JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 92, NUMBER 20 OCTOBER 7, 1970

Physical and Inorganic Chemistry

Absorption Spectra and Reaction Kinetics of NO_2, N_2O_3, and N_2O_4 in Aqueous Solution

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Received January 19, 1970

Abstract: The flash photolysis of NO_2^- ions in aqueous solution gives rise to three transient absorptions assigned to NO_2 (λ_{max} ~400 nm), N_2O_4 (λ_{max} ~340 nm), and N_2O_3 (λ_{max} <250 nm). The formation of O_3^- in air-saturated alkaline solutions of nitrite ions, and of Br_2^- and CO_3^- radicals in the presence of Br^- and CO_3^{2-} ions, indicates that O^- (or OH) radicals are produced by the primary photolytic process $NO_2^- + h\nu \rightarrow NO + O^-$. The mechanism proposed for the generation of the other nitrogen oxides, $O^- + H_2O \rightleftharpoons OH + OH^-$, $OH + NO_2^- \rightarrow NO_2 + OH^-$, $O^- + NO_2^- + H_2O \rightarrow NO_2 + 2OH^-$, $NO_2 + NO_2 \rightleftharpoons N_2O_4$, $NO + NO_2 \rightleftharpoons N_2O_3$, was derived from investigating (a) the effects of temperature and added NO on the transient absorption spectrum, (b) the flash photolysis of $NO_3^- + NO_2^-$ solution, (c) the pulse radiolysis of NO_2^- solutions. The equilibrium constants $K_{N_2O_3} = [NO_2][NO]/[N_2O_3] \sim 2 \times 10^{-5}\ M$ and $K_{N_2O_4} = [NO_2]^2/[N_2O_4] = (1.3 \pm 0.4) \times 10^{-5}\ M$ were derived from flash photolysis and pulse radiolysis experiments, respectively. After equilibration, the three nitrogen oxides decay by first-order processes, with N_2O_3 and N_2O_4 decaying twice as fast as NO_2; in this manner the photolytically decomposed NO_2^- is completely regenerated. The mechanism proposed for the decay of the nitrogen oxides involves NO_2 as a reactive intermediate. On increasing either the N_2O_3 concentration (by adding NO) or its rate of hydrolysis (by raising the pH), N_2O_3 appears to become the reactive intermediate. Some of the difficulties encountered by this mechanism are discussed. From the study of the ozonide decay as a function of $[NO_2^-]$ and pH, the rate constants $k(OH + NO_2^-) = (1.0 \pm 0.1) \times 10^{10}\ M^{-1}\ sec^{-1}$ and $k(O^- + NO_2^-) \sim 2.5 \times 10^8\ M^{-1}\ sec^{-1}$ were determined.

The hydrolysis reactions of the nitrogen oxides are among some of the most basic chemical reactions and are of utmost importance in the chemical industry and in air pollution. Their reaction mechanisms are still, however, relatively obscure. The hydrolysis of NO_2 was usually considered to involve N_2O_4 as the reactive species.[2] In recent works,[3-5] the absorption spectrum of NO_2 in water and its hydrolysis were investigated by flash photolysis and pulse radiolysis methods. The spectrum reported differs from that in the gas phase in its absorption below 350 nm.[4] In two of these works,[3,4] the hydrolysis was interpreted in terms of N_2O_4 as the intermediate, but recent evidence[5] was presented against this mechanism. The effect of pH on the hydrolysis has not been studied. Closely related are the mechanisms of hydrolysis of N_2O_3 and N_2O_4. Lack of information on their spectra in water has hindered direct investigation of their reactions. (Some data are available on the low-intensity absorption of N_2O_3.[6])

In the present work, we have attempted to derive information on some of the properties of NO, NO_2, N_2O_3, and N_2O_4 in water by studying the flash photoly-

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[2] See J. J. Carberry, *Chem. Eng. Sci.*, **9**, 109 (1959), and references cited therein.

[3] M. Ottolenghi and J. Rabani, *J. Phys. Chem.*, **72**, 593 (1968).

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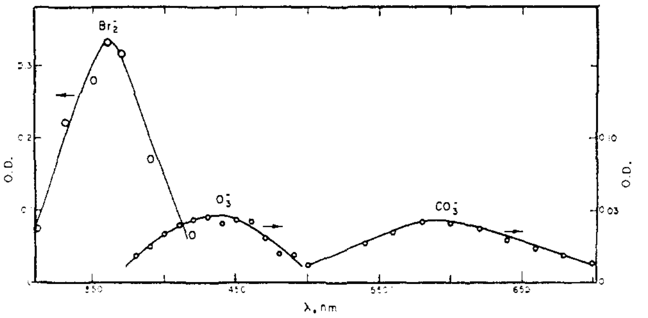

Figure 1. Transient absorption spectra of O_3^-, Br_2^-, and CO_3^- radicals produced on flash photolysis of NO_2^- solutions under the following conditions: O_3^- (4.3×10^{-4} *M* KNO_2 + 2.5×10^{-2} *M* KOH + 2.5×10^{-4} *M* O_2), Br^{2-} (2.6×10^{-4} *M* KNO_2 + 2.5×10^{-2} *M* KBr, air free), CO_3^- (3×10^{-4} *M* KNO_2 + 2.8×10^{-2} *M* K_2CO_3, air free). The spectra were read at 50, 20, and 50 μsec after the flash, respectively.

sis and pulse radiolysis of nitrite ions in solution. The pulse radiolysis has already been investigated in some detail,[4,5] but no attention was given to the spectrum of N_2O_4 produced. Some preliminary results on the flash photolysis of NO_2^- were reported,[7] but the transient absorption was not described or identified. Some information on the properties of NO_3 in water is available.[8] At low $[NO_3]$ it appears to decay by a first-order process, and its reactivity with some molecules would seem to indicate that it is a stronger oxidizing species than the other nitrogen oxides.

