4$ and has been of interest as well for some time in the interpretation of the kinetics of diazotization of amines.[2] Equilibrium 1 was studied in perchloric acid solution (several molar) by Bunton and Stedman[3] and by Turney.[4] Turney obtained a value for the equilibrium constant

$$K_1 = [N_2O_3]a_w/[HNO_2]^2$$

of 0.20 M^{-1} ± 20 °C based on independent determinations by spectrophotometry and solvent extraction. This value was later corrected[5] to account for the influence of ionic strength upon the activities of the dissolved species, leading to a thermodynamic value for K_1 of 0.16 M^{-1} ± 20%. However, this value has recently been questioned. Consideration of thermochemical cycles involving aqueous N$_2$O$_3$[1] suggests that the value of $K_1 = 0.16$ M^{-1} may be too great by a factor of ca. 70. A similar discrepancy is suggested by the estimate[6] of K_1 from the kinetics of N$_2$O$_3$ decomposition and formation reactions, the latter inferred from studies of isotope exchange and diazotization, presumed to take place through a N$_2$O$_3$ intermediate.

A possible explanation for the discrepancy between these estimates of K_1 and the measured value[4] may be that the latter was influenced by the highly acidic medium employed, despite the apparent absence of any direct participation of H$^+$ in the equilibrium. Such an influence of perchloric acid upon the magnitude of K_1, to an extent greater than its influence upon the water activity, may be inferred also from the data of Bunton and Stedman.[3] These considerations have led us to undertake a determination of K_1 at dilute acid concentrations and to examine the dependence of K_1 upon increasing acid concentration.

Dinitrogen trioxide, N$_2$O$_3$, is known in gas, liquid, and solid phases.[7] The liquid is characterized as "cobalt blue". This characteristic blue color is exhibited as well by solutions of N$_2$O$_3$ in water[8] and nonpolar solvents.[9,10] The absorption spectra in nonpolar solvents are typically broad (500–900 nm, $\lambda_{max} \approx 650$ nm) and weak ($\epsilon_{max} \approx 10$–20 M^{-1} cm^{-1}). Such a characteristic blue color and absorption spectrum is exhibited also by solutions of nitrous acid in concentrated sulfuric[11] and perchloric acids.[3,4] This absorption, ascribed to N$_2$O$_3$, served as the basis for the spectrophotometric determination of K_1 in perchloric acid, by Bunton and Stedman and by Turney.

A second, much more intense absorption attributed to N$_2$O$_3$ lies in the ultraviolet region (200–360 nm). In the gas phase

the absorption maximum is ~220 nm with $\epsilon_{max} \approx 6000$ M^{-1} cm^{-1}.[10,12] A similar, somewhat more intense transient absorption spectrum attributed to N$_2$O$_3$ in aqueous solution has been observed in pulse radiolysis[13] and flash photolysis[14] investigations of nitrite solutions saturated with NO. The former study found the formation (on a microsecond time scale) and subsequent decay (milliseconds) of an absorption band reproduced in Figure 1. The kinetics of the appearance of this band was ascribed to production of N$_2$O$_3$ by the aqueous-phase reaction (2) and of the disappearance to hydrolysis by the

$$NO + NO_2 = N_2O_3 \qquad (2)$$
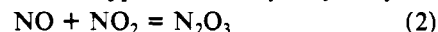
reverse of reaction 1.

Equilibrium and rate constants were obtained for reaction 2 as was the rate constant for the reverse of reaction 1. The absolute value of $\epsilon_{N_2O_3}$ was obtained from K_2 and pulse dosimetry.

The large extinction coefficient of N$_2$O$_3$ in the UV band suggests the possibility of an enhanced sensitivity for determination of K_1 at these wavelengths compared to the visible wavelengths employed by Turney.[4] Such a UV absorption band was observed also by Shaw and Vosper,[10] who present a spectrum of $\epsilon_{N_2O_3}$ calculated by using Turney's value of K_1 (as corrected by Schmid and Krenmayr[5]). Their absorption spectrum, which was unfortunately obtained in acidic solution of unspecified composition and concentration, agrees quantitatively with those obtained in the pulse radiolysis and flash photolysis studies, thus lending support to Turney's value of K_1. The results obtained in the present investigation in relatively dilute acid solution (0.1 M HCl) disagree markedly with those presented by Shaw and Vosper. This discrepancy will be discussed below.

Further aspects of experimental design that must be considered include identification of spectral regions in which the concentration of HNO$_2$ and N$_2$O$_3$ may be determined and the instability of HNO$_2$ to disproportionation by reaction 3.

$$3HNO_2 \rightarrow H^+ + NO_3^- + 2NO + H_2O \qquad (3)$$
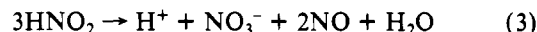
Nitrous acid exhibits a characteristic banded absorption spectrum in the near-ultraviolet[15] region (Figure 1) by which

