photometer (model DU) in the region 216 mμ to 360 mμ; $\epsilon = (1/c) \log I_0/I$, where c is the concentration in moles per liter. Since most of the compounds were rather unstable liquids, at least three distillation cuts of similar boiling point and refractive index were used and the triplicate spectral determinations (in 95% ethanol) were carried out immediately after distillation.

Preparation of Compounds.—In spite of the fact that most of the substances are known, their purity was checked by elementary analysis in addition to b.p. and refractive index. Compounds 1, 3, 16 and 22 were prepared according to Nield,[18] No. 5 according to Pauly and Lieck,[19] Nos. 17 and 19 by decomposition of the corresponding Mannich bases,[20] while Nos. 20 and 21 were gifts of Dr. Jay S. Buckley of the University of Minnesota.[21] The synthesis of diacetylbutadiene (No. 8)[22] will be published at a later date.[23] The following compounds are new:

3,6-Dibromo-3,5-octadien-2,7-dione (No. 7).—This compound was obtained in 56% yield from the corresponding dilactone[23] by following the general method described by Nield.[18] Two recrystallizations from 95% ethanol afforded the desired compound in rosettes of yellow needles, m.p. 102–103°.

Anal. Calcd. for $C_{10}H_8O_2Br_2$: C, 32.46; H, 2.72. Found: C, 32.60; H, 2.79.

3-Bromo-4-(*p*-methoxyphenyl)-3-buten-2-one (No. 24).—α-Keto-β-acetyl-γ-(*p*-methoxyphenyl)-butyrolactone was synthesized in 32% yield by exactly the same procedure employed by Nield[18] for the corresponding γ-phenyl derivative; m.p. 157–158°.

Anal. Calcd. for $C_{13}H_{12}O_5$: C, 62.90; H, 4.88. Found: C, 63.17; H, 5.29.

The bromination and cleavage of the butyrolactone derivative was carried out according to Nield's method[18] at 5° in 85% methanol solution; yield 45%, b.p. 153–155° (0.01 mm.), n^{19}D 1.6579.

Anal. Calcd. for $C_{11}H_{11}O_2Br$: C, 51.79; H, 4.35. Found: C, 51.56; H, 4.62.

α-Bromovinyl-*p*-methoxyphenyl Ketone (No. 18).—The synthesis of α-keto-β-(*p*-methoxybenzoyl)-butyrolactone as modeled after that of the corresponding benzoyl derivative[18]; yield 34%, m.p. 153–154°.

Anal. Calcd. for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30. Found: C, 61.66; H, 4.69.

The bromo derivative was prepared from the above lactone in the usual manner[18] in 41% yield, b.p. 130–131° (0.005 mm.), n^{19}D 1.6028.

Anal. Calcd. for $C_{10}H_9O_2Br$: C, 49.82; H, 3.76. Found: C, 49.71; H, 3.99.

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MEXICO CITY, D. F.
CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF CALIFORNIA]

Reactions of Nitrous Acid. I. Ammonium Nitrite Decomposition[1]

BY JOSEPH H. DUSENBURY AND RICHARD E. POWELL

The rate law for the reaction of nitrous acid with ammonia is $d(N_2)/dt = k_r (NH_4^+)(HNO_2)$, where $k_r = (kT/h) \exp(-7.75/R) \exp(-20{,}000/RT)$ sec.$^{-1}$ mole^{-1} liter. The rate-determining step of the reaction is proposed to be reaction of nitrosyl ion with molecular ammonia.

The kinetics of the reaction between ammonium ion and nitrite ion

$$NH_4^+ + NO_2^- = N_2 + 2H_2O$$

was studied by Abel and co-workers in 1931.[2] They reported the reaction to be kinetically third order: first order with respect to ammonium ion, to nitrite ion and to molecular nitrous acid. Reaction mechanisms involving such an extra molecule of nitrous acid have seemed to us implausible, so we have reinvestigated the kinetics.