The photochemistry of NO_2^- has only been briefly investigated for the simple reason that there is no *net* reaction. This early finding[9] was verified by our preliminary experiment: 2.7×10^{-4} *M* NO_2^- was irradiated with light at 2288 Å from a cadmium lamp for 100 min; the quantum yield of the NO_2^- depletion was found to be less than 10^{-3}. Efficient back-reactions were considered to be responsible for this result, and the reaction

$$NO_2^- \xrightarrow{h\nu} NO + O^-$$

was suggested[10] to be the primary process. It is analogous to the primary photochemical process in organic nitrites.[11]

$$RONO \xrightarrow{h\nu} RO + NO$$

However, no evidence has been presented for the occurrence of a similar reaction in NO_2^-. Recent flash photolysis studies on $S_2O_3^{2-}$,[12] HO_2^-,[13] NO_3^-,[14] and the oxyhalogen ions[15] have shown that the O^- type of dissociation is a common process for excited oxyanions which can readily undergo bond rupture. In the case of HNO_3, photolytic dissociation to OH + NO_2 was also found.[16] It is one of the aims of the present work to show that this dissociation is a major primary process (and probably the only one) of excited NO_2^- ions.

Experimental Section

The flash photolysis setup was described elsewhere.[17a] Flashes of ~1800 J ($\tau_{1/2}$ = 8 μsec) and optical cells with an optical path of 20 cm were used. Thermostating was achieved by circulating water from a thermostat through the outer jacket of the quartz optical cell; the temperature of the solution was measured within the cell. In room-temperature experiments, the jacket was filled with water or with the appropriate solution filter. KNO_2 and all other chemicals were of the purest research grade available and were used as received. Nitric oxide (Matheson) was purified by bubbling through three washing bottles containing concentrated H_2SO_4, 50% KOH over pellets of NaOH, and water, respectively. Borate buffer was used at concentrations comparable to those of KNO_2 (in the pH range 6–8, the results were not affected by the presence of the buffer). In all cases where the results were sensitive to pH, the pH of the solution was measured immediately after its rejection from the optical cell; usually it differed little from that of the original solution.

The pulse radiolysis setup has been described.[17b] Electrons of 2.3-MeV energy and 30-nsec duration were used and a 2-cm optical path cell was employed. Extinction coefficients were derived based on the dosimetry procedure given elsewhere.[17b]

Results and Discussion

I. Flash Photolysis of NO_2^-. A. Primary Process, Production, and Decay of O_3^-. The flash photolysis of air-saturated solutions of NO_2^- at pH >12 gave rise to a transient absorption with a maximum at 430 nm, identical with that of O_3^- radicals; see Figure 1. Up to 3 μmol of O_3^- could be produced by one flash. In the presence of Br^- or CO_3^{2-} ions, the photolysis of NO_2^- ions showed the presence of the transient spectra of Br_2^- and CO_3^- radicals (Figure 1). These results suggest that the primary photolytic mechanism of nitrite ions produces O^- radicals, according to

$$NO_2^- \xrightarrow{h\nu} NO + O^- \qquad (1)$$

$$O^- + H_2O \rightleftharpoons OH + OH^- \qquad (2)$$

The radicals Br_2^- and CO_3^- are formed by the reactions

$$Br^- + OH \longrightarrow Br\cdot + OH^-$$

$$Br\cdot + Br^- \rightleftharpoons Br_2^-$$

$$CO_3^{2-} + OH \longrightarrow CO_3^- + OH^-$$

The decay rate of ozonide radicals obeyed the law

$$\frac{-d[O_3^-]}{dt} = k_0[O_3^-]$$

where

$$k_0 = \frac{[NO_2^-]}{p[NO_2^-] + q[O_2]}$$

p is a constant and *q* is a function of pH. The dependence of k_0 on $[NO_2^-]$ and pH is shown in Figure 2. The same law was found to be applicable to the decay of O_3^- produced from HO_2^- [13] and the oxybromine and oxyiodine systems.[15] This suggests a similar mechanism for the generation and decay of O_3^-, reactions 1–6

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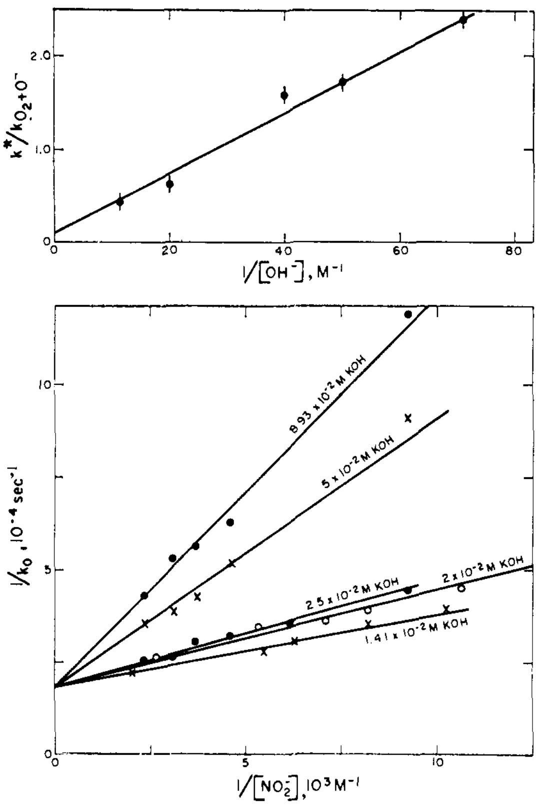

Figure 2. Dependence of the first-order decay of O_3^- upon OH^- and NO_2^- concentrations (see eq 7).

$$OH + NO_2^- \longrightarrow NO_2 + OH^- \tag{3}$$

$$O^- + NO_2^- \xrightarrow{+H_2O} NO_2 + 2OH^- \tag{4}$$

$$O^- + O_2 \longrightarrow O_3^- \tag{5}$$

$$O_3^- \longrightarrow O_2 + O^- \tag{6}$$

This mechanism leads to the following relation

$$1/k_0 = 1/k_6 + \frac{k_5[O_2]}{k_6k^*}\frac{1}{[NO_2^-]} \tag{7}$$

with

$$k^* = k_4 + \frac{k_3K_w}{K_{OH}}\frac{1}{[OH^-]}$$

where $K_w = [H^+][OH^-]$ and $K_{OH} = [H^+][O^-]/[OH]$.

