The process controlling the rate of formation of phosphorus nitride from phosphorus and nitrogen at temperatures above 1800°, therefore, is viewed as the catalyzed dissociation of diatomic phosphorus into atoms. The process probably involves adsorption of diatomic phosphorus on the tungsten, release of phosphorus atoms from the surface and reaction of the phosphorus atoms with nitrogen in the gas phase.

The ratio N:P in the phosphorus nitride products was always greater than unity. This occurrence could result from the presence of phosphorus atoms in accordance with the mechanism postulated below.

Phosphorus atoms—produced at the tungsten surface—react with nitrogen molecules to form the complex PNN, which then reacts with another phosphorus atom. The resultant groupings may combine to yield the polymer $(PN)_n$. Or they may continue to grow through alternate collisions with nitrogen molecules and phosphorus atoms until the reaction ends at an N:P ratio in the range from unity, as in $(PN)_n$, to 5:3, as in the polymer $(P_3N_5)_n$, which has the highest nitrogen content of the known phosphorus nitrides.

Other mechanisms were considered: (a) the atom chain reaction

$$P + N_2 \longrightarrow PN + N$$
$$N + P_2 \longrightarrow PN + P$$

leading into a polymerization reaction, and (b) reaction of the diatomic molecules

$$P_2 + N_2 \longrightarrow P_2N_2\ddagger \longrightarrow 2PN$$

also leading into a polymerization reaction. Calculations based upon the dissociation energies of N_2 and PN and the probable energy of polymerization[26] of PN indicate that the energy level of mechanism (a) is nearly twice as high as the experimental activation energy. The chain reaction might proceed, however, in the vicinity of an electric arc. The magnitude of the experimental activation energy, 59 kcal., is inconsistent also with mechanism (b), because the formation of P_2 molecules requires only 26.8 kcal. mole^{-1}, and the estimated energy level of a P_2N_2 complex is considerably below that of phosphorus atoms.

The reaction velocities found experimentally were compared with those calculated according to the absolute rate equation[27] which applies to the postulated mechanism

$$v_x = C_{P_2}{}^{1/2}c_S \frac{kT}{h} \times \frac{f\ddagger}{F_{P_2}{}^{1/2}f_S}\, e^{-E_0/RT}$$

The number of active sites per square centimeter of catalyst surface, c_s, is a function of the composition of the catalyst and the degree of covering by the adsorbate. From the adsorption isotherm[27] applicable to the mechanism suggested here, the degree of covering is estimated to be 1 to 10%. An assumption that the phosphorus–tungsten complexes are the active sites leads to absolute reaction rates five to ten times as great as the experimental values—a fairly good agreement in view of the uncertainties as to the surface area of the catalyst and the efficiency of condensation of the nitride.

Acknowledgment.—Henry Eyring, Consultant to TVA, gave helpful advice concerning the study. Mary Griffin Rountree and A. J. Smith assisted with the experimental measurements. J. A. Brabson, O. W. Edwards and Inez Jenkins Murphy dealt with the problems of chemical analysis. Thad D. Farr made useful suggestions about the manuscript.

WILSON DAM, ALABAMA

[26] National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Series I, Vol. I, Table 19-10, Washington, D. C., December 31, 1947, and March 31, 1949.

[27] Reference 18, p. 358.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

Interaction of Nitrous Acid with Hydrogen Peroxide and with Water

BY MICHAEL ANBAR[1] AND HENRY TAUBE

RECEIVED JUNE 24, 1954

The rate law for the exchange of oxygen between nitrite and water in the *p*H range 4–6 is $k(H^+)^2(NO_2^-)$; at $\mu = 1.00$ and 25°, $k = 2.6 \times 10^8$ l.^{2} mole^{-2} min.$^{-1}$. The rate is unaffected by phosphate buffer at low concentration. The form of the rate law, the inhibition by H_2O_2 of the exchange, and the kinetics of the reaction of NO_2^- and H_2O_2 are explained by the formation from the activated complex of an intermediate (possibly NO^+), and competition of H_2O and H_2O_2 for reaction with the intermediate. At low nitrite concentrations, two oxygen atoms are transferred from peroxide for each mole nitrate formed, corresponding to decomposition of an intermediate pernitrate ($ON\overset{*}{O}\overset{*}{O}H$) by internal rearrangement. At high nitrite and low peroxide one atom of peroxide oxygen appears in each nitrate formed, a result which corresponds to the process: $ON\overset{*}{O}\overset{*}{O}H + NO_2^- \rightarrow ONO^{*-} + {}^*ONO_2^- + H^+$. When nitrite and peroxide are high, peroxide oxygen appears in the nitrite (but nitrite oxygen does not appear in the peroxide). The exchange results are applied in testing mechanisms which have been proposed for the reaction of amines and nitrites.