(1) S. E. Schwartz and W. H. White, *Adv. Environ. Sci. Eng.*, in press.
(2) J. H. Ridd, *Q. Rev., Chem. Soc.*, **15**, 418 (1961).
(3) C. A. Bunton and G. Stedman, *J. Chem. Soc.*, 2440 (1958).
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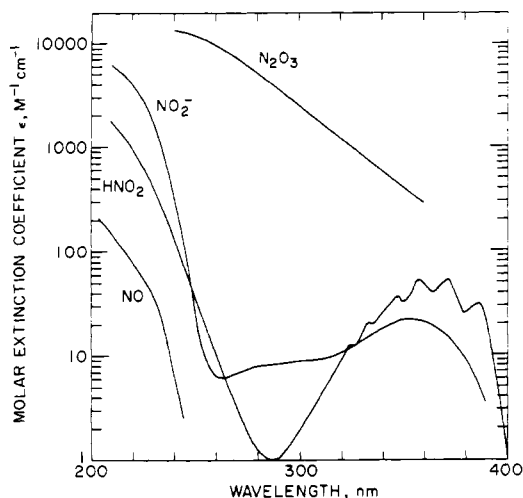
Figure 1. Aqueous-phase absorption spectra of N_2O_3 (ref 13), HNO_2 and NO_2^- (ref 15 and this work), and NO (ref 21).

its concentration may be readily determined. The extinction coefficient decreases but then increases at the shorter wavelengths (240–260 nm) of the most intense N_2O_3 absorption, although remaining well below that of N_2O_3. A somewhat greater extinction coefficient in that region is exhibited by nitrite ion,[15] but the concentration of that species may be suppressed by working in acid solution. Nitrous acid is a relatively weak acid

$$HNO_2 = H^+ + NO_2^-$$

with K_a values reported from $(3-7) \times 10^{-4}$ M.[16-18] In order to maintain a high, constant ratio of $[HNO_2]$ to $[NO_2^-]$ we have chosen to work in 0.1 M acid solution.
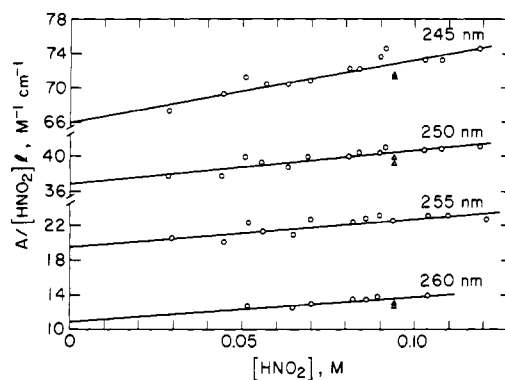
A less tractable problem is that of decomposition of nitrous acid. The kinetics of this decomposition have been examined in detail by Abel and Schmid,[19] who give the rate law

$$-d[HNO_2]/dt = k_4[HNO_2]^4/p_{NO}^2 \qquad (4)$$

Clearly this decomposition may be suppressed by the presence of NO, and consequently all studies were carried out under a pressure of NO of 1 atm. Nitric oxide dissolves in water with solubility 1.93×10^{-3} M atm^{-1}.[20] Dissolved NO absorbs in the UV[21] region, but the extinction coefficient at wavelengths greater than 220 nm is low compared to those of other species of interest here (see Figure 1). The rate of decomposition may be further suppressed by working at low concentrations of HNO_2. The rate constant k_4 given by Abel and Schmid (46 M^{-3} atm^2 min^{-1}) predicts a decomposition rate of ~5% min^{-1} for $P_{NO} = 1$ atm and $[HNO_2] = 0.1$ M and is correspondingly less for lower $[HNO_2]$. Such a rate of decomposition requires the ability to measure HNO_2 and N_2O_3 concentrations in close succession. The necessity of working at low nitrous acid concentrations is an additional motivation for determining the N_2O_3 concentration by means of the intense UV absorption.

Experimental Section

Spectrophotometric measurements were achieved by using a two-compartment vessel fused to a quartz optical cell (2 or 10 mm). Solutions of sodium nitrite and acid (HCl or $HClO_4$) were placed in the separate compartments and purged first with N_2 (to remove

(15) G. Kortüm, *Z. Phys. Chem., Abt. B*, **43**, 418 (1939).
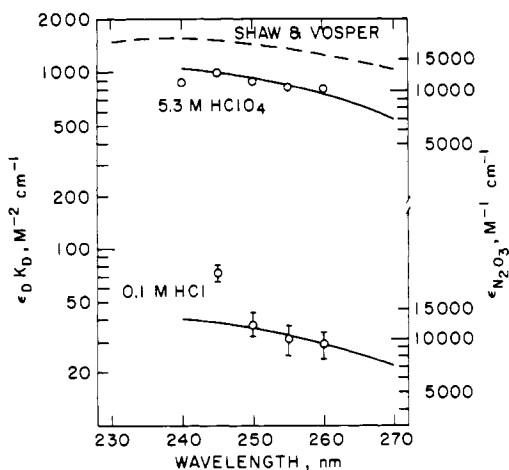(16) H. Schmid, R. Marchgraber, and F. Dunkl, *Z. Elektrochem.*, **43**, 337 (1937).
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(19) E. Abel and H. Schmid, *Z. Phys. Chem.*, **134**, 279 (1928).
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(21) R. Grajower and J. Jortner, *J. Am. Chem. Soc.*, **85**, 512 (1963).