From the parameters of the lines in Figure 2 we could calculate $k_6 = (5.5 \pm 0.5) \times 10^3$ sec^{-1} (in good agreement with previous data[13,15]), $k_3/k_5 = 4.0 \pm 0.4$, and $k_4/k_3 \sim 40$. Taking $k_5 = 2.5 \times 10^9$ M^{-1} sec^{-1},[18] the values $k_3 = (1.0 \pm 0.1) \times 10^{10}$ M^{-1} sec^{-1} and $k_4 \sim 2.5 \times 10^8$ M^{-1} sec^{-1} were derived, which are close to those recently reported.[19] Equation 7 is based on the assumption that equilibrium 2 is established. In all our experiments, $k_3[NO_2^-]$ and $k_4 \cdot [NO_2^-]$ were lower than 5×10^6 and 10^5 sec^{-1}, respectively, whereas $k_2[H_2O]$ and $k_{-2}[OH^-]$ were at least one order of magnitude higher.[19] This assumption is thus justified.

B. Identification of NO_2. According to the above mechanism, equimolar amounts of NO and NO_2 should be produced by the photolysis and, as in the gas phase, they are expected to be in equilibria with N_2O_4 and N_2O_3. The absorption of NO in water is significant only below ~220 nm, where NO_2^- absorbs strongly, but the other three nitrogen oxides absorb at longer wavelengths.[6] For their identification, the formation of O_3^- was avoided by using air-free solutions, or air-saturated solutions at pH below 10.

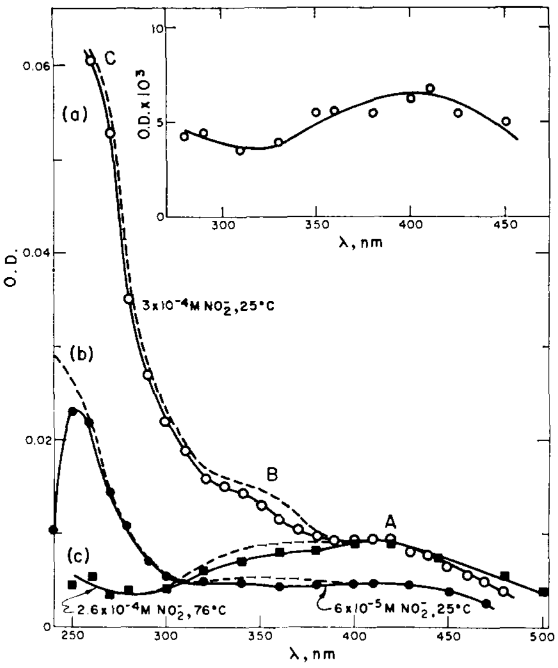

Figure 3. Absorption spectra of transients produced on flash photolysis of NO_2^-, pH 6–8, at different temperatures and $[NO_2^-]$, OD read 150 μsec after start of flash: dashed curves, spectra corrected for depletion of NO_2^- (see text); insert, spectrum produced on flash photolysis of 0.1 M KNO_3 + 1.7×10^{-4} M KNO_2, 25°, OD read at 200 μsec after start of flash.

Figure 3 shows some transient spectra produced under these conditions. On flash photolysis of 3×10^{-4} M NO_2^- at 25°, the spectrum displays three distinct bands: two weak bands appearing as "shoulders" at ~400 nm (band A) and at ~340 nm (band B) and the ascending branch of a relatively intense band (band C) at shorter wavelengths. The three bands decay within the millisecond range (see section III), and at the end of the decay no depletion of NO_2^- could be detected even at 230 nm, where $\epsilon_{NO_2^-} = 2400$ M^{-1} cm^{-1}. The latter result (which was obtained with 2×10^{-5} M NO_2^-) confirms that there is no *net* photolysis of NO_2^-, despite the high efficiency of its primary decomposition.

Neither N_2O nor O_2 had any distinct effect on the transient spectrum, which indicates (a) that solvated electrons do not play a significant role in the photolysis (the effect of N_2O was tried with $[N_2O]/[NO_2^-] \sim 100$); (b) that the reaction of NO with O_2 in solution is slow relative to other processes in this system which involve NO. In general, a decrease in the amount of transients (either by changing their initial yield or their decay processes) affects bands B and C more than band A. Thus, when the intensity of band A is doubled, that of C increases by a factor of ~4 (Figure 3, curves a and b). It was difficult to examine the effect on band B, a more detailed study of which was conducted by pulse radiolysis (see section II). This

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explains our observation that the absorbance values measured within bands B and C were considerably scattered. This and the low intensity of band A made it necessary to average the results of several measurements, usually more than three.

The spectrum of NO_2 in aqueous solution displays a broad band peaking at ~400 nm, with $\epsilon \sim 200\ M^{-1}\ cm^{-1}$.[3-5] The assignment of band A to NO_2 is thus suggested and further supported by the following results.

(a) The intensities of bands B and C were found to decrease on raising the temperature of the solution, and at 76° only band A was detected after the flash (Figure 3, curve c). The dashed curve shows the spectrum corrected for the depletion of NO_2^-; the correction was based on the assumption that 2 mol of NO_2^- is consumed for each mole of NO_2 produced (eq 1–3) and on the known spectrum of NO_2^-. The spectrum of NO_2^- measured by us was identical with that reported in the literature. This correction is significant near 360 nm, where NO_2^- has an absorption maximum. (Figure 3 includes such corrections for curves a and b, but here the conversion of NO_2 to N_2O_4 was also taken into account.) Band A appears to undergo temperature broadening. It also intensifies on warming, but this is not shown in Figure 3, where spectrum a represents the average of eight measurements. In the gas phase the degree of dissociation of N_2O_4 and N_2O_3 markedly increases with temperature (the heats of dissociation are 14.6 and 10.3 kcal, respectively[20]); therefore at 76° the spectra of N_2O_4 and N_2O_3 should be practically quenched and that of NO_2 intensified.

(b) NO_2 was also generated by flash photolysis of the $NO_3^- + NO_2^-$ mixture. The concentrations of NO_3^- and NO_2^- were so adjusted that in effect all the light was absorbed by NO_3^-, and all the OH radicals produced[14] by the reaction

$$NO_3^- \xrightarrow{h\nu} NO_2 + O^- \qquad (8)$$

were scavenged by NO_2^-, reaction 3. The insert in Figure 3 shows the spectrum produced by flashing a solution of 0.1 M NO_3^- + 1.7×10^{-4} M NO_2^-. It was corrected for NO_2^- depletion: 1 mol of NO_2^- is consumed for 2 mol of NO_2 produced. (This is a small correction and need be considered only near 360 nm.) In addition to the transient absorption, a permanent absorption peaking near 360 nm was observed after the flash; it is due to NO_2^- generated from NO_3^- by other[14] processes. The transient absorption includes a contribution from N_2O_4 (1.7 μmol of NO_2 was produced by the flash; *i.e.*, $[N_2O_4]/[NO_2] \sim 0.1$; see section II). Still the spectra produced by methods a and b are rather similar. In particular, both differ from the spectrum of NO_2 previously reported[4] (and resemble more closely the gas-phase spectrum[21]) by showing a smaller absorption below 300 nm. We believe that in the pulse work other transients contribute to the short-wavelength absorption (see section II).