The reaction

$$NO_2^- + H_2O_2 = NO_3^- + H_2O \qquad (1)$$

takes place very rapidly in acid solution, but the rate decreases markedly as the acidity is reduced. The rate law for the reaction has been shown to be[2] $-d(\text{peroxide})/dt = k(H^+)(HNO_2)(H_2O_2)$ with $k = 8.3 \times 10^3$ l.^{2} mole^{-2} min.$^{-1}$ at 19°. It also has been shown[3] that in acid solution pernitrite (presumably ONOOH) is formed in equivalent amounts. This was done by making the solution containing NO_2^-, H_2O_2 and acid alkaline soon after mixing. In some experiments as much as 0.7 of the nitrite

[1] UNESCO Fellow on leave from Weizmann Institute, Rehovoth, Israel.

[2] E. Halfpenny and P. L. Robinson, *J. Chem. Soc.*, 928 (1952).

[3] K. Gleu and R. Hubold, *Z. anorg. Chem.*, **223**, 305 (1935).

appears as pernitrite. The pernitrite persists in alkaline solution, but decomposes rapidly in acid to yield NO_3^-. It seems reasonable to suppose that pernitrite is an intermediate for reaction (1) at moderate acidities, even though not enough is present at the steady state under these conditions to make its presence easily recognizable.

We have been concerned mainly with experiments on the system using O^{18} as a tracer. The slow exchange of H_2O_2 and NO_3^- with water makes it possible to obtain meaningful results in such a study. The tracer results are especially searching in the present system, because the reactant NO_2^- and water can also be used isotopically distinct in composition. They are given added interest by comparison with those obtained in the reaction of sulfite and peroxide,[4] which showed that each sulfate formed contains *two* oxygen atoms derived from the peroxide.

Experimental

Definitions and Conditions.—Time is expressed in minutes, and concentrations in moles/liter.

N represents the mole fraction of O^{18} in a particular species. Subscripts represent the time of reaction.

E represents the enrichment ratio, *i.e.*, N in a sample compared to N for a sample of normal isotopic composition.

n represents the number of oxygen atoms derived from peroxide in each nitrate ion formed in the reaction.

The temperature of reaction in all experiments was 25 ± 0.2°.

Materials.—Chemicals were A.R. quality. Water, used as solvent, was purified by redistillation from alkaline permanganate. H_2SO_5 in solution was obtained by the reaction of $K_2S_2O_8$ and sulfuric acid. Solutions used soon after preparation contained less than 5% of the oxidizing agent as H_2O_2.

Procedures.—The oxygen isotope composition of the nitrite was determined using the reaction with azide ion

$$HN_3 + HNO_2 = N_2O + N_2 + H_2O$$

and analyzing the N_2O in the mass spectrometer. Other work has shown exchange of N_2O with solvent to be very slow.[5] The reaction medium was a phosphate buffer at pH 2.5, and the reaction was conducted, adding the nitrite to the azide contained in the buffer. When pH is much lower, the exchange of nitrite with solvent during the reaction becomes too great; at higher pH, the reaction is too slow. Attempts to analyse by acidifying mixtures of N_3^- and NO_2^- contained in alkali revealed a remarkable result: the exchange of NO_2^- and water in alkali is ordinarily very slow, but with azide present it takes place rather rapidly.

