The 3-vinylcyclohexene was prepared by polymerizing butadiene at 450° and 600–700 mm. The dimer was twice distilled at 2 mm. pressure, the first and last samples being rejected each time. The sample had a b. p. 128–130° and $n^{20}D$ 1.4658. Our sample of limonene, b. p. (20 mm.) 67–68°, was purchased from Eastman Kodak Co. The 3-*p*-menthene was prepared by the dehydration of menthol. Sulfuric acid and aluminum oxide were both used as dehydrating agents but there was no difference in the products obtained by pyrolyzing the two samples. The material had a b. p. 168–169° and on hydrogenation gave 0.98 double bond.

The gaseous products were analyzed in a modified Shepherd[14] gas analysis apparatus containing a hydrogenation unit.[15] The products condensing in the traps were transferred to a low temperature Podbielniak still, fractionated, and then further analyzed in the gas analysis apparatus.

Isoprene was identified by its b. p., by giving two double bonds on hydrogenation and by the maleic anhydride derivative, m. p. 63°. 2-Phenylbutadiene was characterized by its b. p. and maleic anhydride derivative, m. p. 105°. 1,3-Butadiene was identified by its b. p. and hydrogenation value.

Summary

1. The thermal decomposition of a number of substituted cyclohexenes has been studied in the expectation that they would follow the pattern of the cyclohexene decomposition and yield a substituted butadiene and ethylene.

2. This was found to be the case for 1-methyl, 3-vinyl and 1-phenyl cyclohexene. In the case of ethylcyclohexene, we could not detect the expected ethylbutadiene.

3. Dipentene gave, as was to be expected, a high yield of isoprene. On the other hand, 3-*p*-menthene gave a high yield of propylene but no isopropylbutadiene could be detected.

WASHINGTON, D. C. RECEIVED FEBRUARY 19, 1944

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[14] Shepherd, *Bur. Standards J. Research*, **6**, 121 (1931).

[15] McMillan, Cole and Ritchie, *Ind. Eng. Chem., Anal. Ed.*, **8**, 105 (1936).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

The Effect of Dielectric Constant and Temperature on the Catalyzed Decomposition of Azodicarbonate Ion

BY CECIL V. KING AND JESSE J. JOSEPHS

In recent years much interest in reaction kinetics in solution has centered in two factors: (1) prediction by electrostatic theory of the effects of changing dielectric constant and ionic strength and (2) the interpretation of temperature coefficients in terms of activation energy and entropy.

(1) For a reaction between ions A and B present electrostatic theory may be summarized in the well-known Christiansen–Scatchard equation[1]

$$\log k = \log k_\infty - \frac{Z_A Z_B \epsilon^2 N}{2.3DRT} \cdot \frac{1}{r_A + r_B} + \frac{Z_A Z_B \epsilon^2 N}{2.3DRT} \cdot \frac{\kappa}{1 + a\kappa} \quad (1)$$

where the symbols have their usual significance and the last term refers to the salt effect, the next to last term to the dielectric constant effect. A similar equation has been developed by Eyring and his associates and includes a separate estimation of the radius of each ion and the critical complex.[2,3] (2) Introduction of the Eyring theory that rates may be expressed in terms of a universal frequency and an equilibrium constant K^* (reactants-critical complex) necessitates

$$k = RT/Nh \times K^*$$

defining the Arrhenius "energy of activation" as a free energy, and leads to the equation, for reactions in solution[4,5]

$$\log k = \log e \frac{RT}{Nh} - \frac{E_{\text{exp.}}}{2.3RT} + \frac{\Delta S^*}{2.3R} \quad (2)$$

where $E_{\text{exp.}}$ is the activation energy as determined from the slope of log k *vs.* $1/T$ plots and ΔS^* has been defined as the entropy of activation. This may be compared with the corresponding "collision theory" equation

$$\log k = \log Z - \frac{E_{\text{exp.}}}{2.3RT} + \log P \quad (3)$$

where the collision frequency Z may be calculated from the equations of the kinetic theory and P is the probability factor for effective collision.