(c) The assignment of band A to NO_2 leads to a 1:1 ratio for the yields of NO_2 and O^- (or OH), in agreement with the proposed mechanism (eq 1–4). The initial yield of NO_2 was calculated by extrapolating the maximum absorbance of A to zero time and correcting for the conversion of NO_2 to N_2O_4, using $\epsilon_{NO_2} = 200\ M^{-1}\ cm^{-1}$ and $K_{diss}(N_2O_4) = 1.3 \times 10^{-5}\ M$ (section II). No correction for N_2O_3 was introduced. Such correction may increase the yields of NO_2 by ~10% (section I.C). Under the same conditions, the initial yield of O^- was determined from the yields of O_3^-, Br_2^-, or CO_3^- produced when all the O^- (or OH) radicals are scavenged by O_2, Br^-, or CO_3^{2-}, respectively. All the absorbance values were extrapolated to zero time. The values of ϵ_{max} used (in units of $M^{-1}\ cm^{-1}$) were 1.9×10^3, 7.8×10^3, and 1.86×10^3 for O_3^-, Br_2^-, and CO_3^-, respectively.[22] The three scavengers led to the following values for $[NO_2]/[O^-]$: 1.1 (from O_3^-), 0.9 (from Br_2^-), and 1.5 (from CO_3^-).

(d) In neutral solution the decay kinetics of transient A closely resembles that of NO_2 (see section III).

In the presence of ethanol band A was not produced. With Br^- the, suppression of C could be shown, but the intense Br_2^- absorption prevented reaching any conclusions about the other two bands (the decay of Br_2^- was accompanied by the buildup of a weak absorption below 300 nm, which may be due to NOBr[23]). With CO_3^{2-} no transient absorption was detected below 450 nm, but this could also be interpreted as a pH effect (see section III.C) since the pH of the solution was 11.1. Altogether, these results suggest that OH radicals are the precursors of the transients which are responsible for bands A, B, and C (Figure 3).

The generation of NO_2 (band A) was also achieved by confining the absorption of light from the flash to the 360-nm band of NO_2^-. To show this, 0.1 M NO_2^- solution was flashed with 0.1 M phthalic acid as a filter (cutoff at ~300 nm). This filter led to a considerable reduction in the yield of NO_2. This and the fact that NO_2 (and the other two transients) was produced from very dilute NO_2^- solutions ($\sim 2 \times 10^{-5}\ M$) suggest the absence of a wavelength effect on the mechanism of the photolysis of NO_2^- at $\lambda \gtrsim 220$ nm.

C. The Identification of N_2O_3. The effect of NO on the photolysis of NO_2^- was studied. The spectrum obtained on flashing 9.5×10^{-4} M NO_2^- + 1.9×10^{-3} M NO is shown in Figure 4. Band A has apparently vanished and the spectrum now consists of a single band which resembles band C (Figure 3). Thus NO appears to convert transient A to transient C. Keeping the NO concentration constant, the intensity of this single band was found to increase with $[NO_2^-]$, tending to some limiting value. The set of reactions which occurs in this system most likely includes reactions 1 and 2, with reaction 3 competing with the reaction

$$OH + NO \longrightarrow HONO \qquad (9)$$

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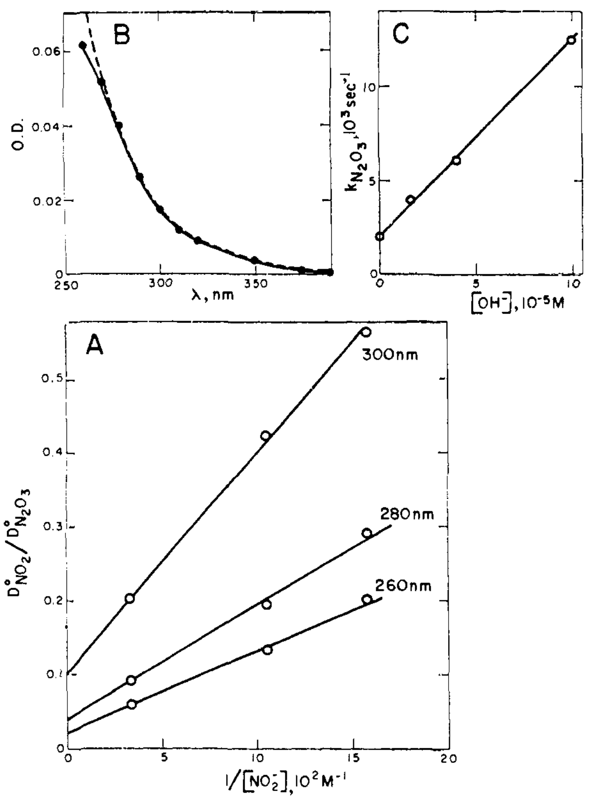

Figure 4. Decay kinetics and transient spectrum produced on flash photolysis of NO_2^- solutions saturated with NO (1.9×10^{-3} *M*) at 25°: (A) competition kinetics between NO_2^- and NO for OH radicals; (B) transient spectrum of N_2O_3 obtained with 9.5×10^{-4} *M* NO_2^- (OD read at 100 μsec), dashed curve is the normalized spectrum of N_2O_3 in the gas phase (ref 24); (C) first-order decay constant of N_2O_3 as a function of pH.

and NO_2 reacting with NO.