Experimental

The reaction vessel was a three-necked flask equipped with a gas-tight motor stirrer,[3] a pressure-equalizing funnel for adding the sodium nitrite solution to the other reactants, and a gas buret in which the evolved nitrogen was measured. The reactor was immersed in an oil thermostat whose temperature was controlled to ±0.05°. The apparatus was swept with nitrogen before each run. At the completion of each run the evolved gas was shaken with permanganate solution to determine the nitric oxide liberated by the incidental decomposition of nitrous acid. Under our experimental conditions the amount of such decomposition was negligible.

Reaction mixtures were made up from stock solutions of sodium nitrite and ammonium perchlorate, whose concentrations were checked by analysis. The acidity of the reaction mixtures was controlled by phosphate buffers made with phosphoric acid and NaH_2PO_4, and was measured before and after each run with a glass-electrode *p*H meter. The ionic strength was brought to the desired value with sodium perchlorate.

Individual measurements of initial rates were reproducible within about 2%.

Results and Discussion

In one series of rate measurements, only the initial concentration of ammonium ion was varied (Table I, Fig. 1). In another series, only the initial concentration of total nitrous acid was varied (Table II, Fig. 2). These data demonstrate that the reaction is first order with respect to (stoichiometric) ammonia and first order with respect to (stoichiometric) nitrous acid. We find no evidence of the second-order dependence on stoichiometric nitrous acid which Abel, *et al.*, reported. The probable explanation of the discrepancy is that we buffered our reaction mixtures, whereas they omitted doing so.

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[1] Presented at the 115th National Meeting of the American Chemical Society, San Francisco, California.

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TABLE I

EFFECT OF AMMONIA CONCENTRATION[a]

pH	ΣHNO_2, M	ΣNH_3, M	Initial rate, mole liter^{-1} sec.$^{-1}$ $\times 10^{-8}$
2.86	0.00904	0.395	128
2.87	.00896	.197	64
2.82	.00916	.098	34.9
2.84	.00924	.049	16.6

[a] Temperature 30.0°, ionic strength 1.00, total concentration of phosphate buffer 0.567 M.

TABLE II

EFFECT OF TOTAL NITROUS ACID CONCENTRATION[a]

pH	ΣHNO_2, M	ΣNH_3, M	Initial rate, mole liter^{-1} sec.$^{-1}$ $\times 10^{-8}$
2.98	0.0940	0.186	643
2.92	.0507	.196	338
2.90	.0488	.196	335
2.91	.0249	.196	156
2.91	.0100	.198	65.0
2.94	.00490	.198	32.6
2.90	.00243	.198	17.5

[a] Temperature 30.0°, ionic strength 1.00, total concentration of phosphate buffer 0.567 M.

The dependence of the rate upon pH (Table III, Fig. 3) permits us to decide which of the various nitrous acid species (HNO_2, NO_2^- or possibly NO^+) may react with which of the ammonia species (NH_4^+, NH_3 or possibly NH_2^-) in the rate-determining step. For comparison with the experimental data, we compute a family of curves giving the expected rate as a function of pH for all possible pairs of reactant species. The ratio of the rate at any given acidity, (H^+), to the rate at 1 M H^+ is given by the expression

$$(H^+)^{Z+1}\left(\frac{1+K_1}{(H^+)+K_1}\right)\left(\frac{1+K_2}{(H^+)+K_2}\right) \qquad (1)$$

where Z is the charge on the activated complex, which is the sum of the charges on the two reactant species. K_1 and K_2 are the known ionization constants of HNO_2 and NH_4^+, respectively.[4,5] The several theoretical curves are displayed in Fig. 4.

TABLE III

EFFECT OF HYDROGEN ION CONCENTRATION[a]

pH	ΣHNO_2, M	ΣNH_3, M	Initial rate, mole liter^{-1} sec.$^{-1}$ $\times 10^{-8}$
0.43[b]	0.0477	0.197	517
0.96	.0475	.196	513
1.81	.0439	.193	371
2.95	.0481	.197	305
3.68	.0485	.197	140
4.11	.0476	.196	51.7
4.33	.0487	.198	30.5
5.00[c]	.0480	.197	9.15
6.18[d]	.0492	.198	0.588

[a] Temperature 30.0°, ionic strength 1.00, total concentration of phosphate buffer 0.567 M. [b] Acidified with sulfuric acid. [c] Rate was measured at 43.0° and recomputed to 30.0° on basis of 20 kcal. heat of activation. [d] Rate was measured at 60.0° and recomputed to 30.0° on basis of 20 kcal. heat of activation.