The oxygen isotope composition of nitrate was determined on N_2O formed by the reaction of NH_4^+ with NO_3^-. To apply this method to nitrate formed in the reaction mixture, all deleterious substances were first removed. Excess nitrite was destroyed by hydrazine, sulfate and phosphate were removed as the lead compounds, using $PbCl_2$ as the precipitant. Solid NH_4Cl was then added, the solution adjusted with sodium hydroxide to a faintly acidic condition, and water was removed by evaporation at room temperature. The reaction mixture, containing mainly Na^+, NO_3^-, NH_4^+ and Cl^- was dried thoroughly, transferred to a platinum crucible, then heated at *ca.* 300° to liberate N_2O. This gas was first condensed over solid NaOH to remove any acidic substances formed as side products, then over concentrated sulfuric acid, and collected for mass spectrometric analysis.

Isotopic analyses of the hydrogen peroxide were made, oxidizing it with Ce(IV) and examining the isotopic ratio in the oxygen.

The isotopic enrichment of the stock enriched water was determined by comparing isotopic ratios on CO_2 equilibrated with O^{18} enriched and with ordinary water. The enrichment ratio of water in any solution was estimated, taking account of the dilution by ordinary water, and any oxygen exchangeable species.

The pH values of solutions were determined with a Beckman meter, model G.

Calculations.—The experiments on the exchange of NO_2^- and solvent required measurement of the isotopic composition of NO_2^- as a function of time. The logarithms of $(N_t - N_\infty)/(N_0 - N_\infty)$ were plotted against time, and the specific rate determined from this plot is related to the rate, R, of the reaction carrying the exchange by the equation

$$R = k_{ex}\frac{2(NO_2^-)(H_2O)}{2(NO_2^-) + (H_2O)}$$

where R is expressed in the units moles of O per liter per minute.

The experiments on oxygen atom transfer required comparison of the isotopic composition of the nitrate formed with that of the nitrite and peroxide undergoing reaction. The hydrogen peroxide used was of normal isotopic composition, but the solvent, and the nitrite in isotopic equilibrium with it were enriched in O^{18}. To correct as far as possible for fractionation effects (these arise as a result of equilibrium isotope discrimination in the pair NO_2^--H_2O, the fractionation of oxygen in the reactions to produce N_2O, and as a result of side reactions during liberation of N_2O), the oxygen isotopic composition of nitrite in equilibrium with solvent of normal isotopic composition and that of nitrate formed from it by reaction with hydrogen peroxide of normal composition were compared, and the ratio found (1.04) was applied to all the data.

The greatest source of error in the rate data appears to be in the determination of (H^+); in addition to the difficulties in principle with using pH as an index of this quantity, is the imprecision in the measurements. This imprecision is magnified in the values of k, since they depend on the square of (H^+).

Experimental Results

The results on the exchange of NO_2^- and solvent are presented in Table I. Each value of R entered is calculated from a slope determined by 4 or more points. The lines through the points were straight, indicating, as was shown directly, that there was no appreciable change in pH, and that net decomposition was only slight.

TABLE I

THE EXCHANGE OF OXYGEN BETWEEN NITRITE AND WATER

Phosphate used as buffer except in 1.09, 1.61 and 1.62.

Exp.	(NO_2^-)	Buffer	Other	μ	pH	$R \times 10^3$	$k \times 10^{-8}$
1.01	0.25	0.11	....	0.69	8.00	0.0003	100
1.02	.25	.11	....	.44	6.30	.038	6
1.03	.25	.11	....	.44	6.30	.031	5
1.04	.25	.11	....	.45	6.00	.14	5.6
1.05	.25	.15	....	.45	5.95	.16	4.9
1.06	.25	.10	....	.37	5.70	.50	5.0
1.07	.25	.10	....	.35	5.10	4.0	2.7
1.08	.25	.10	....	.35	5.00	4.9	2.0
1.09	.25	.10[a]	....	.32	5.00	3.8	1.5
1.10	.25	.10	$NaClO_4$, 0.22	.57	5.00	6.3	2.6
1.11	.25	.11	....	.35	4.67	21	2.0
1.12	.25	.11	....	.32	4.40	39	(1.1)
1.31	.45	.91	....	1.36	5.00	31	7.1
1.32	.114	.91	$NaClO_4$, 0.34	1.36	5.00	9.9	8.8
1.41	.50	0.05	....	.55	5.47	2.1	3.6
1.42	.50	.025	....	.55	5.30	4.6	3.7
1.43	.20	.10	NaBr, 0.2	.50	5.70	0.35	4.4
1.44	.20	.10	$NaClO_4$, 0.2	.50	5.67	0.43	4.8
1.51	.005	...	$NaClO_4$, 0.99	1.00	4.53	1.00	2.4
1.52	.01	...	$NaClO_4$, .99	1.00	4.43	3.3	2.6
1.53	.05	...	$NaClO_4$, .95	1.00	4.35	26	2.8
1.54	.10	...	$NaClO_4$, .90	1.00	4.30	52	2.3
1.55	.10	...	....		0 10	99	1.8
1.61	.10	.02[b]	$C_6H_5NH_2$, 0.1	.22	5.75	0.5	15.6
1.62	.10	.02[b]	$C_6H_5NH_2$, 0.4	.52	5.40	1.84	10.5