$$NO_2 + NO \rightleftharpoons N_2O_3 \qquad (10)$$

Under the conditions employed, HNO_2 rapidly dissociates to NO_2^- and almost all the NO_2 was converted to N_2O_3, as was indicated by the disappearance of band A (and also by the value of the equilibrium constant; see later). Thus this simple competition scheme leads to the following relations

$$\frac{OD_{NO_2}{}^{400}}{OD_{N_2O_3}{}^{\lambda}} = \frac{1}{\epsilon_{rel}{}^{\lambda}} + \frac{1}{\epsilon_{rel}{}^{\lambda}}\frac{k_9[NO]}{k_3}\frac{1}{[NO_2^-]}$$

where $OD_{NO_2}{}^{400}$ and $OD_{N_2O_3}{}^{\lambda}$ are the OD values for NO_2 at 400 nm (in the absence of NO) and for N_2O_3 at wavelength λ (in the presence of 1.9×10^{-3} *M* NO), respectively, obtained by flashing the same NO_2^- solution. (The absorbance was extrapolated to zero time and OD_{NO_2} was corrected for the conversion of NO_2 to N_2O_4.) $\epsilon_{rel}{}^{\lambda}$ is $\epsilon_{N_2O_3}{}^{\lambda}/\epsilon_{NO_2}{}^{400}$. Figure 4A shows the validity of this relation at three wavelengths; from the parameters of the lines ϵ_{rel} and k_9/k_3 could be calculated. Owing to the small value of the intercepts, the values derived from the 260- and 280-nm lines are only approximate. Thus, we found $\epsilon_{rel}{}^{300} = 10$, $k_9/k_3 = 1.6 \pm 0.4$; $\epsilon_{rel}{}^{280} \sim 25$, $k_9/k_3 \sim 2$; $\epsilon_{rel}{}^{260} \sim 40$, $k_9/k_3 \sim 2$. The proposed scheme is supported by (a) the apparent constancy of k_9, and (b) the ratio $\epsilon^{300}:\epsilon^{280}:\epsilon^{260} = 10:25:40$ being close to that exhibited by the spectrum shown in Figure 4B. Using our value $k_3 = (1.0 \pm 0.1) \times 10^{10}$ M^{-1} sec^{-1}, we obtain $k_9 = (1.6 \pm 0.5) \times 10^{10}$ M^{-1} sec^{-1}. This is considerably higher than the value previously reported,[18] but seems quite reasonable.

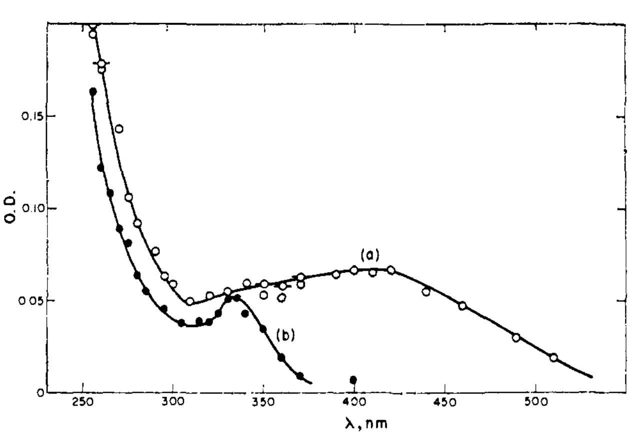

Figure 5. Pulse radiolysis of aqueous solutions of 9.5×10^{-4} *M* KNO_2, pH 5.0, saturated with N_2O (1 atm). Transient spectrum (a) read at 0.1 μsec and (b) read at 160 μsec after a 30-nsec electron pulse. -O- represents OD corrected for depletion of NO_2^- (assuming that 1 mol of NO_2^- is depleted for each mole of NO_2 produced).

The spectrum of N_2O_3 in the gas phase has been reported recently.[24] Its shape is close to that of the spectrum recorded here (see dashed curve, Figure 4B) but its intensity is much lower (by a factor of ~5). Before reaching any conclusion this spectrum should be checked.

In conclusion we believe that band C is due mainly to N_2O_3. Only little of the absorption below 300 nm can be ascribed to NO_2 and N_2O_4 (section II). From Figure 3 we could estimate that $[N_2O_3] \sim 0.12[NO_2]$. Assuming $[NO] = [NO_2]$ (section III.C), we obtain $K_{N_2O_3} = [NO][NO_2]/[N_2O_3] = 2 \times 10^{-5}$ *M*. In the gas phase $K_{N_2O_3}$ is much higher.[6b] The same type of solvent effect is also exhibited by N_2O_4 (section II).

II. Pulse Radiolysis of NO_2^- Solutions. Band B in Figure 3 should be related to a third species; its assignment to N_2O_4 will now be considered. For this purpose the pulse radiolysis of aqueous solutions of NO_2^- was studied, under conditions where high concentrations of NO_2 could be produced. The radiolysis of water produces the reactive species OH, e_{aq}^-, and H.

$$H_2O \rightsquigarrow OH, e_{aq}^-, H, H_2, H_2O_2$$

In the presence of N_2O, e_{aq}^- can be converted to OH radicals (>98%), with $k_{e_{aq}^- + N_2O} = 6.5 \times 10^9 M^{-1}$ sec^{-1}.[18]

$$e_{aq}^- + N_2O \longrightarrow OH + N_2 + OH^-$$

Figure 5 shows the transient spectra produced on pulse radiolysis of 9.5×10^{-4} *M* KNO_2 saturated with N_2O ($\sim 2.5 \times 10^{-2}$ *M*), pH 5.0, with the OD measured at 0.1 and 160 μsec after the pulse. The former spectrum resembles that obtained in earlier studies,[4,5] and our value $\epsilon_{max} = 190 \pm 20$ M^{-1} cm^{-1} for the 400-nm band is also in agreement. However, the short-wavelength part of this spectrum is not due to NO_2 (section I.B). The absorption below ~300 nm could be accounted in part to the NO_2^{2-} radical[4]

(24) C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **50**, 3075 (1969).

Table I. First-Order Rate Constants for Decay of the Transients Absorbing at 400 and 280 nm[a]

System	k_{400}, sec^{-1}	k_{280}, sec^{-1}	$\frac{k_{280}\text{ (av)}}{k_{400}\text{ (av)}}$
10^{-4} M NO_2^-, air satd	235, 275	...	...
1.2×10^{-4} M NO_2^-, N_2O satd	265	520	1.96
2.6×10^{-4} M NO_2^-, N_2 satd, borate buffer (pH 8.0)	268, 345, 318, 356 (k_{av} = 322)	508	1.58
2.6×10^{-4} M NO_2^-, air satd, borate buffer (pH 7.4)	392	...	...
3×10^{-4} M NO_2^-, N_2 satd	240, 319, 220, 309 (k_{av} = 272)	499, 564, 540, 520 (k_{av} = 531)	1.95
3×10^{-4} M NO_2^-, air satd	...	380	...
6.9×10^{-4} M NO_2^-, air satd	...	579	...
4×10^{-2} M NO_2^-, air satd	390, 440	...	...
0.1 M NO_2^-, air satd	230, 350, 340	...	...
0.1 M NO_2^-, N_2 satd	370	...	...
0.1 M NO_3^- + 1.7×10^{-4} M NO_2^-, N_2 satd	190, 250 (k_{av} = 220)	248	1.1

[a] Temperature = 25 ± 2°.