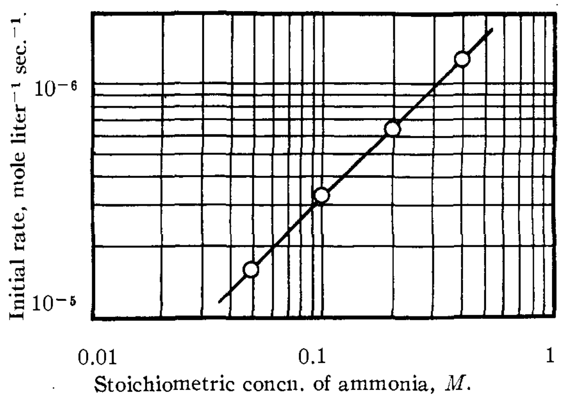

Fig. 1.—Dependence of rate on ammonia concentration The straight line has a slope of unity.

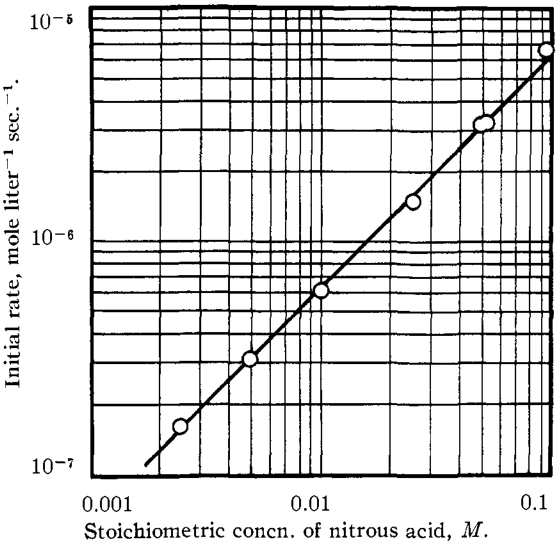

Fig. 2.—Dependence of rate on nitrous acid concentration. The straight line has a slope of unity.

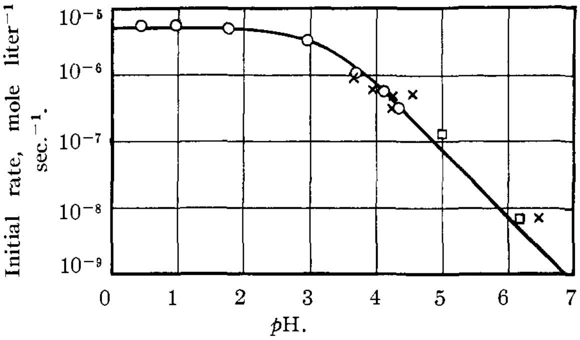

Fig. 3.—Dependence of rate on acidity. Circles, measurements at 30°. Squares, measurements at higher temperatures recomputed to 30°. Crosses, measurements by Abel *et al.*, computed from data in ref. (2). The curve is the theoretical curve for $Z = +1$.

The experimental data (Fig. 3) are in excellent agreement with the theoretical curve for $Z = +1$, but in no kind of agreement with any of the other curves. The activated complex for the reaction therefore carries a +1 charge. It has the formula of the nitrosoammonium ion NH_3NO^+ or a hydrated form thereof, and could be formed

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(4) A. Klemenc and E. Hayek, *Monatsh.*, **54**, 407 (1929).