[a] Acetate buffer. [b] Phthalate buffer.

---

[4] J. Halperin and H. Taube, THIS JOURNAL, **74**, 380 (1952).

[5] A. Bothner-By and L. Friedman, *J. Chem. Phys.*, **20**, 4591 (1952).

The values of specific rate entered in the last column of the table were calculated from the rate law

$$R = k(\mathrm{H^+})^2(\mathrm{NO_2^-})$$

In this rate law, $(\mathrm{H^+})$ = antilog (−*p*H), and NO_2^- represents the concentration of nitrite ion, calculated from the stoichiometric nitrite, allowing for the association to form HNO_2. The value of $K_{\mathrm{diss.}}$[6] used for this calculation was 5.0×10^{-4}, at all ionic strengths. In the most extreme case, at the lowest *p*H studied, this correction amounts to only 16%.

The first fourteen experiments described were performed before a new method of making isotopic analyses on NO_2^- had been worked out. The values of R entered for these are not as precise as they are for the remainder of the experiments.

Some experimental results on the exchange of oxygen between NO_2^- and H_2O in the presence of H_2O_2 are recorded in Table II. In these experiments, nitrite and peroxide were of normal isotopic composition and the solvent was enriched in H_2O^{18}.

TABLE II

Exp.	(NO_2^-)	Buffer	(H_2O_2)	μ	*p*H	$R \times 10^3$	$k \times 10^8$
2.01	0.25	0.2	1.0	0.45	4.75	8.8	1.1
2.02	.25	.2	4.0	.45	4.30	12.9	0.2

Table III contains the record of experiments in which the isotopic composition of the nitrite initially was between that of the solvent and that of the hydrogen peroxide. The hydrogen peroxide of normal isotopic composition was used at high concentration.

TABLE III

THE EXCHANGE OF NO_2^- WITH H_2O AT HIGH HYDROGEN PEROXIDE CONCENTRATION

(NO_2^-), 0.63; (H_2O_2), 4.0; $\Sigma(PO_4^{\equiv})$, 0.15; *p*H 5.0; $\mu = 0.78$

A

Time	3	6.5	12	20	—
E	2.391	2.276	2.366	1.636	3.500[a]

(NO_2^-), 0.50; (H_2O_2), 2.00; *p*H 5.0; $\mu = 0.50$

B

Time	2	13	26	42	—
E	4.185	4.193	4.086	3.960	4.270[a]

[a] Calcd. for NO_2^- in isotopic equilibrium with the solvent.

The rate of reaction of hydrogen peroxide and nitrite was studied spectrophotometrically, and the results of this series of experiments are summarized in Table IV. The wave length 357 mμ which corresponds to the band maximum for NO_2^- was used to follow the reaction. This wave length is much more strongly absorbed by the pernitrite[7] than by nitrite. There was no evidence for the growth of pernitrite, indicating that its stationary concentration is very slow.

TABLE IV

THE RATE OF REACTION OF HYDROGEN PEROXIDE AND NITRITE AS A FUNCTION OF HYDROGEN PEROXIDE CONCENTRATION AT HIGH PEROXIDE CONCENTRATION

$\Sigma PO_4^{\equiv}$, 0.30 *M*; temp., 25.0°.