(or its protonated forms), to N_2O_3, and/or to HNO[25] (with maxima at ∼250 and 380 nm) produced from reactions with e_{aq}^- or H atoms.

$$e_{aq}^- + NO_2^- \longrightarrow NO_2^{2-} \xrightarrow{H_2O} NO + 2OH^-$$

$$H + NO_2^- \longrightarrow NO_2^{2-} + H^+$$

$$H + NO \longrightarrow HNO$$

$$e_{aq}^- + NO \longrightarrow HNO + OH^-$$

The formation of NO_2^{2-} was confirmed (by pulse radiolysis of 8×10^{-4} M KNO_2 + 0.5 M t-butyl alcohol, pH 8.9, air free), $\lambda_{max} \simeq 265$ nm, ϵ_{max} 800 ± 150 M^{-1} cm^{-1}; the decay rate of NO_2^{2-} was found to be $k = 7.7 \times 10^4$ sec^{-1}.

The NO_2 generated by pulse radiolysis was found to undergo two distinct stages of decay: in the microsecond and millisecond ranges, respectively, the first stage has already been studied[4,5] and was ascribed to the equilibration process $2NO_2 \rightleftarrows N_2O_4$. Here we focused our attention on the second stage, which seemed more relevant to the flash photolysis work, where the equilibration process was completed within the duration of the flash.

After reaching equilibrium the system clearly displays a new absorption with λ_{max} 335 nm (Figure 5, curve b). Its location and shape suggest its assignment to N_2O_4 (λ_{max} 343 and 333 for N_2O_4 in hexane and MeCN, respectively[26]). Since the reactions with water are slow compared with the rate of equilibration, $\epsilon_{N_2O_4}$ and $K_{N_2O_4} = [NO_2]^2/[N_2O_4]$ could be calculated by using the following expressions

$$\epsilon_{N_2O_4} = \frac{2OD_{N_2O_4}}{\Delta OD_{NO_2}}\epsilon_{NO_2}$$

$$K_{N_2O_4} = \frac{2(OD_{NO_2})^2}{\epsilon_{NO_2} l \Delta OD_{NO_2}}$$

where $OD_{N_2O_4}$ and OD_{NO_2} are the maximum absorbance values for N_2O_4 and NO_2, respectively, both being in equilibrium; ΔOD_{NO_2} is the drop in absorbance of NO_2 relative to its initial value; l is the optical path; $\epsilon_{NO_2} = 200$ M^{-1} cm^{-1}. From four measurements we derived $\epsilon_{N_2O_4}{}^{335} = (320 \pm 60)$ M^{-1} cm^{-1}, $K_{N_2O_4} = (1.3 \pm 0.4) \times 10^{-5}$ M. The latter value is in agreement with previous results.[4,5] The lowering of $K_{N_2O_4}$ in solution compared to the gas phase is mainly an entropy effect; in solvents which function as Lewis bases, like water, $K_{N_2O_4}$ is further lowered because N_2O_4 is a better Lewis acid than NO_2.[27] There is no previous report on the spectrum of N_2O_4 in water, but compared with other results (ϵ_{max} 179 and 233 in the gas phase and in hexane, respectively[26]) our result is reasonable. Thus spectrum b of Figure 5 appears to represent the spectrum of N_2O_4 in the 300–380-nm region. Its absorption below 300 nm may be somewhat lower than that shown in the figure since some N_2O_3 should also be present in the system (NO is produced by the H atoms). Our values of $K_{N_2O_4}$ and $\epsilon_{N_2O_4}$ may also need some correction owing to the presence of N_2O_3.

III. The Hydrolysis of the Nitrogen Oxides. A. The $2NO_2 \rightleftarrows N_2O_4$ System. The reaction

$$N_2O_4 + H_2O \longrightarrow NO_3^- + NO_2^- + 2H^+ \tag{11}$$

has been hitherto the accepted mechanism for the hydrolysis of NO_2. For such a mechanism to be valid, the decay of NO_2 in equilibrium with N_2O_4 should be second order when $[N_2O_4] \ll [NO_2]$. In our experiments $[N_2O_4]/[NO_2]$ varied from 1.8 (in the pulse work) to 0.02 (the limit of detection for the flash photolysis of NO_3^- + NO_2^-), and all over this range the decay was first order with $k \sim 300$ sec^{-1} (Table I). This finding is in agreement with recent pulse radiolysis work.[5] In addition, in our pulse work we find (a) in both cases the kinetics of the decay is unaffected by varying the pH in the range 5.0 to 11.4; and (b) the decay of N_2O_4 is also first order, with a rate constant $k_{N_2O_4} \sim 2k_{NO_2}$. The reason for the latter result is simple: as long as equilibrium conditions prevail $[N_2O_4]$ is proportional to $[NO_2)^2$, and so $[NO_2] = [NO_2]_0 \exp[-k_{NO_2}t]$ leads to $[N_2O_4] = [N_2O_4]_0 \exp(-2k_{NO_2}t)$.

The reaction of NO_2 with H_2O in the gas phase is also first order with respect to NO_2[28] (Carberry[2] claims that no reaction occurs between NO_2 and water vapor). However, it appears to be slower than that in liquid

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(25) W. A. Seddon, Progress Report, Chemistry and Material Division, Atomic Energy of Canada Ltd., PR-CMa-10, 1969; E. Hayon, unpublished results.

(26) C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 3142 (1958).

(27) T. F. Redmond and B. Wayland, *J. Phys. Chem.*, **72**, 1626 (1968).

(28) P. A. Leighton, "Photochemistry of Air Pollution," Academic Press, New York, N. Y., 1961, p 190.

water: assuming that the reaction is first order in water, the reported data[28] lead to a rate constant which is ~10^3 times smaller. This may reflect the changes in the reactivity of water molecules induced by H bonding; further investigation of the gaseous system is needed before reaching any definite conclusion.