Figure 2. Departure of extinction from Beer's law. Absorbance is plotted according to eq 6; finite slope represents component of absorbance quadratic in $[HNO_2]$: circles, [HCl] = 0.1 M; triangles, [HCl] = 0.3 M.

O_2) and then saturated with NO (Matheson). The solutions were then mixed by tilting the device and pouring the solutions back and forth between the two compartments.

Optical absorbance was measured at 371 nm (for HNO_2), followed by 260, 255, 250, and 245 nm, and again at 371 nm to ascertain the extent of decomposition. Usually the time for these measurements was less than 4 min, and the decrease in HNO_2 concentration was less than 2%. A Cary-14 spectrophotometer was employed. All experiments were carried out at 22 ± 2 °C.

Absorption spectra of HNO_2 and NO_2^- were determined in separate experiments. The extinction coefficients at the peaks of the banded nitrous acid spectrum are, in 0.1 M HCl solution, 28.6, 49.4, 47.7, and 32.8 M^{-1} cm^{-1} at 386, 371, 358, and 347 nm, respectively.

From the known extinction coefficients of nitrous acid and nitrite ion it was possible, as a byproduct of this study, to determine the acid dissociation constant K_a for nitrous acid under conditions of low concentration (to avoid decomposition) and low ionic strength. The extinction coefficients obtained at 230, 225, and 220 nm were 395, 650, and 950 M^{-1} cm^{-1} for nitrous acid and 1680, 2920, and 4090 M^{-1} cm^{-1} for nitrate ion, respectively. Solutions of known formal concentration of sodium nitrite and various amounts of hydrochloric acid were prepared, and the pHs were determined by a pH meter. From the measured optical density at the three wavelengths the acid dissociation constant of nitrous acid was determined as $K_a = (10 \pm 3) \times 10^{-4}$ M, in fair agreement with, but somewhat greater than, values reported previously $((3-7) \times 10^{-4}$ M).[16-18]

Results and Analysis

Initial qualitative experiments established the strong influence of concentrated acid upon the formation of the blue colored species (presumably N_2O_3). Solutions of 0.1 M nitrous acid in 5 M $HClO_4$, H_2SO_4, or H_3PO_4 were observed to exhibit a distinct blue tinge not present in 0.1 M HCl or in a mixture of 0.1 M HCl and 5 M $NaClO_4$. These observation indicate that there is a shift at high acid concentrations in the equilibrium responsible for the formation of the blue colored species and that this shift is due to the acid and not merely to the high ionic strength.

An attempt was made to reproduce the ultraviolet absorption spectrum ascribed to N_2O_3 by Shaw and Vosper.[10] We were unable to reproduce such a spectrum in dilute acid, by utilizing nitrous acid produced either by acidification of sodium nitrite or, following Shaw and Vosper, by air oxidation of NO. However, an absorption spectrum similar to that of Shaw and Vosper was obtained in 5.3 M $HClO_4$.

A series of quantitative measurements was carried out in 0.1 M HCl of the optical density at ultraviolet wavelengths 245–260 nm as a function of nitrous acid concentration. The results of these measurements are given in Figure 2 in which the ratio of the absorbance to nitrous acid concentration is plotted vs. nitrous acid concentration. (We were unable to extend the range of these measurements, limited at long wavelengths by the small changes in absorbance and at short

Figure 3. Wavelength dependence of extinction. Points (left-hand scale) represent component of extinction quadratic in [HNO_2]. Error bars at 0.1 M HCl represent estimated standard deviation. Solid curves (right-hand scale) represent N_2O_3 spectrum of ref 13 adjusted to coincide with present data. Dashed curve represents data of ref 10 reconstructed as discussed in text.

wavelengths by the opacity of the solutions.) The positive slopes obtained indicate the formation, with increasing [HNO_2] of an additional species absorbing at these wavelengths. Assuming that the increase in absorbance is due to a species resulting from the association of two nitrous acid molecules, we may describe the absorbance as

$$A/l = \epsilon_{HNO_2}[HNO_2] + \epsilon_{NO_2^-}[NO_2^-] + \epsilon_D[D] \qquad (5)$$

where D (denoting "dimer") represents the product of the association reaction

$$2HNO_2 = D \qquad (D)$$

and l is the path length. Introducing the equilibrium constant

$$K_D = [D]/[HNO_2]^2$$

valid for a given water activity or acid concentration and making use as well of the acid dissociation equilibrium for HNO_2, we obtain eq 6, where $\epsilon_0 = \epsilon_{HNO_2} + \epsilon_{NO_2^-}K_a/[H^+]$ is

$$A/l[HNO_2] = \epsilon_0 + \epsilon_D K_D[HNO_2] \qquad (6)$$

independent of [HNO_2]. Equation 6 predicts a linear dependence of $A/l[HNO_2]$ upon [HNO_2] with intercept ϵ_0 and slope $\epsilon_D K_D$. Within the scatter of the measurements, which may be due in part to decomposition during the measurements, the data exhibit the predicted linear dependence permitting evaluation of $\epsilon_D K_D$. The spectrum of $\epsilon_D K_D$ is shown in Figure 3, where the error bars represent the square root of the estimated variance in the least-squares slope.[22] The intercepts obtained from the least-squares fit agree closely with ϵ_{HNO_2} at several wavelengths, as anticipated for $K_a/[H^+] \ll 1$. Thus the data establish the formation of a species exhibiting a quadratic dependence upon [HNO_2]. We have assumed that this species is N_2O_3, but the possibility cannot be excluded that the observed increase in extinction is due to some other species whose concentration varies quadratically with [HNO_2].