Exp.	(H_2O_2)	*p*H	$k' \times 10^{-3}$
4.01	0.08	4.60	0.63
4.02	0.20	4.65	1.17
4.03	0.40	4.60	1.9
4.04	1.00	4.65	2.2
4.05	2.40	4.85	3.1
4.06	4.80	5.10	3.4
4.07	8.00	4.60	2.6

The system is well behaved kinetically, and in buffered solutions, the reaction is strictly first order in NO_2^-, to at least 90% decomposition, which was about the limit for meaningful data. The specific rates tabulated are defined by the rate law

$$\frac{-\mathrm{d}(\mathrm{NO_2^-})}{\mathrm{d}t} = k'(\mathrm{H^+})^2(\mathrm{NO_2^-})$$

An attempt was also made to obtain data for systems at low acid, not containing buffer. The curves in a plot of log (extinction − extinction) *vs.* t were found to be concave down. This feature is readily accounted for in the following way. When $(NO_2^-) >> (HNO_2) >> (H^+)$, for the major portion of the reaction, (HNO_2) remains constant as NO_2^- disappears. Thus it follows that $(H^+) = K(HNO_2)/(NO_2^-)$ varies inversely as (NO_2^-), and the rate law $k'(H^+)^2(NO_2^-)$ assumes the form const./(NO_2^-) with const = $kK^2(HNO_2)^2$. The data for individual experiments were found to conform well to the integrated form

$$(\mathrm{NO_2^-})^2_0 - (\mathrm{NO_2^-})^2 = 2k'K^2(\mathrm{HNO_2})^2t$$

but the specific rates from experiment to experiment were erratic. This effect is attributed to the uncertainty and instability in *p*H in the low acid range studied (*p*H *ca.* 5). The data in general are in agreement with those obtained with phosphate buffer added.

The results of the tracer experiments on transfer of oxygen to nitrite during reaction are presented in Table V.

TABLE V

OXYGEN ATOM TRANSFER IN THE REACTION OF PEROXIDES AND NITRITE

Reaction to completion except in 5.10, in which it was 10% complete.

Expt. no.	(NO_2^-)	(H_2O_2)	*p*H	Other	Buffer	E for NO_2^-	E for NO_3^-	n
5.01	1.56	1.23	1.8	.....	0.04	6.30	4.22	1.17
5.02	1.33	1.33	3.5	.....	.17	5.88	3.92	1.21
5.03	1.33	1.33	4.5	.....	.17	5.88	3.90	1.22
5.04	1.33	1.33	6.0	.....	.17	5.88	3.88	1.23
5.06	2.00	0.80	5.5	.....	1.5	7.00	5.00	1.00[a]
5.07	0.50	3.64	1.7–2.0	.....	.8	6.30	2.90	1.93[b]
5.08	.40	2.66	2.0	.....	.8	6.45	2.83	1.99[b]
5.09	.50	2.00	1.5–1.8	.....	.8	5.93	2.60	2.02
5.10	3.33	2.67	5.5	.....	.5	6.95	4.49	1.24
5.11	0.50	2.00	1.7	Pt	.5	5.82	3.02	1.71
5.12	1.56	1.23	4.4	Pt	.04	6.30	4.52	1.07
5.13	1.67	1.33	4.5	Pt	.3	6.00	4.50	.91
5.14	1.67	1.33	5.5	Pt	.3	6.00	4.20	1.08
5.15	1.34	2.14	6.2	Pt	.4	7.00	4.80	1.10
5.21	1.41	1.13	4.0	Mo(VI)	.1	6.00	4.28	1.03
5.22	1.56	1.23	4.8	Mo(VI)	.04	6.12	4.24	1.10
5.23	0.50	2.66	5.5	Mo(VI)	.4	7.00	3.50	1.57[b]
5.24	.40	4.00	1.9	Mo(VI)	.5	6.45	2.90	1.95[b]
5.31	.50	.28[c]	0	.....	..	3.94	2.96	1.00

[a] H_2O_2 added slowly to nitrite. [b] Nitrite added slowly to H_2O_2. [c] H_2SO_5 as oxidant.

Discussion

The results reported in Table I show that the leading term in the rate law for the exchange of oxy-

---

(6) A. Klemenc and F. Hayek, *Monatsh.*, **53/54**, 407 (1929).