As usually determined, in iso-composition solutions, both $E_{\text{exp.}}$ and ΔS^* contain factors due to the change in dielectric constant with temperature; and it has been suggested[6] that temperature coefficients for use in these equations should be determined in media of the same dielectric constant rather than the same composition.

Presumably there should be no entropy of activation unless the free energy of activation varies with temperature, or if the dielectric constant is kept unchanged as the temperature is varied (using rate constants at zero ionic strength).[7,8] However, since ΔS^* is deter-

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[1] Scatchard, *Chem. Rev.*, **10**, 229 (1932).

[2] Laidler and Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).

[3] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 428, 430.

[4] Ref. 3, p. 199.

[5] LaMer, *J. Franklin Inst.*, **225**, 709 (1938).

[6] Svirbely and Warner, THIS JOURNAL, **57**, 1883 (1935); Warner, *Ann. N. Y. Acad. Sci.*, **39**, 345 (1940).

[7] LaMer, *J. Chem. Phys.*, **1**, 289 (1933 .

[8] Ref. 3, pp. 433–434.

mined as a difference it does not represent correct entropy values unless all other factors in equation (2) can be properly evaluated. For instance there may be a fractional "transmission coefficient" by which the Eyring frequency factor *eRT/Nh* should be multiplied in any particular case, but there is no independent method of ascertaining this. Also it has been suggested that the rate constant *k* should be based on mole fraction rather than volume concentrations for the calculation of $E_{\text{exp.}}$[9,10,11]

The Azodicarbonate Decomposition.—This reaction has been studied in detail.[12] It is highly sensitive to general acid catalysis; the hydrogen ion catalyzed rate is measurable in dilute sodium hydroxide solutions, while catalysis by molecular water is small. The rate-controlling process is second order, presumably

$$N_2(COO)_2^{=} + H_3O^+ \longrightarrow X^{-1}$$

while the stoichiometric equation is

$$2N_2(COO)_2^{=} + 4OH^- \longrightarrow N_2 + N_2H_4 + 4CO_3^{=}$$

The rate equation is, neglecting water catalysis and change in ionic strength μ during the reaction

$$\frac{k_{\mu}^{H}K_{\mu}^{w}\,t}{2.3(b - 2a)} = \log\frac{a}{a - x} + \frac{2x}{2.3(b - 2a)} \qquad (4)$$

where a and b are initial molar concentrations of azodicarbonate and hydroxyl ions, respectively, k_{μ}^{H} and K_{μ}^{w} are molar rate constant and the water constant ($C_{H_3O^+}\,C_{OH^-}$) at finite values of μ, and x and t have their usual meaning.

Experimental.—Sodium azodicarbonate was prepared as before[12]; two samples evolved 95 and 98% of the theoretical nitrogen, in acid solution. The rates were followed by measuring the pressure of the nitrogen evolved as before. Five temperatures were used, 14.9, 19.9, 24.9, 29.9 and 34.9°, each ±0.02°. Slight condensation of water vapor in exposed parts of the apparatus at the two higher temperatures did not seem to affect the measurements. Since the temperature coefficient is approximately 2% per 0.1° throughout, all rate constants were arbitrarily increased by 2% to correspond to round temperatures.

To vary the dielectric constant dioxane–water mixtures were used. Solutions were made up at approximately 25°, using, per 100 cc., 0, 10, 20, 30, 40, 50 and 60 cc. of dioxane (purified as described by Kraus and Fuoss.)[13] Using the density data of Hertz and Lorentz[14] these solutions are calculated to contain 0, 10.2, 20.2, 30.1, 39.9, 49.7 and 59.5% dioxane by weight. Dielectric constants of these mixtures were interpolated from the measurements of Åkerlöf and Short[15] and the water dissociation constants from a large plot of the data of Harned and Fallon.[16] The latter values were corrected to the volume concentration scale.