While the focus of the present study was an examination of equilibrium 1 under conditions of low acidity, in order to examine the effect of strong acid upon K_D and to compare this study to previous work, a second series of absorption measurements was carried out, in perchloric acid solution at a concentration (5.3 M) comparable to the concentrations employed in the studies of Bunton and Stedman[3] and of Turney.[4]
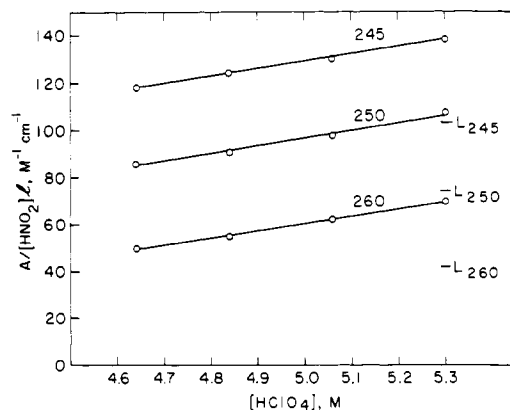
Figure 4. Dependence of extinction upon perchloric acid concentration. Limits indicate component of absorbance linear in [HNO_2] at 5.3 M $HClO_4$.

The observed slopes in a graph of $A/[HNO_2]l$ vs. [HNO_2] (not shown) were greatly enhanced over those obtained in dilute (0.1 M) acid solution. The resulting spectrum of $\epsilon_D K_D$ is also given in Figure 3 and lies some 25-fold higher than that obtained in the dilute solution.

A further examination was made of the effect of strong acid concentration upon the absorbance of the solution by varying the acid concentration at fixed formal concentration of HNO_2. Between 4.6 and 5.3 M perchloric acid there was a marked change in absorbance as shown in Figure 4. Also shown in Figure 4 are the intercepts from the graph of $A/l[HNO_2]$ vs. [HNO_2] at 5.3 M $HClO_4$, representing that component of the extinction that is linear in [HNO_2]. The effect of changing perchloric acid upon the excess extinction, i.e., the extinction in excess of the linear component, is quite marked—60–70% decrease between 5.3 and 4.64 M.

An examination was made as well of the effect of acid concentration upon the extinction of nitrous acid in dilute acid solutions. As indicated in Figure 2, within the sensitivity of the measurements, which was limited to a few percent because of the instability of the solutions, there was no increase in the extinction of 0.94 M HNO_2 solutions upon increasing the acid concentration from 0.1 to 0.3 M.

Discussion

Magnitude of $\epsilon_D K_D$. The primary data of the present study consist of the product of the extinction coefficient, ϵ_D, of a species whose concentration is quadratic in [HNO_2] times the equilibrium constant for the formation of that species, K_D. Spectra of $\epsilon_D K_D$ obtained in dilute acid and in 5.3 M perchloric acid exhibit a similar wavelength dependence (albeit over a rather restricted wavelength range), with the exception of the datum for 245 nm. It thus seems reasonable to suppose that the two spectra are due to the same species and that the change in $\epsilon_D K_D$ is due to a change in K_D with acid concentration, although the presence cannot be ruled out of a second absorbing species quadratic in HNO_2 having a similar absorption spectrum. This point will be discussed further below.

The present spectra may be directly compared also to that of Shaw and Vosper,[10] who present a spectrum of the extinction coefficient (attributed to N_2O_3), derived from their measured absorbance spectrum, with the concentration of N_2O_3 computed by using the Schmid–Krenmayr[5] value of K_1. By reversing their computation we may calculate their primary spectrum of $\epsilon_{N_2O_3}K_D$, a portion of which is given in Figure 3. It may be seen that the present spectrum of $\epsilon_D K_D$ obtained in dilute (0.1 M) acid solution lies some 50-fold lower than that obtained by Shaw and Vosper, whereas the spectrum obtained in 5.3 M perchloric acid lies much closer to theirs (factor of ~1.6). As noted above, we were unable to reproduce their absorbance spectrum in dilute acid but obtained a similar

(22) M. G. Natrella, *NBS Hand. (U.S.)*, No. **91**, 5–1, (1963).

spectrum in ~5 M perchloric acid. We cannot explain this discrepancy unless their spectrum, which was taken in acidic solution in order to suppress nitrite ion, was obtained in acid of concentration substantially greater than 0.3 M.

Magnitude of K_D and Dependence on Acidity. The present spectra of $\epsilon_D K_D$ may be compared, within a constant factor, to the spectrum ascribed to N_2O_3 by Grätzel et al.[13] in their pulse radiolysis study. This comparison is given in Figure 3 for the two data sets taken in dilute acid and in 5.3 M perchloric acid, where the solid curves represent a smooth curve drawn through the extinction coefficient data, adjusted to fit the present spectrum of $\epsilon_D K_D$. Except for the point at 245 nm in dilute acid, there is agreement, within experimental error, in the shapes of the spectral envelopes, lending support to the identification of the dimeric association product of nitrous acid obtained in the present study with the transient product of association of NO and NO_2, observed by Grätzel et al.

