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

Reactions of Nitrous Acid. II. The Reaction of Nitrous Acid with Methylamine

BY JOSEPH H. DUSENBURY AND RICHARD E. POWELL

The rate law for the reaction of nitrous acid with methylamine is $d(N_2)/dt = k_r(CH_3NH_3^+)(HNO_2)$, where $k_r = (kT/h) \exp(-27.8/R) \exp(-14{,}000/RT)$ sec.$^{-1}$ mole^{-1} liter. The rate-determining step of the reaction is proposed to be reaction of nitrosyl ion with molecular methylamine.

The kinetics of the reaction between nitrous acid and methylamine

$$CH_3NH_2 + HNO_2 = N_2 + CH_3OH + H_2O$$

was investigated by T. W. J. Taylor.[1] He reported the reaction to be kinetically third order: first order with respect to methylammonium ion, to nitrite ion, and to molecular nitrous acid. In a later review of his investigation, he writes[2] "A reaction complex is formed consisting of the amine nitrite and a molecule of nitrous acid, the latter being liberated unchanged in the decomposition of the reaction complex. Until the role of this apparently unnecessary molecule of nitrous acid is understood, the problem of the mechanism of the reaction can hardly find a satisfactory solution."

Since it appeared to us that the methylamine reaction ought to have the same kinetics as the ammonia reaction with nitrous acid,[3] we have reinvestigated the kinetics of this reaction.

Experimental

The apparatus and technique were the same as for the ammonia reaction,[3] except for the minor changes that the buffer was made up with phosphoric acid and sodium hydroxide, and the ionic strength was adjusted with sodium chloride. Methylamine hydrochloride was recrystallized 5 times from *n*-butanol and vacuum dried. Its m.p. was 231.8–233.4°, and it contained 52.40% Cl (theoretical is 52.51% Cl).

Results and Discussion

TABLE I

EFFECT OF METHYLAMINE CONCENTRATION[a]

*p*H	ΣHNO_2, *M*	ΣCH_3NH_2, *M*	Rate/ΣHNO_2, sec.$^{-1}$ × 10^{-4}
2.68	0.00962	0.0994	0.323
2.72	.00943	.199	0.631
2.71	.00929	.399	1.21

[a] Temperature 30.0°, ionic strength 1.00, total phosphate buffer 0.500 *M*.

TABLE II

EFFECT OF TOTAL NITROUS ACID CONCENTRATION[a]

*p*H	ΣHNO_2, *M*	ΣCH_3NH_2, *M*	Rate/ΣCH_3NH_2, sec.$^{-1}$, × 10^{-4}
2.72	0.00469	0.200	1.45
2.72	.00943	.199	2.99
2.75	.0181	.198	6.40

[a] Temperature 30.0°, ionic strength 1.00, total phosphate buffer 0.500 *M*.

TABLE III

EFFECT OF HYDROGEN ION CONCENTRATION[a]

*p*H	ΣHNO_2, *M*	ΣCH_3NH_2, *M*	Rate/(ΣHNO_2)(ΣCH_3NH_2) sec.$^{-1}$ mole^{-1} liter × 10^{-4}
1.12	0.00933	0.199	4.23
2.10	.00940	.199	4.02
2.68	.00962	.0994	3.25
2.72	.00943	.199	3.17
3.70	.0230	.199	1.03
4.50	.0203	.200	0.187

[a] Temperature 30.0°, ionic strength 1.00, total phosphate buffer 0.500 *M*.

TABLE IV

EFFECT OF IONIC STRENGTH[a]

Ionic strength	k_r at *p*H 2.7 × 10^{-4}	k_r at *p*H 2.1 × 10^{-4}
0.50	4.99	4.85
1.00	4.21	4.28
1.50	3.51	3.84

[a] Temperature 30.0°.

The experimental results are collected in Tables I–V. Our experimental results with methylamine are parallel in every respect to our earlier results with ammonia. The reaction is kinetically first order with respect to stoichiometric methylamine (Fig. 1), and first order with respect to stoichiometric nitrous acid (Fig. 2). The "unnecessary

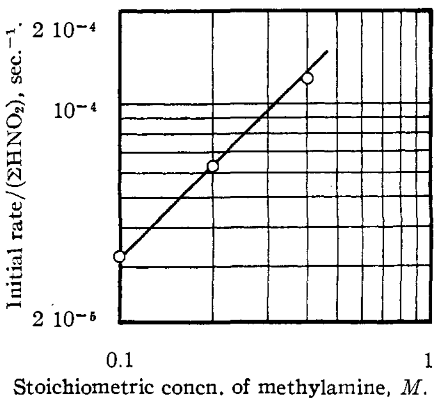

Fig. 1.—Dependence of rate on methylamine concentration. The straight line has a slope of unity.

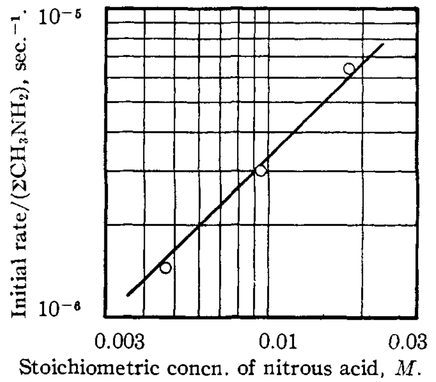

Fig. 2.—Dependence of rate on nitrous acid concentration. The straight line has a slope of unity.