In order to explain these results we propose that reactions 12 and 13 also occur in this system, with

$$NO_2 + H_2O \longrightarrow X \qquad (12)$$

$$X + NO_2 \xrightarrow{H_2O} NO_3^- + NO_2^- + 2H^+ \qquad (13)$$

reaction 13 being much faster than (12). In the gas phase, HNO_3 + HNO_2 should result from reaction 13. Reactions 11, 12, 13 and the equilibrium reaction

$$2NO_2 \rightleftharpoons N_2O_4 \qquad (14)$$

lead to the relation

$$-\frac{d[NO_2]}{dt} - 2\frac{d[N_2O_4]}{dt} = 2k_{12}{}^1[NO_2] + 2k_{11}{}^1[N_2O_4] \qquad (15)$$

where $k_{12}{}^1 = k_{12}[H_2O]$ and $k_{11}{}^1 = k_{11}[H_2O]$. In the slowly decaying system equilibrium conditions should prevail. Thus the rates of decay are related by

$$2[NO_2]\frac{d[NO_2]}{dt} = K_{N_2O_4}\frac{d[N_2O_4]}{dt}$$

Substituting this relation in (15) we obtain

$$-\frac{d[NO_2]}{dt} = 2k_{12}{}^1[NO_2]\frac{1 + (k_{11}{}^1/k_{12}{}^1)[N_2O_4]/[NO_2]}{1 + 4[N_2O_4]/[NO_2]} \qquad (16)$$

Equation 16 describes the behavior of the system if we assume that $k_{11}{}^1 \sim 4k_{12}{}^1$ and that both rate constants are pH independent. The concentration of **X** may be too low for detection. The simplest formula of **X** is H_2NO_3 (or HNO_3^-, etc.). A radical of the same formula has been observed by pulse radiolysis of NO_3^-;[29] further study of this radical may help in establishing the proposed mechanism.

B. The N_2O_3 System. With the NO_2^- + NO system (section I.C), one could study the kinetics of N_2O_3 in aqueous solution. It was found to decay by a first-order process, with $k_{N_2O_3}$ increasing linearly with $[OH^-]$ (Figure 4): $k_{N_2O_3}(sec^{-1}) = 2 \times 10^3 + 10^8 \times [OH^-]$. Thus N_2O_3 appears to react with both H_2O and OH^-.

$$N_2O_3 + H_2O \longrightarrow 2NO_2^- + 2H^+ \qquad (17)$$

$$N_2O_3 + OH^- \longrightarrow 2NO_2^- + H^+ \qquad (18)$$

C. The Hydrolysis Reactions in the Photolysis of NO_2^-. These hydrolysis reactions bring about complete regeneration of NO_2^-; namely, their overall stoichiometry must be

$$NO_2 + NO + H_2O \rightleftharpoons 2NO_2^- + 2H^+ \qquad (19)$$

Still, in the pH range 6–8, the decay kinetics of NO_2 was found to be identical with that displayed by the NO_2 + N_2O_4 system, where the overall stoichiometry is

$$NO_2 + NO_2 + H_2O \longrightarrow NO_2^- + NO_3^- + 2H^+ \qquad (20)$$

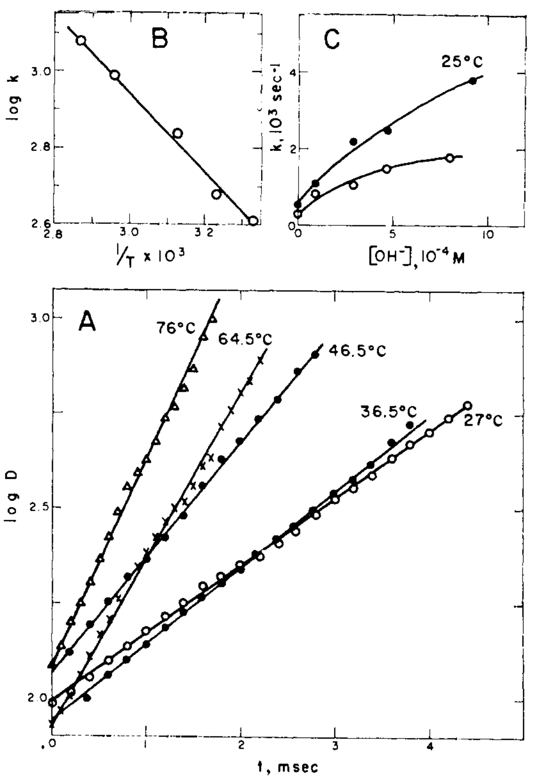

Figure 6. Effect of temperature and pH on the decay rate of NO_2: (A) first-order plots at various temperatures, pH 7.9, decay monitored at 400 nm ("zero" time is not the same for all the runs, but this has no influence on the determination of k); (B) Arrhenius plot for the rate constants, derived from (A); (C) decay constants as a function of $[OH^-]$ at 400 nm (○) and 280 nm (●).

This is shown in Table I, which records some of the kinetic data obtained at room temperature. The decay of NO_2 (the 400-nm band) is first order with k = (3 ± 1) × 10^2 sec^{-1}. (For comparison, Table I includes data on NO_2 produced from the NO_3^- + NO_2^- mixture.) The decay is hardly affected by (a) varying the concentration of NO_2^- in the range 10^{-4}–10^{-1} M, (b) the presence of O_2 or N_2O. The effect of temperature on the rate constant is shown in Figure 6: it follows the Arrhenius law, with $k = 10^6 \exp(-4700/RT)$. (If the reaction is first order in water then the second-order rate constant is 55 times lower.) The low preexponential factor may be due to uncompensated loss of translational and rotational entropy occurring when the activated complex is formed. But it could also be interpreted in terms of a complex mechanism with one or more equilibrium stages. As already discussed,[5] the independence of k on the NO_2^- and NO_3^- concentrations excludes the equilibria $N_2O_4 \rightleftarrows NO_2^+ + NO_2^-$ or $N_2O_4 \rightleftarrows NO^+ + NO_3^-$ as part of the rate-determining mechanism. Moreover, this mechanism cannot account for the first-order kinetics in the gas phase. The identical kinetics of reactions 19 and 20 indicates that both have a common rate-determining step. This can be explained if one assumes that in the presence of NO, reaction 13 is replaced by the fast reaction

$$X + NO \xrightarrow{+H_2O} 2NO_2^- + 2H^+ \qquad (21)$$

The decay of band C (Figure 3) is also first order, with k nearly twice that for NO_2 (Table I). This is in agreement with the general response of bands A