Identification of the present spectra of $\epsilon_D K_D$ with the spectrum $\epsilon_{N_2O_3}$ of Grätzel et al. permits evaluation of the association constants K_D at the two acid concentrations examined. In dilute acid the average of the three points (250–260 nm) gives $K_D = (3.04 \pm 0.23) \times 10^{-3}$ M^{-1}. In 5.3 M $HClO_4$ the average of the four points (245–260 nm) gives $K_D = 7.8 \times 10^{-2}$ M^{-1}. The apparent variation of K_D with $[HClO_4]$ at fixed $[HNO_2]$ may be estimated as follows. From eq 6 it may be seen that

$$\frac{d}{d[HClO_4]} \frac{A/l}{[HNO_2]^2} = \epsilon_D \frac{dK_D}{d[HClO_4]}$$

provided that only K_D and none of the extinction coefficients varies with $[HClO_4]$. The measurements given in Figure 4 and the values of ϵ_D derived from Grätzel permit the apparent change in K_D to be evaluated; the value of K_D at 4.64 M $HClO_4$ estimated in this way is 3.8×10^{-2} M^{-1}, demonstrating an apparent factor-of-2 change in K_D within this concentration range.

As noted above, the measured values of K_D pertain to a given acid concentration and, i.e., do not reflect the water activity in eq 2. In dilute solution (0.1 M acid) the water activity is sufficiently close to unity (0.996) that this correction is negligible, but at several molar perchloric acid this correction is appreciable.[23] In order to compare the present results to those of previous studies and to establish that the variation of the equilibrium constant with $[HClO_4]$ greatly exceeds that of a_w, we report these data also as K_D', calculated as

$$K_D' = K_D a_w \tag{7}$$

In dilute acid $K_D' = (3.03 \pm 0.23) \times 10^{-3}$ M^{-1}. The derived values for K_D' in perchloric acid increase over the range studied from 2.4×10^{-2} (4.64 M) to 4.4×10^{-2} M^{-1} (5.3 M). The strong variation in K_D' with acid concentration greatly exceeds the magnitude (~25%) that might be expected due to the effect of ionic strength upon the activity coefficients of the neutral species[5] and is indicative rather of a specific interaction, presumably involving solution acidity.

The values of K_D' in perchloric acid may be compared to the values of K_1 given previously by Bunton and Stedman[3] and by Turney.[4] Bunton and Stedman measured the absorbance at 625 nm to determine $[N_2O_3]$ by means of the extinction coefficient of N_2O_3 in toluene, assuming that this extinction coefficient applied as well to aqueous solution. Their results, also corrected for water activity by eq 7 are shown in Figure 5. These values of K_D' exhibit a similar dependence on $[HClO_4]$ to those found here, differing, however, by a factor of 2.8. This discrepancy may be due to a difference in ex-
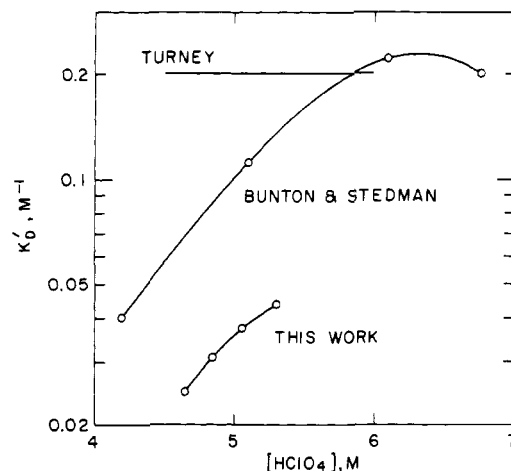

Figure 5. Dependence of association constant K_D' upon perchloric acid concentration.

tinction coefficient between the two solvents; solvent-to-solvent differences of this magnitude are not uncommon and were found for N_2O_3 in various nonaqueous solvents by Shaw and Vosper.[10] We thus feel that there is rather good agreement between the present results and those of Bunton and Stedman, both in the dependence of K_D' on $[HClO_4]$ and in the absolute magnitude of K_D' in ~5 M perchloric acid.

Equilibrium 1 in perchloric acid was examined also by Turney by two independent methods. In a study similar to that of Bunton and Stedman optical extinction at 656 nm was examined as a function of N^{III} concentration, leading to a determination of both K_D' and ϵ_{656}. No dependence of K_D' on $[HClO_4]$ was discerned for $HClO_4$ concentrations ranging from 4.5 to 6 M (as inferred from the reported water activities). A second determination of K_D' in 5.2 M $HClO_4$ was made by extraction with toluene, under the assumption that only N_2O_3 and not HNO_2 is extracted into toluene. The value of K_D' determined in this way (0.22 ± 0.04 M^{-1}) agreed closely with that determined spectrophotometrically (0.18 ± 0.04 M^{-1}) leading to the average 0.20 ± 0.05 M^{-1}.