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[1] T. W. J. Taylor, *J. Chem. Soc.*, 1099 (1928).

[2] T. W. J. Taylor and W. Baker, editors of N. V. Sidgwick's "The Organic Chemistry of Nitrogen," Oxford University Press, 1937, p. 24.

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

molecule of nitrous acid" is accordingly nonexistent.

TABLE V

EFFECT OF TEMPERATURE[a]

Temperature, °C.	k_r, sec.$^{-1}$ mole^{-1} liter × 10^{-4}
20.0	1.91
25.0	2.91
30.0	4.20
34.8	6.26
35.0	6.46

[a] Ionic strength 1.00.

The dependence of the rate upon *p*H can be compared with the family of theoretical curves in Fig. 4 of ref. 3, which apply to methylamine as well as ammonia. The experimental data (Fig. 3) are in agreement with the theoretical curve for $Z = +1$. The activated complex for the reaction therefore carries a +1 charge, and has the formula of the nitrosomethylammonium ion $CH_3NH_2NO^+$ or a hydrated form thereof. We can write the rate law in the form

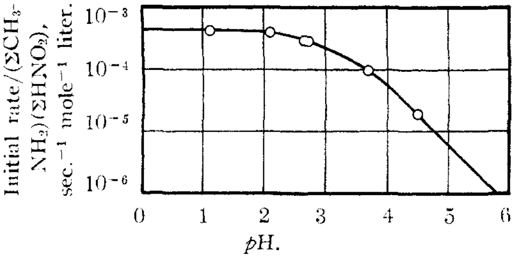

Fig. 3.—Dependence of the rate on acidity. The curve is the theoretical curve for $Z = +1$.

$$d(N_2)/dt = k_r(CH_3NH_3^+)(HNO_2) \quad (1)$$

though the reaction mechanism probably involves not the methylammonium ion and molecular nitrous acid, but the nitrosyl ion and molecular methylamine

$$H^+ + HNO_2 = H_2O + NO^+ \text{ (rapid)} \quad (2)$$

$$CH_3NH_3^+ = H^+ + CH_3NH_2 \text{ (rapid)} \quad (3)$$

$$NO^+ + CH_3NH_2 \longrightarrow CH_3NH_2NO^+ \text{ (rate determining)} \quad (4)$$

The rate of the reaction is the same in 0.25, 0.50 or 0.75 *M* phosphate buffer. The reaction shows a small negative salt effect (Table IV), which is probably caused by the effect of ionic strength on the ionization of nitrous acid.

The rate data in the temperature range 20 to 35° (Table V) are reproduced by the equation

$$k_r = (kT/h)e^{-27.8/R}\, e^{-14{,}000/RT} \text{ sec.}^{-1} \text{ mole}^{-1} \text{ liter} \quad (5)$$

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Theory of Radiation Chemistry. I. Some Effects of Variation in Ionization Density[1,2]

BY JOHN L. MAGEE

The ionization density in a homogeneous medium exposed to steady irradiation is a function of space and time. The space–time ionization density pattern depends on both the ionization density of the particles used in the irradiation and also the number of particles incident per unit time and area (*i.e.*, the rate of irradiation). In this paper a simple model is presented which describes the life of a particle track in the steady-state condition and thus also gives a description of the variations in ionization density. The author believes that this model contains the essentials of the actual physical situation, and it has the particular advantage that mathematical treatment can be carried out rigorously. In the model account is taken of the background ionization density which is present when a track is formed; this background ionization density can be higher or lower than that of the track itself depending upon the diffusion rate of the ions and radicals formed, their recombination rate constants and the rate of irradiation. Yields in radiation chemistry depend upon whether the background is high or low; this situation is discussed in terms of the model with application to some problems of radiation chemistry.

Introduction

A system exposed to a steady irradiation of charged particles has an ionization density which varies in both space and time. High concentrations of ions are produced locally with each track; at any time there will be randomly spaced tracks of various ages, and at any point in space there will be a time variation of ionization density as various tracks cross the point. The space-time pattern of ionization density, therefore, depends on both the density of ionization in the particle tracks and also upon the number of tracks per unit time falling in a region. In this paper there is reported a study of the ionization density pattern of steady state irradiations. This initial study is essentially physical and mathematical but the ultimate objective is to make application of the results to radiation chemistry, and it is hoped that progress will soon be made in this effort.

Most theoretical considerations of mechanism in radiation chemistry have essentially paralleled treatments long customary in photochemistry, and the assumption usually exists that all intermediates are created homogeneously in space. Special effects of charged particle "tracks" have been ignored. The much-quoted theory of Eyring, Hirschfelder and Taylor,[3] for example, employs this technique. We do not mean to deprecate the theoretical work in radiation chemistry, and particularly this pioneering effort of EHT,[3] but we would like to emphasize that eventually the chemical theories must recognize that the effect of a charged particle is localized in a "track." Experimentalists have for a long time recognized that there are char-

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(1) Paper presented at Symposium on Chemistry and Physics of Radiation Dosimetry at the Army Chemical Center, Maryland, September 18, 1950.

(2) A contribution from the Radiation Chemistry Project operated by the University of Notre Dame Chemistry Department under Atomic Energy Commission Contract AT(11-1)-38.

(3) Eyring, Hirschfelder and Taylor, *J. Chem. Phys.*, **4**, 479 (1936).