peratures below 80°K., the stannic compound has the lower molal heat capacity, despite the extra atom of sulfur in its molecular composition. A similar phenomenon is evident in Millar's[2] results for stannic and stannous oxides, the former having the lower molal heat capacity at temperatures below about 155°K.

Entropies at 298.16°K.—The entropy increments for the measured temperature range, 51.00 to 298.16°K., were obtained by Simpson-rule integrations of plots of C_p against log T. The extrapolated portions, between zero and 51.00°K., were evaluated by means of the following empirical sums of Debye and Einstein functions which fit the measured heat capacities to within the limits and for the temperature ranges shown in parentheses.

$$\mathrm{SnS_2}: D(172/T) + E(369/T) + E\left(\frac{415}{T}\right) \ (1.0\%, 51\text{–}170°\mathrm{K.})$$

$$\mathrm{SnS}: \quad D(146/T) + E(311/T) \ (1.0\%, 51\text{–}150°\mathrm{K.})$$

Results of the entropy calculations are in Table II. The measured portions constitute 89.7 and 84.5%, respectively, of the totals at 298.16°K. for stannic and stannous sulfides.

TABLE II

ENTROPIES AT 298.16°K. (CAL./DEG. MOLE)

	SnS_2	SnS
0–51°K. (extrap.)	2.15	2.84
51–298.16°K. (meas.)	18.78	15.52
$S°_{298.16}$	20.9 ± 0.2	18.4 ± 0.2

Employing entropy values for white tin and rhombic sulfur listed by Kelley,[4] the entropies of formation of stannic and stannous sulfides are, respectively, $\Delta S_{298.16} = -6.6 \pm 0.2$ and $\Delta S_{298.16} = -1.5 \pm 0.2$ cal./deg. mole.

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[4] K. K. Kelley, U. S. Bur. Mines Bulletin 477 (1950).

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Decomposition of Nitrosyl Disulfonate Ion. II. The Relation to the Mechanisms of Diazotization and Deamination

BY JAMES C. M. LI AND D. M. RITTER

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In connection with the study of the decomposition of nitrosyl disulfonate ion,[1] we have studied the reaction of nitrous acid with nitrosyl disulfonate ion and with sulfamate ion[2]; and we have found both cases significantly related to the mechanisms proposed for diazotization and deamination.

The first reaction in one molar sodium acetate solution was kinetically second order with respect to molecular nitrous acid and zero order to nitrosyl disulfonate ion. This rate law was deduced from the concentration and pH dependence of the rate of disappearance of the colored nitrosyl disulfonate ion and the evolution of nitrous oxide product.

As one evidence for the validity of the treatment the dissociation constant of nitrous acid was obtained from a plot of $1/\sqrt{k}$ *vs.* $1/[\mathrm{H}^+]$ as required by the relation

$$\frac{1}{\sqrt{k}} = \frac{K}{\gamma_- \sqrt{k'}} \cdot \frac{1}{[\mathrm{H}^+]} + \frac{1}{\sqrt{k'}} \qquad (1)$$

In equation (1) k is the rate constant at a given pH, K the dissociation constant of nitrous acid, γ_- the activity coefficient of NO_2^- and k' the pH independent constant for the proposed rate law: rate = $k'(\mathrm{HNO_2})$.[2] The value obtained was $5 \pm 0.5 \times 10^{-4}\ \gamma_-$ close to $5.15 \times 10^{-4}\ \gamma_\pm^2$ obtained by Schmid, Marchgraber and Dunkl[3] at 25°.

Following Hammett's suggestion[4] for the second-order participation of nitrous acid, we have deduced the following mechanism

$$2\mathrm{HNO_2} \xrightarrow{k_1} \mathrm{N_2O_3} + \mathrm{H_2O}$$

$$(\mathrm{SO_3})_2\mathrm{NO}^= + \mathrm{N_2O_3} + 2\mathrm{H_2O} \xrightarrow{\text{fast}} 2\mathrm{SO_4}^= + \mathrm{NO}^+ + \mathrm{NO} + \mathrm{NOH} + \mathrm{H_3O}^+$$

$$(\mathrm{SO_3})_2\mathrm{NO}^= + \mathrm{NO} + \mathrm{H_3O}^+ \xrightarrow{\text{fast}} (\mathrm{SO_3})_2\mathrm{NOH}^= + \mathrm{NO}^+ + \mathrm{H_2O}$$

with NO^+ and 2NOH giving nitrous acid and nitrous oxide, respectively. The rate constant k_1 = 7,000 l./mole-min. was obtained at 25°. From the temperature dependence of k_1 between 35 and 10°, k_1 = 300 was obtained at 0° by extrapolation.