The present results in perchloric acid differ from Turney's results both in exhibiting a dependence on perchloric acid concentration and in the magnitude of K_1. However, reexamination of the data presented by Turney suggests that his spectroscopic value of K_1, which depends on the ratio of a slope to an extrapolated intercept, exhibits an uncertainty substantially greater than that estimated by Turney, which would encompass the values measured here. We thus conclude that the available evidence, including the present study, supports the interpretation that the equilibrium constant K_D' exhibits a marked increase with increasing perchloric acid concentration in the range 4–6 M that has been studied previously. The present data also give evidence for substantial (order of magnitude) increase in K_D' on going from dilute acid to 5 M perchloric acid.

It is of interest briefly to explore an alternative interpretation of the present measurements, i.e., that K_D' is independent of perchloric acid concentration but that ϵ_D decreases with decreasing acid concentration. If we accept, e.g., a value of K_D' = 0.1 M^{-1}, as given by Bunton and Stedman at $[HClO_4]$ = 5 M, then the present dilute-acid value $\epsilon_D K_D' = 38$ M^{-1} cm^{-1} at 250 nm would lead to a value of $\epsilon_D = 380$ M^{-1} cm^{-1}. In view of the fact that the gas-phase extinction coefficient for N_2O_3 at this wavelength (3100 M^{-1} cm^{-1})[12] exceeds that value by almost 1 order of magnitude, it seems highly unlikely that a constant value of K_D' as great as 0.1 M^{-1} can be consistent with the present observations.

Alternatively we raise the possibility that K_D' is constant at the value of ~3 × 10^{-3} M^{-1} obtained in dilute acid solution

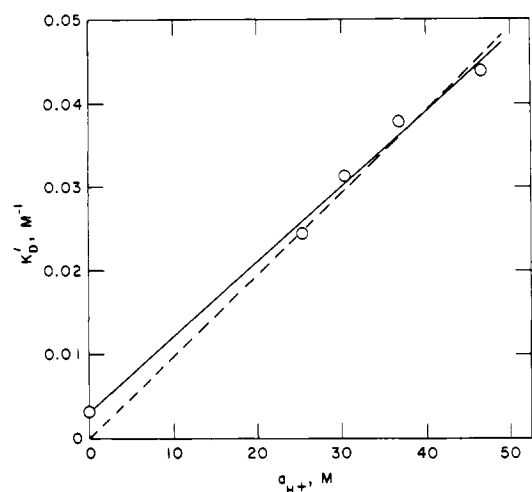(23) R. Haase, K.-H. Dücker, and H. A. Küppers, *Ber. Bunsenges. Phys. Chem.*, **69**, 97 (1965).

Figure 6. Dependence of association constant K_D' upon hydrogen ion activity. Dashed line is fit to eq 10; solid line is fit to eq 12.

and that the observed increase in $\epsilon_D K_D'$ results from an increase in ϵ_D with increasing acid concentration. Such an explanation for the present observations would imply that the extinction coefficient in 5 M HClO$_4$ becomes the order of 2×10^5 M^{-1} cm^{-1}, a magnitude that may be excluded on theoretical grounds[24] since it would imply an oscillator strength of approximately 10.

It is tempting to speculate why $\epsilon_D K_D$ exhibits the observed strong increase with increasing acid concentration. In perchloric acid of concentration greater than 5 M the protonated form of nitrous acid, nitrous acidium ion H$_2$NO$_2^+$, and/or its dehydration product, nitrosonium ion NO$^+$, is known[25] to account for an increasingly greater fraction of N^{III} with increasing acidity ($\sim$1% at 5.5 M HClO$_4$ up to $\sim$100% at 8.7 M). However, the presence of this species cannot account for the present observations, since its concentration would be linear in nitrous acid concentration at a given perchloric acid concentration and would thus not account for a contribution to the absorbance quadratic in [HNO$_2$]. The possibility is thus raised that the species responsible for the "quadratic" component of the absorbance is a protonated form of N$_2$O$_3$, dinitrogen trioxidium cation, HN$_2$O$_3^+$. The role of N$_2$O$_3$ as a proton acceptor does not appear to have been suggested previously, although N$_2$O$_3$ has been shown[26] to act as a Lewis base in forming an adduct with BF$_3$ and may thus be susceptible to protonation as well. If HN$_2$O$_3^+$ were responsible for the observed departure from Beer's law, then we would predict that the slope of eq 6 would be given by

$$\epsilon_D K_D = \epsilon_{HN_2O_3^+} K_9 a_{H^+} / a_w \tag{8}$$

where K_9 is the equilibrium constant for

$$2HNO_2 + H^+ = HN_2O_3^+ + H_2O \tag{9}$$
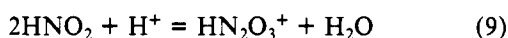
$$K_9 = [HN_2O_3^+] a_w / [HNO_2]^2 a_{H^+}$$

To test this, a plot was made (Figure 6) of K_D' vs. hydrogen ion activity, the latter evaluated from tabulated data[23] as a_{H^+}, $= \alpha y_\pm C$, where α is the fractional dissociation, $y_\pm$ the mean ionic activity coefficient, and C the molal concentration of HClO$_4$. Over the rather restricted concentration range available the data are fit reasonably well by eq 10 as predicted

$$K_D' \propto a_{H^+} \tag{10}$$

by eq 8. This linear dependence of K_D' on a_{H^+} supports the

suggestion that the "quadratic" component of the extinction is dominated in this range of perchloric acid concentration by a species of stoichiometry HN$_2$O$_3^+$.