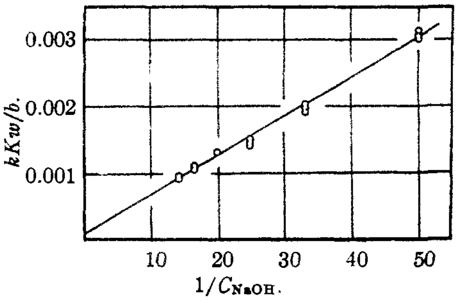

Fig. 1.—The rate in 30% dioxane, at constant ionic strength.

Solutions were made with carbonate-free sodium hydroxide and carbon dioxide free water and no attempt was made to study the effect of other acids than the hydrogen ion. All experiments were made at least in duplicate. Average values only are given except in Table I.

Results.—To check the nature of the reaction in dioxane mixtures experiments were carried out in 30% dioxane (by volume), with varying sodium hydroxide concentration and the ionic strength maintained constant at 0.1225 by additions of sodium chloride. The rates are given in Table I and plotted *vs.* the reciprocal of hydroxyl concentration in Fig. 1. The rate is proportional to the hydrogen ion concentration except for the small water catalysis whose value is obtained by extrapolation to $1/C_{OH^-} = 0$.

TABLE I

The rate in 30% dioxane (by volume) as a function of sodium hydroxide concentration; 25°, μ = 0.1225, C azo-salt = 0.0075 *M*.

C_{NaOH}, *M*	*kKw/b*	C_{NaOH}, *M*	*kKw/b*
0.02	0.00302	0.05	0.00131
	.00305		.00131
	.00314		.00130
.03	.00194		
	.00197	.06	.00106
	.00205		.00111
	.00205		
		.07	.000966
.04	.00141		.000938
	.00144		.000938
	.00147		.000966

In Table I rate constants are given as *kKw/b* since these values are comparable to first order rate constants with unchanging hydrogen ion concentration.[12] In Table II averaged constants with $C_{OH^-} = 0.02$ and varying temperatures and dioxane concentration are given in terms of $k_{\mu}^{H}K_{\mu}^{w}$ since these are used directly to evaluate k_0^H, the molar hydrogen ion catalytic constant at zero ionic strength.

In the application of equation (1) it is customary to evaluate and eliminate the last term (effect of ionic strength), usually by determining rate constants at a number of ionic strengths and extrapolating to $\mu = 0$. In the present case the accuracy attainable did not seem to justify the very large number of experiments necessary to make satisfactory extrapolations.

Instead, the salt effect term, including the effect of ionic strength on the water constant

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[9] Scatchard, *J. Chem. Phys.*, **7**, 657 (1939); *Ann. N. Y. Acad Sci.*, **39**, 341 (1940).

[10] Davis and LaMer, *J. Chem. Phys.*, **10**, 585 (1942).

[11] Svirbely and Peterson, THIS JOURNAL, **65**, 166 (1943).

[12] King, *ibid.*, **62**, 379 (1940).

[13] Kraus and Fuoss, *ibid.*, **55**, 21 (footnote 7) (1933).

[14] Hertz and Lorentz, *Z. physik. Chem.*, **A140**, 406 (1929).

[15] Åkerlöf and Short, THIS JOURNAL, **58**, 1241 (1936).

[16] Harned and Fallon, *ibid.*, **61**, 2374 (1939).

TABLE II

The rate in dioxane mixtures. C azo-salt = 0.0075 M, $C_{\mathrm{NaOH}} = 0.02\ M$, $\mu = 0.0425$.

Dioxane, vol. %	$k_\mu^H K_\mu^w \times 10^5$ 15°	20°	25°	30°	35°
0	3.25	6.78	13.54	26.8	43.3
10	3.34	5.95	11.32	23.0	41.0
20	2.75	4.91	8.96	18.1	35.5
30	2.12	3.46	6.60	14.3	26.1
40	1.47	2.53	4.94	10.2	16.8
50	1.00	1.78	3.51	6.40	12.9
60	0.64	1.12	2.19	3.94	8.30

(since this is known only at zero ionic strength), was calculated as follows. Introducing activity coefficients (f) for the ions involved

$$k_\mu^H K_\mu^w = k_0^H K_0^w f_2/f_1^2 \tag{5}$$

and using the Debye–Hückel "second approximation" for $\log f$, k_0^H becomes

$$\log k_0^H = \log k_\mu^H K_\mu^w - \log K_0^w + \frac{\epsilon^2 N}{2.3DRT}\,\frac{\kappa}{1 + a\kappa} \tag{6}$$