Compare this reaction with the diazotization of aniline[5] at 0° and mild acidity where the concentration dependences were zero order for amine and second order for nitrous acid. In the calculation, a value[3] of 3.55×10^{-4} was used for the dissociation constant of nitrous acid at 0° and the activity coefficient of NO_2^- was taken as 0.8 in the phthalate buffer solution. The following table shows results of calculations based upon data transcribed from the latter paper

pH	Rate/$(\Sigma\ \mathrm{HNO_2})^2$	$[1 + (K/[\mathrm{H}^+]\gamma^-)]^2$	k_1
4.80	0.30	840	252
5.00	.14	2060	289
5.20	.063	5100	321

The agreement suggests that N_2O_3 is the actual reacting species in the acid decomposition of nitrosyl disulfonate ion as well as in some diazotization reactions.

The second reaction between sulfamate ion and nitrous acid was found kinetically first order with respect to each reactant in an acetate buffer solution, and the pH dependence showed the following rate law at 25° and 0.17 ionic strength

$$\frac{d(\mathrm{N_2})}{dt} = 7.0 \times 10^4(\mathrm{HNO_2})(\mathrm{H}^+)(^-\mathrm{SO_3NH_2}) \text{ moles/liter-min.}$$

in agreement with Dusenbury and Powell[6] who suggested NO^+ or $H_2NO_2^+$ as the deamination agent.

We also have re-examined[7] the data of Taylor[8]

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[1] J. H. Murib and D. M. Ritter, THIS JOURNAL, 74, 3394 (1952).

[2] Forthcoming papers III, IV of this series.

[3] H. Schmid, R. Marchgraber and F. Dunkl, *Z. Elektrochem.*, 43, 337 (1937).

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

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

[6] J. H. Dusenbury and R. E. Powell, THIS JOURNAL, 73, 3266, 3269 (1951).

[7] See also, A. T. Austin, E. D. Hughes, C. K. Ingold and J. H. Ridd, *ibid.*, 74, 555 (1952).

[8] T. W. J. Taylor, *J. Chem. Soc.*, 1099, 1897 (1928).

and of Abel, Schmid and Schafranik[9] for methylamine and ammonia, respectively, using the curve-matching method of Dusenbury and Powell.[6] When all the values were considered, the rates corresponded exactly with the Taylor–Abel third-order rate equation over *p*H 3.5–4.6. The observed rates were somewhat larger than they should have been over *p*H 0.2–2.1, but they were closer to the third order rate law than to any other.

The results can all be reconciled by assuming two mechanisms. One is predominantly that followed in deamination

$$NO^+ + NH_3 \underset{k_b}{\overset{k_a}{\rightleftarrows}} N_2{-}H_3O^+$$

$$N_2 - H_3O^+ + B^- \xrightarrow{k_c} N_2 + HB + H_2O$$

where B^- is a generalized base. Steady state computation gives

$$\frac{d(N_2)}{dt} = \frac{k_a k_c (NO^+)(NH_3)(B^-)}{k_b + k_c(B^-)}$$

which gives at low (B^-) the Taylor–Able mechanism (when B^- is only NO_2^-) and at high (B^-) the mechanism of Dusenbury and Powell and those cases where chloride or bromide ions are catalysts. The second mechanism involving N_2O_3 appears peculiar to diazotization. However, only where the amine dependence is zero is it kinetically distinguishable from the Taylor–Abel case.

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

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Absorption Spectra of Solutions of Pheophytin a in Methanol Containing Acid or Base[1]

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In the study of the kinetics of a photosensitized reaction it was necessary to use the extinction coefficients of pheophytin **a** at several different wave lengths and in solutions of varying acidity. Since such data were not available,[2] the absorption spetra of pheophytin **a**, dissolved in methanol containing a wide range of concentrations of added acid or base, were measured.