Having implicated the participation of H$^+$ in the more concentrated acid, we must now address the failure of $\epsilon_D K_D'$ to exhibit a dependence on [H$^+$] at lower acid concentrations. Such a dependence is ruled out by the lack of increase in the UV extinction as [H$^+$] was increased from 0.1 to 0.3 M at constant [HNO$_2$], and hence these observations would tend to exclude HN$_2$O$_3^+$ as the absorbing species. However, evaluation of K_D' by eq 10 at 0.3 M [H$^+$] leads to a value 10-fold less than that observed in dilute acid. It thus seems reasonable to infer that both species, N$_2$O$_3$ and HN$_2$O$_3^+$, contribute to the "quadratic" term in the extinction of N$_2$O$_3$, i.e., that $\epsilon_D K_D'$ consists of two components, a constant, independent of acid concentration that is due to N$_2$O$_3$, and a term linearly proportional to hydrogen ion activity that is due to HN$_2$O$_3^+$. The observed quantity $\epsilon_D K_D'$ would thus be expressed in terms of the extinction coefficients and equilibrium constants for the two species as eq 11. K_1 would be identified

$$\epsilon_D K_D = \epsilon_{N_2O_3} K_1 + \epsilon_{HN_2O_3^+} K_9 a_{H^+} \tag{11}$$

with the dilute-acid value of K_D', viz., $(3.03 \pm 0.23) \times 10^{-3}$ M^{-1}, and the acid dependence of K_D' would be expressed as eq 12. The fit to eq 12 is also shown in Figure 6. The

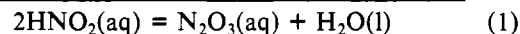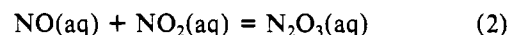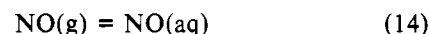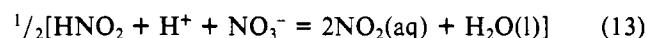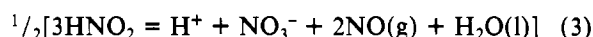$$K_D' = K_1 + K' a_{H^+} \tag{12}$$

numerical value of the acid-dependent term is related to that of the constant term by

$$\epsilon_{HN_2O_3^+} K_9 / \epsilon_{N_2O_3} K_1 = 0.30$$

appropriate to the range of wavelengths examined (245–260 nm). This interpretation would account for the observed independence of K_D upon acid concentration in the range 0.1–0.3 M and thus lends support to the applicability of K_1 determined at pH 1 to solutions of higher pH.

A primary motivation of the present study has been to permit comparison of the value of K_1 measured here to that which may be obtained by a thermochemical cycle involving equilibrium 3 that was studied by Grätzel et al.[13] This cycle may be constructed as

$$^1/_2[3HNO_2 = H^+ + NO_3^- + 2NO(g) + H_2O(l)] \tag{3}$$

$$^1/_2[HNO_2 + H^+ + NO_3^- = 2NO_2(aq) + H_2O(l)] \tag{13}$$

$$NO(g) = NO(aq) \tag{14}$$

$$\underline{NO(aq) + NO_2(aq) = N_2O_3(aq)} \tag{2}$$

$$2HNO_2(aq) = N_2O_3(aq) + H_2O(l) \tag{1}$$

permitting K_1 to be evaluated as

$$K_1 = K_4^{1/2} K_{13}^{1/2} K_{14} K_3 \tag{15}$$

Studies leading to the determination of these several equilibrium constants have recently been reviewed elsewhere;[1] the conclusions of that review are briefly summarized here. Equilibrium 3 is well established ($K_3 = 30.1$ atm^2 M^{-1}, 25 °C), as is the solubility equilibrium for NO ($K_{14} = 1.93 \times 10^{-3}$ M atm^{-1}). On the other hand, equilibria involving aqueous NO$_2$ and/or N$_2$O$_3$, eq 13 and 2 as well as eq 1, are much less well established. Equilibrium 13 was studied by Vetter[27] by measuring the departure from Nernstian behavior of the HNO$_2$/HNO$_3$ half-cell potential due to occurrence of reaction 13. Although those studies were carried out in rather concentrated ($\geq$7 M) nitric acid, examination of the dependence of K_{13} upon nitric acid activity[1] permitted estimation of the dilute solution value of K_{13} as $(2.6 \pm 1) \times 10^{-10}$ M^{-1}.

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(25) K. Singer and P. A. Vamplew, *J. Chem. Soc.*, 3971 (1956).
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Equilibrium 2 was studied by Grätzel et al.,[13] as noted above. In that study NO_2 was formed in solution rapidly after the pulse; the equilibrium constant K_2, determined from the decrease in NO_2 absorbance as equilibrium 2 was established, was found to be 1.4×10^4 M^{-1} (20 °C).