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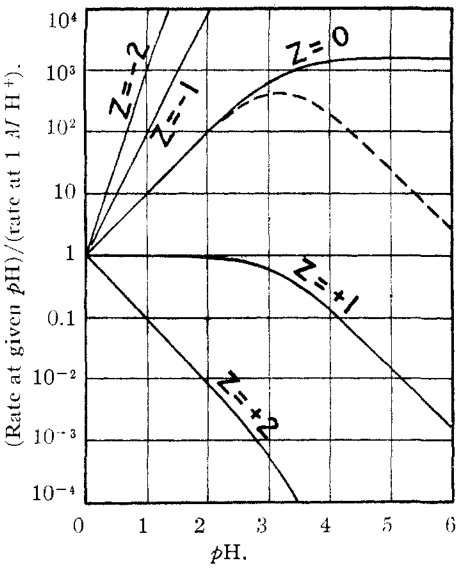

Fig. 4.—Theoretical dependence of rate on acidity. The dashed line is for Abel's third-order rate law.

either by the reaction of NH_4^+ with HNO_2 or by the reaction of NO^+ with NH_3. Of course, it is quite impossible to decide between these two mechanisms on the basis of kinetics. For the sake of having the rate law in terms of conventional species, we write

$$d(N_2)/dt = k_r(NH_4^+)(HNO_2) \qquad (2)$$

It does not in fact seem reasonable to us that the activated complex NH_3NO^+ be formed by a direct reaction of neutral HNO_2 with the already 4-coördinated nitrogen in NH_4^+ ion. We are inclined to prefer the sequence in which the reactants are nitrosyl ion and molecular ammonia formed by preliminary reversible equilibria

$$H^+ + HNO_2 = H_2O + NO^+ \text{ (rapid)} \qquad (3)$$

$$NH_4^+ = H^+ + NH_3 \text{ (rapid)} \qquad (4)$$

$$NO^+ + NH_3 \longrightarrow NH_3NO^+ \text{ (rate determining)} \qquad (5)$$

The nitrosyl ion (NO^+ or $HONOH^+$) has been proposed previously, both as a stable species and as a kinetic intermediate. The reaction of NO^+ with NH_3 would be an acid–base reaction in the Lewis sense, and would be expected to proceed with only a small activation energy, or possibly to be diffusion-controlled in solution.

The rate of reaction is the same in 0.226, 0.576 or 0.849 *M* phosphate buffer, so the reaction is not subject to general acid catalysis by the phosphoric acid species.

At higher ionic strengths the reaction is noticeably slower (Table IV), as Abel, *et al.*, observed also. This phenomenon is surprising, for we would have expected the rate of reaction of an ion with a neutral molecule to be nearly independent of ionic strength. As a clue to its cause, we note that the ionic strength effect is much smaller at higher acidity. At the lower acidity, a substantial part of the total nitrous acid is present as NO_2^- ion. Decreasing the ionic strength increases the activity coefficients of NO_2^- ion and H^+ ion, thereby shifting to the left the equilibrium $HNO_2 = H^+ + NO_2^-$. As the concentration of molecular HNO_2 rises, so does the reaction rate. At a higher acidity, most of the nitrous acid is already converted into HNO_2, and this sort of ionic strength effect must be less important.

TABLE IV

EFFECT OF IONIC STRENGTH[a]

pH	ΣH_3PO_4, *M*	Ionic strength	k_r, sec.$^{-1}$ mole^{-1} liter $\times 10^{-4}$
3.0	0.226	0.50	7.22
3.0	.226	1.00	5.00
3.0	.226	1.45	3.28
2.0	.576	0.50	5.85
2.0	.567	1.00	5.03
2.0	.567	1.28	4.63

[a] Temperature 30.0°.

Over the temperature range 20 to 35° the specific rate is given by the equation

$$k_r = (kT/h)e^{-7.75/R}\, e^{-20,000/RT} \text{ sec.}^{-1} \text{ mole}^{-1} \text{ liter} \qquad (6)$$

which reproduces the data of Table V.

TABLE V

EFFECT OF TEMPERATURE[a]

Temperature, °C.	k_r, sec.$^{-1}$ mole^{-1} liter[b] $\times 10^{-4}$
20.17	1.55
25.00	2.78
30.00	5.00
35.00	8.32

[a] pH 3.0, total ammonia 0.20 *M*, total nitrous acid 0.050 *M*, ionic strength 1.00, total concentration of phosphate buffer 0.567 *M*. [b] In computing k_r from the measured rates, we used as the ionization constant for HNO_2: at 20° 5.17 × 10^{-4}; at 25° 5.70 × 10^{-4}; at 30° 6.26 × 10^{-4}; at 35° 6.87 × 10^{-4}.

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