(7) G. Kortüm and B. Finckh, *Z. physik. Chem.*, **B48**, 32 (1941).

gen between nitrite and water for the *p*H range ~4 to 6 is $k(H^+)^2(NO_2^-)$. When $\mu = 1.0$ and the temperature is 25°, k is approximately 2.6×10^8. At low acid, the rate of reaction is not accounted for entirely by this term, and evidently a term of lower order in (H^+) enters. Phosphate and acetate buffers at concentrations of 0.1 *M* and lower have little specific effect on the rate of exchange, but at high phosphate buffer, a specific effect of this agent can be recognized (*cf.* 1.31 and 1.32 with 1.51 to 1.55).

This rate law is consistent[8] with the assumption that the rate-determining act in the reaction for water exchange is the S_N1 process

$$H_2NO_2^+ \longrightarrow H_2O + NO^+ \qquad (2)$$

Other observations prove that an S_N1 process is in fact the principal path for the activated complex of composition $H_2NO_2^+$. Inhibition by H_2O_2 of the exchange between NO_2^- and water is marked: thus in 4 *M* H_2O_2, the specific rate for exchange is only $^1/_{12}$ of what it is when H_2O_2 is absent. The kinetic data of Table IV demonstrate the complementary effect, that at high (H_2O_2) the order of the reaction with respect to this reagent is less than one. A limiting rate, independent of the concentration of H_2O_2 and corresponding to essentially complete consumption of NO^+ by H_2O_2 is achieved at about 4 *M* H_2O_2. The limiting specific rate for the oxidation of nitrite by H_2O_2 (3.5×10^8, see below) agrees satisfactorily with the specific rate for water exchange calculated by the same rate law. The slight difference can be attributed to the effect of the higher buffer concentration in the oxidation experiments. The exchange data, and the specific rate data lead to estimates for the ratio k_3/k_{-2}, where k_{-2} is the first-order specific rate for the reverse of reaction 2, and k_3 is the specific rate for

$$NO^+ + H_2O_2 \longrightarrow ONOOH \qquad (3)$$

The exchange experiments 2.01 and 2.02, taking the exchange rate at $(H_2O_2) = 0$ as 2.6×10^8, yield for this ratio the values 1.4 and 3. When the rate experiments in Table IV are treated according to the rate law

$$\frac{-d(H_2O_2)}{dt} = \frac{k_3k_2(H^+)^2(NO_2^-)(H_2O_2)}{k_{-2} + k_3(H_2O_2)}$$

plotting $1/k'$ *vs.* $1/(H_2O_2)$, they yield for k_2 the value 3.5×10^8 and for k_3/k_{-2}, 2.4. The best value for the ratio k_3/k_{-2} is obtained from the rate data.

The data considered leave little room for S_N2 reaction paths, either with H_2O or H_2O_2 as the reagents attacking nitrite. Experiment 1.43 in comparison to 1.44 demonstrates that Br^- at 0.2 *M* does not catalyse exchange in the system H_2O–NO_2^-, and shows that the S_N2 process

$$HNO_2(\text{or } H_2NO_2^+) + Br^- \rightarrow$$

contributes little under these conditions. This observation has added interest in connection with the suggestion by Austin, *et al.*, that Cl^- catalyzes the reaction of nitrite and certain amines.[9]

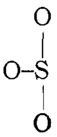
The tracer results, and certain features of the exchange results, are explained by assuming ONOOH as an intermediate deriving two oxygen atoms from the peroxide, and reacting by the competing paths

$$O\overset{*}{N}\overset{*}{O}OH \longrightarrow O_2{}^*NO^- + H^+ \qquad (4)$$

$$O\overset{*}{N}\overset{*}{O}OH + NO_2^- \longrightarrow ONO^{*-} + O_2NO^{*-} + H^+ \qquad (5)$$

When the stationary concentration of the nitrite is low (the extreme was achieved by adding nitrite slowly to peroxide as in exp. 5.08), reaction (4) predominates, and n approaches 2. When nitrite is high, reaction (5) predominates. If furthermore peroxide is low, the nitrite left labeled with peroxide oxygen by the transfer of an oxygen atom to another nitrite exchanges before it is oxidized, and n approaches 1. These conditions were apparently satisfied in experiment 5.06. When both nitrite and peroxide are high, values of n between 1 and 2 are expected, for even though pernitrite reacts by transfer to another nitrite, the nitrite ion left labeled will be oxidized to nitrate before it exchanges. In the limit of high nitrite and high hydrogen peroxide, the value of n expected is 1.67[10] for complete consumption of nitrite; for consumption of 0.1, as in experiment 5.10, it is 1.36. The defect, only slightly outside of experimental error, can be attributed to partial exchange of peroxide-labeled nitrite with water.