The magnitude of K_1 evaluated by eq 16, $(2.3 \pm 1) \times 10^{-3}$ M^{-1}, agrees within the estimated error bound with that determined in this study $((3.03 \pm 0.23) \times 10^{-3}$ M$^{-1})$. This agreement lends support to the present interpretation of the measurements made in dilute acid, viz., that the species responsible for the quadratic component of the UV absorption in the present study is the same species (presumably N_2O_3) that gives rise to the UV absorption spectrum in the pulse radiolysis studies. This close agreement contrasts with the strong disagreement (70–90-fold) between the value of K_1 evaluated by eq 15 and that determined by Turney[4] (in ~5 M perchloric acid) or that given by Schmid and Krenmayr[5] (based on the value of Turney but corrected to dilute solution). As noted above, it was this disagreement that stimulated the present investigation. The present results establish that this disagreement is a consequence of the shift in the empirical association constant K_D' with increasing acidity. We have suggested above that this shift is due to the formation of a species whose concentration is dependent upon hydrogen ion activity as well as exhibiting a quadratic dependence on $[HNO_2]$. Since the shift in K_D' is observed in studies both in the UV (this work) and in the visible regions (Bunton and Stedman,[3] as well as the qualitative observations noted above), we infer that the absorption at λ 500–800 nm that gives rise to the blue color of the acidic solutions also arises from the acidic species, rather than from the neutral N_2O_3 as has been supposed in the previous studies. A study of the dependence of the weak visible absorption band upon acid concentration might give further insight into the identity of the species responsible for the blue color. We note in this context that the presence of "blue nitrous acid" is generally associated with highly acidic media.[11,28,29]

The low value of K_1 found in the present study would appear also to resolve an anomaly in the interpretation of the kinetics of diazotization of amines via N_2O_3 intermediate. As pointed out by Ridd,[2] the apparent reaction rate between N_2O_3 and amines is far less than the encounter rate of the species when $[N_2O_3]$ is evaluated by using Turney's value for K_1, whereas for diazotization via nitrosyl halide intermediates the rate coefficients approach those of encounter reactions. However, for the lower value of $[N_2O_3]$ calculated by using K_1 obtained in the present study, the rate coefficient for reaction between N_2O_3 and, e.g., aniline is found to be 7×10^8 M^{-1} s^{-1} at 25 °C, within 1 order of magnitude of the encounter rate of the species and much more in keeping with the rate constants obtained for reaction with nitrosyl chloride and nitrosyl bromide.

Determination of K_1 permits the free energy of formation of N_2O_3(aq) to be evaluated, making use of the known[30] free energies of formation of HNO_2 and H_2O(l); the resulting value is $\Delta G_f°(N_2O_3(aq)) = 33.53 \pm 0.05$ kcal/mol, where the error bar represents the propagated uncertainty in K_1. This value may be used in turn to evaluate the physical (Henry's law) solubility of N_2O_3 as the equilibrium constant of reaction 16.

$$N_2O_3(g) = N_2O_3(aq) \qquad (16)$$
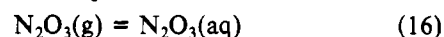
Making use of the known[30] free energy of formation of N_2O_3(g), one obtains $K_{16} = 0.70 \pm 0.05$ M atm^{-1}, where again the uncertainty reflects the uncertainty in the present value of K_1. Because of the reactivity of N_2O_3, K_{16} cannot be directly measured. The value of K_{16} derived here agrees as well as may be expected with the value (1 M atm^{-1}) estimated by Turney and Wright[31] on the basis of physical properties of N_2O_3 in analogy with other molecules whose solubility coefficients are known.

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Kinetics and Mechanism of Oxidation of Hypophosphorous Acid with Silver(II) in Aqueous Perchloric Acid Solutions

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The title reaction at constant $[HClO_4]$ and $[ClO_4^-]$ follows the rate law $-d[Ag(II)]/dt = 2k_2[Ag(II)][H_3PO_2]/(1 + K_5[Ag(I)])$, where k_2 was found to be $(7.6 \pm 0.7) \times 10^2$ M^{-1} s^{-1}, at 30 °C and $I \approx 4.0$ M, and K_5 is the formation constant of $AgH_3PO_2^+$, and its value from kinetics results was 38 ± 2.5 M^{-1} at 30 °C and $[HClO_4] = 4.0$ M. There is evidence for the complexes $AgClO_4^+$ and $Ag(ClO_4)_2$ in perchlorate solutions of Ag(II). Silver(II) oxide appears to disproportionate to Ag(III) even in the solid state.

The authors recently studied[1] the silver(I)-catalyzed oxidation of hypophosphorous acid with cerium(IV) to ascertain the role of the catalyst. Though no evidence for the Ag(I)/Ag(II) cycle was obtained, a study of the reaction of Ag(II) with hypophosphorous acid seemed desirable to confirm the absence of this cycle in the catalyzed reaction. The kinetic studies made with silver(II) have been few, owing to its reaction with water in acidic solutions of $HClO_4$,[2,3] H_2SO_4,[4] H_3PO_4,[5] and HNO_3,[6] and some of them are incomplete from

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