Experimental Materials and Methods

Pheophytin **a** was prepared as follows: 0.6 ml. of a 2.4 *m* solution of HCl in methanol was added to 150 ml. of a 4 × 10^{-4} *m* solution of purified chlorophyll **a**[3] in ether. After standing for about 6 hours at room temperature, the pheophytin was transferred to about 10 ml. of petroleum ether A, and was purified chromatographically on powdered sugar, using petroleum ether A containing 0.5% isopropyl alcohol as a developer. Only a single band appeared on the column. The absorption spectrum of an ethereal solution of this material agreed closely with the spectrum published by Zscheile and Harris.[4]

Methanolic hydrochloric acid was prepared by bubbling dry hydrogen chloride into purified methanol.[5] Solutions of sodium methoxide were prepared by dissolving clean sodium in purified methanol. The concentrations of these solutions were determined by titration with standard aqueous solutions of acid and base.

The spectrophotometric measurements were made (at approximately 25°) with a Beckman DU spectrophotometer, using 10.0-mm. Corex cells. A few experiments were performed, with a Carey recording spectrophotometer, to test for the possible existence of a transient, reversible form of pheophytin in basic solutions.

Results and Conclusions

Values of log I_0/I of 1.5 × 10^{-5} *m* pheophytin **a**, from λ3400 to 7000 Å., were measured at 100 Å. intervals for methanolic solutions containing the following added substances at the concentrations indicated: (1) 10^{-1} *m* HCl, (2) 10^{-2} *m* HCl, (3) 10^{-3} *m* HCl, (4) 10^{-4} *m* HCl, (5) 3 × 10^{-5} *m* HCl, (6) 10^{-5} *m* HCl, (7) 5 × 10^{-6} *m* HCl, (8) 10^{-6} *m* HCl, (9) 7.5 × 10^{-2} *m* $CH_2Cl{\cdot}COOH$ + 7.5 × 10^{-3} *m* $CH_2Cl{\cdot}COONH_4$, (10) no added substance, (11) 10^{-3} *m* CH_3CONa, and (12) 10^{-1} *m* CH_3CONa. The absorption spectra of solutions (1) and (2) correspond to curve A of Fig. 1; of solutions (8), (9) and (10) to curve N; and of solutions (11) and (12) to curve B.

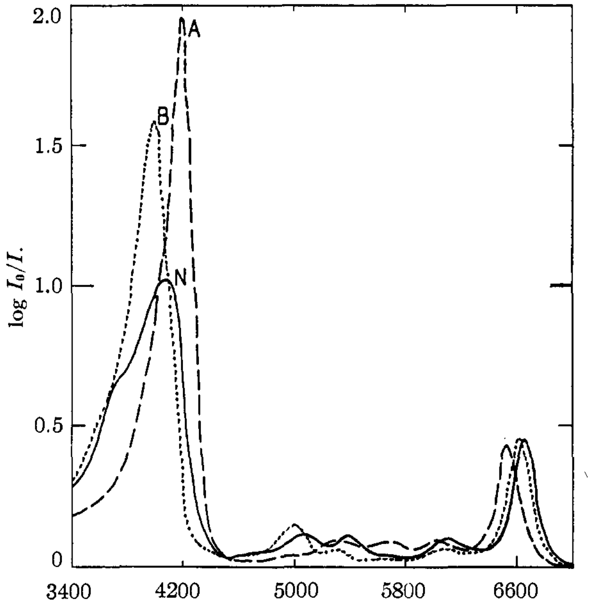

Fig. 1.—Absorption spectra of pheophytin in neutral, acidic and basic methanolic solutions: A, solutions containing HCl at concentrations of 10^{-2} *m* or greater; N, solutions in pure methanol; B, solutions formed by dissolving pheophytin in strongly basic solutions.

TABLE OF PRINCIPAL MAXIMA

Solutions	λ, Å.	log I_0/I	λ, Å.	log I_0/I
A	4180	1.95	6525	0.43
N	4080	1.04	6670	0.45
B	4000	1.57	6630	0.44

The spectra of solutions (3) to (7) exhibit (principal) isobestic points at λ4030 and 6600 Å. Spectra

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[1] This work was made possible by the support of the Office of Naval Research (NR 059,028, Contract N6ori-212, T.O.I) to which the authors are indebted. R. Pariser, Ph.D. Thesis, Univ. of Minnesota, 1950.

[2] Compare, however, W. Broser and W. Lautsch, *Naturwissenschaften*, **38**, 209 (1951).

[3] R. Livingston, D. Sickle and A. Uchiyama, *J. Phys. Chem.*, **51**, 775 (1947).

[4] F. Zscheile and D. Harris, *Bot. Gaz.*, **104**, 515 (1943).

[5] R. Livingston and R. Pariser, THIS JOURNAL, **70**, 1510 (1948).