Experiments A and B in Table III demonstrate directly the labeling of residual nitrite by peroxide oxygen as the reaction progresses. In both experiments, the isotopic composition changes in the opposite direction from that corresponding to exchange with water. Analyses were made of the isotopic composition of the hydrogen peroxide during reaction. Only a slight change occurred, of magnitude expected for an isotope fractionation effect.

The assumption of a reaction of the type of (5) is supported by the experiments with H_2SO_5 as oxidizing agent, which shows that with this peroxide, a single atom of oxygen is transferred per mole of nitrite oxidized. H_2SO_5 and HOONO differ from H_2O_2 in two respects: S(VI) and N(III) are much less labile to substitution than is H(I); the groups  $\text{O–}\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle O}{|}}{S}}$ and NO^+ have much stronger inductive effects than H^+, facilitating the rupture of the O–O bond by transfer of O (or OH^+) to a reducing agent.

The experiments with Mo(VI), undertaken to discover whether the peroxide of Mo(VI) reacts by O atom transfer, did not yield clear-cut results. In almost all cases, with Mo(VI) present, n is lower than in a similar experiment without it. However, the difference is not large, and in the absence of kinetic data, establishing independently the relative contributions by the Mo(VI) and the direct path, a definite number cannot be assigned to transfer by Mo(VI) peroxide. The system is further

---

[8] The data show that an intermediate is formed from the activated complex $H_2NO_2^+$. The product NO^+ seems an attractive possibility, but it must be admitted that an isomeric change in $H_2NO_2^+$ fits the data equally well.

[9] A. T. Austin, E. D. Hughes, C. K. Ingold and J. H. Ridd, THIS JOURNAL, **74**, 555 (1952).

[10] The relationship of x, the mole fraction of oxygen in the nitrite which is derived from peroxide, and a/a_0, the fraction of the nitrite left is $1 - x = \sqrt{a/a_0}$. The number of oxygens lost to the solvent for complete reaction of a_0 molecules of nitrite $= -\int_a^0 x\,da = 1/3a_0$. The integration to $a = 0$ does not correspond to a situation realizable experimentally, for at low (NO_2^-), reaction 4 intervenes.

complicated by an important side reaction, a catalytic (or induced) decomposition of H_2O_2.

Experiment 5.15 shows that Pt provides a path for the reaction of nitrite and hydrogen peroxide. Under the conditions of this reaction, an insignificant amount of nitrate is formed by the direct reaction. In the other experiments with Pt present, n is lower than in corresponding experiments without it. The defect may be the result of the lower prevailing concentration of H_2O_2, caused by the decomposition which consumes the bulk of the peroxide.

The exchange results have implications for reactions of nitrite with other nucleophilic reagents besides H_2O_2. It has been suggested that the nitrosating agent in reactions of amines with nitrite is N_2O_3[11] and that when the amine is at high concentration, the formation of N_2O_3 by the reaction