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(29) M. Simic and E. Hayon, unpublished results.

and C to a change in the amount of transients (section I.B). This behavior supports both the assignment of band C to N_2O_3 and the proposed mechanism of hydrolysis. According to this mechanism [NO] = $[NO_2]$ throughout the photolysis and therefore $[N_2O_3]$ should be proportional to $[NO_2]^2$. Hence $[NO_2] = [NO_2]e^{-kt}$ leads to $[N_2O_3] = [N_2O_3]e^{-2kt}$. Here it is of interest to note that the spectrum produced from the NO_3^- + NO_2^- system (section I.B) shows the same decay rate at 400 and 280 nm (Table I). This supports our conclusion that in this case the whole spectrum (insert of Figure 3) is primarily due to NO_2.

The flash photolysis of alkaline NO_2^- solutions revealed new features. (For this purpose only air-free solutions were studied to avoid the formation of O_3^-.) In contrast to the $NO_2 + N_2O_4$ system, the NO_2 + NO ($+N_2O_4$, etc.) system exhibited a pronounced pH effect; the rate of decay of the three transients increased with pH; above pH 11 most of the decay occurred within the flash duration and so the transients, which normally had low absorptions, could hardly be detected. The overall spectrum of the transients could still be measured at pH 10.5 and was found to have the same general shape as that produced in neutral solutions. At 76°, when only NO_2 was produced (section I.B), no effect of pH on the decay could be detected, in agreement with the pulse data (section II).

Qualitatively our results can be ascribed to the effect of pH on $k_{N_2O_3}$ (section III.B), but quantitatively they could not be explained within the frame of the simple mechanism proposed. Reactions 10, 12, 17, and 18 lead to

$$-\frac{d[NO_2]}{dt} - \frac{d[N_2O_3]}{dt} = k_{12}{}^1[NO_2] + k_{N_2O_3}[N_2O_3] \quad (22)$$

where $k_{N_2O_3} = k_{17}[H_2O] + k_{18}[OH^-]$. Under equilibrium conditions and $[NO] = [NO_2]$, the relation $2\cdot[NO_2]d[NO_2]/dt = K_{N_2O_3}d[N_2O_3]/dt$ is valid, which, together with eq 22, yields

$$-\frac{d[NO_2]}{dt} = \frac{k_{12}{}^1[NO_2] + k_{N_2O_3}[N_2O_3]}{1 + 2[N_2O_3]/[NO_2]} \quad (23)$$

Since in the flashed solution $[N_2O_3] \sim 0.1[NO_2]$, this relation reduces to

$$-\frac{d[NO_2]}{dt} \simeq k_{12}{}^1[NO_2] + (k_{N_2O_3}/K_{N_2O_3})[NO_2]^2 \quad (24)$$

Thus as long as $(k_{N_2O_3}/K_{N_2O_3})[NO_2]^2 \ll k_{12}{}^1[NO_2]$ the reaction should be first order and pH independent. On the other hand, a pH dependence should be reflected in deviations from first order and approach to second order. Such deviations were not found. The decay of both NO_2 and N_2O_3 was first order over the entire pH range studied, with $k_{400}/k_{280} \sim 1/2$ (Figure 6), despite the large variation of the rate constants. Moreover, even in neutral solutions the effect of N_2O_3 (the second term in eq 24) should be important. Taking $k_{12}{}^1 \simeq 300$ sec^{-1} (the rate constant for the decay in absence of NO), $k_{N_2O_3} = 2 \times 10^3$ sec^{-1} (section III.B), and $[N_2O_3] = 0.1[NO_2]$, we could estimate that in neutral solution 40% of the decay should proceed through N_2O_3. From the pH dependence of $k_{N_2O_3}$ it appears that already at pH 10 the reaction should mainly involve the hydrolysis of N_2O_3; namely the decay of NO_2 should be nearly second order.[30]

The pulse radiolysis of air-free solutions of NO_2^- (in the absence of additives) is expected to give rise to almost equimolar mixtures of NO and NO_2 (from the reaction e_{aq}^- or H + NO_2^- and OH + NO_2^-, respectively), with $[N_2O_3]/[NO_2]$ higher than in the flashed systems. However, the pulsed system appears to be more complicated.[5] Still, the striking result is that the decay of NO_2 proceeds with the same rate law, first order, with $k \sim 300$ sec^{-1}. Even addition[5] of 4×10^{-5} *M* NO does not affect this result. At $[N_2O_3]/[NO_2] \gg 1$, eq 23 reduces to $-d[NO_2]/dt = {}^1/{}_2k_{N_2O_3}\cdot[NO_2]$; *i.e.*, the rate constant should approach 10^3 sec^{-1} in neutral solutions. Altogether we conclude that the proposed simple mechanism does not fully account for the decay kinetics of a system containing both N_2O_3 and NO_2 in significant amounts. The reason for this is still unclear.

Finally, it is of interest to note that the photolysis of HNO_2 does lead to a net chemical reaction[31]

$$3HNO_2 \longrightarrow 3NO + NO_3^-$$

We believe that also in this case equimolar amounts of NO and NO_2 are produced (by the reactions, $HNO_2 + h\nu \rightarrow OH + NO$ and $OH + HNO_2 \rightarrow H_2O + NO_2$, which are similar to those postulated[16] for HNO_3) but that now the decay occurs through reaction 20.

Acknowledgment. We are indebted to Dr. J. Rabani for some valuable discussions.

(30) The assumption that equilibrium conditions prevail may be incorrect at pH $\gtrsim 10$. Assuming that reaction 10 is diffusion controlled, with $k_{10} \sim 10^9$ M^{-1} sec^{-1} and $K_{N_2O_3} = 2 \times 10^{-5}$ *M*, we estimate $k_{-10} \gtrsim 2 \times 10^4$ sec^{-1}. The lowest value is comparable with $k_{N_2O_3}$ at pH 10.

(31) B. K. Mukergi and N. R. Dhar, *Z. Electrochem.*, 31, 255 (1925).