$$2HNO_2 \longrightarrow N_2O_3 + H_2O \qquad (6)$$

becomes rate determining.[12] This reaction also has been suggested as the rate-determining step for the decomposition of $(SO_3)_2NO^=$ catalyzed by HNO_2.[13] From the latter work, the rate constant for reaction 1 at 25° was calculated as 7×10^3 l. mole^{-1} min.$^{-1}$, a value which after correction for the difference in temperature is in agreement with that calculated from data on the rate of diazotization of aniline.[14] If reaction 6 occurs it must provide a path for the exchange of oxygen between NO_2^- and solvent. Our data show that the reaction carrying the exchange, up to solutions as concentrated in NO_2^- as $0.5M$, is first order in nitrite, rather than second order. This alone is not evidence against reaction 6 as it is applied to nitrosating reactions, because reaction 2 may be part of a detailed mechanism for reaction 6. However, a comparison of rates demonstrates the incompatibility of the interpretation of nitrosation kinetics and the observed rate of water exchange: when the specific rate cited for reaction 6 is applied to the concentration conditions of our experiments, the rates calculated are greater by a factor of 50 than those observed, when (NO_2^-) is 0.5 M. We conclude, therefore, that the mechanism proposed for the reaction of nitrites and amines is incomplete, if not incorrect. If in fact a process second order in HNO_2 to form N_2O_3 does take place, it requires for the activated complex in addition to $2HNO_2$ substances which are not contained in our solutions, with or without added buffer. It should also be noted that the agreement among the values deduced for the specific rate of reaction 6 is not complete. Thus Schmid and Woppmann[15] report for k_6 at 0°, 55 l. mole^{-1} min.$^{-1}$, to be compared with *ca.* 300 at the same temperature suggested by Li and Ritter.[14]

The exchange results indicate the necessity for re-examining the mechanisms of the reactions in question, but have not sufficed to resolve for us some of the apparent paradoxes in the field. Leading among these is the report by some authors that the reaction are first order in HNO_2, and by others that they are second order. Results in direct contradiction have been reported: Dusenberry and Powell[16] demonstrating the first-order law for the reaction of NH_4^+ and NO_2^-, and Abel, Schmid and Schafranik,[17] the second-order law for the same reaction. The interpretation[9] that the difference is caused by the phosphate buffer (which was used in the studies by Dusenberry and Powell, but not in the others) introducing a new path is not valid. This interpretation requires the rates in the buffered system to be so much greater than in the other, as to swamp the second-order path. The rates reported, at least under some conditions, are approximately the same in both systems. Nor can it be argued that the buffer changes the reaction path by consuming nitrite. A spectrophotometric study which we have done showed no effect on the nitrite absorption by phosphate buffer at 5×10^{-2} to 1 M. Even more convincing is the observation that buffer, at least at low concentration but equivalent to the nitrite, has no effect on the exchange of oxygen between nitrite and water.

The experiment on the exchange in the reaction mixture containing aniline was done at acidity sufficiently low[9] so that the rate of diazotization is independent of the concentration of aniline. According to the interpretation that reaction 6 is rate determining, water exchange by this path should be eliminated. The rate of water exchange, however, was observed to be greater than in the other reaction mixtures of Table I at the same acidity. The conclusion suggests itself, that aniline, or some other component in this buffer mixture, may be involved in the rate term which is second order in HNO_2, and that it also provides a new path for the water exchange. This suggestion however does not help to resolve the paradox presented by comparison of the two researches on the reaction $NH_4^+ + NO_2^-$.

The rate laws for the NO_2^-–H_2O exchange which we have observed, and the actual rates, are consistent with the interpretation that NO^+, formed from an activated complex of composition H_2ONO^+, is the nitrosating agent in the reaction[16] of NH_4^+ and NO_2^-, and in the reaction of sulfamic acid[18] and NO_2^-.

Acknowledgment.—This work was supported by the Office of Naval Research under Contract N6-ori-02026. The funds for the purchase of the mass spectrometer used in the research were supplied by the Atomic Energy Commission under Contract At(11-1)-92.

CHICAGO 37, ILL.

---

[11] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 294.

[12] E. D. Hughes, C. K. Ingold and J. H. Ridd, *Nature*, **166**, 642 (1950).

[13] J. C. M. Li and D. M. Ritter, THIS JOURNAL, **75**, 5823 (1953).

[14] J. C. M. Li and D. M. Ritter, *ibid.*, **75**, 3024 (1953).

[15] H. Schmid and A. Woppmann, *Monatsh.*, **83**, 346 (1952).

[16] J. H. Dusenberry and R. E. Powell, THIS JOURNAL, **73**, 3266 (1951).

[17] E. Abel, H. Schmid and J. Schafranik, *Z. physik. Chem.* (Bodenstein Festband), 510 (1931).

[18] J. C. M. Li and D. M. Ritter, THIS JOURNAL, **75**, 5828 (1953).