The value to be used for a was estimated from the salt effect experiments with sodium chloride recorded in Table II of the previous paper.[12] Log $k_\mu^H K_\mu^w$ was plotted *vs.* the last term of the equation

$$\log k_\mu^H K_\mu^w = \log k_0^H K_0^w - 1.02\sqrt{\mu}/(1 + 0.328a\sqrt{\mu}) \tag{7}$$

using various values for a (in Å.) until the points conformed to the slope 1.02. The plot, using a = 6 Å., is shown in Fig. 2. This method has the disadvantage of using one average a value for all the ions involved. Previous work indicates that a varies little with changing temperature or dielectric constant.

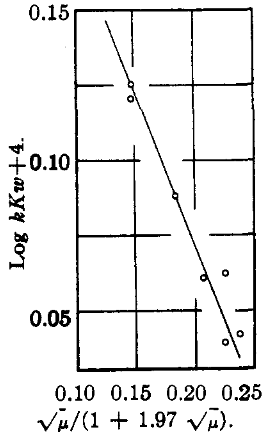

Fig. 2.—Evaluation of a from salt effect data; slope of line = −1.02.

Table III shows in detail the calculation of k_0^H. Equation (1) may now be put in the form

$$\log k_0^H = \log k_{0\ D=\infty}^H - \frac{Z_A Z_B\,\epsilon^2 N}{2.3DRT}\,\frac{1}{r_A + r_B} \tag{8}$$

from which it is seen that a plot of log k_0^H *vs.* $1/D$, at each temperature, should be linear, with a slope from which $(r_A + r_B)$ can be calculated.

These plots are shown in Fig. 3. The points approximate a linear relation at dielectric constant above 50. Previous work[5,6,17] has shown that departure from linearity at lower dielectric constant, in the direction found here, is to be expected. It has been possible to measure rate constants of some reactions with higher dielectric constants than in water, by the addition of amino-acids to the solutions, in which case the linear relation is found to hold over a wider range. That could not be done in this case because of the general acid catalysis.

TABLE III

THE EVALUATION OF LOG k_0^H; a = 6 Å.

t, °C.	Dioxane, vol.%	D	log $k_\mu^H K_\mu^w$	log K_0^w	$\frac{\epsilon^2 N}{2.3DRT}\cdot\frac{\kappa}{1 + a\kappa}$	log k_0^H
15	0	82.3	−4.49	−14.35	0.21	10.07
	10	73.0	−4.48	−14.64	.24	10.40
	20	63.8	−4.56	−14.99	.29	10.72
	30	54.8	−4.67	−15.39	.35	11.07
	40	45.5	−4.83	−15.83	.44	11.44
	50	36.6	−5.00	−16.40	.58	11.98
	60	27.8	−5.19	−17.09	.82	12.72
20	0	80.4	−4.17	−14.16	.21	10.20
	10	71.2	−4.23	−14.47	.24	10.48
	20	62.2	−4.31	−14.81	.29	10.79
	30	53.5	−4.46	−15.31	.35	11.20
	40	44.3	−4.60	−15.66	.45	11.51
	50	35.6	−4.75	−16.19	.59	12.06
	60	27.0	−4.95	−16.93	.83	12.81
25	0	78.5	−3.87	−14.00	.21	10.34
	10	69.5	−3.95	−14.30	.25	10.60
	20	60.5	−4.05	−14.64	.30	10.89
	30	52.1	−4.18	−15.04	.36	11.22
	40	43.1	−4.31	−15.50	.45	11.64
	50	34.6	−4.45	−16.05	.60	12.20
	60	26.2	−4.66	−16.77	.84	12.95
30	0	76.7	−3.57	−13.83	.21	10.47
	10	67.8	−3.64	−14.13	.25	10.74
	20	59.0	−3.74	−14.48	.30	11.04
	30	50.8	−3.84	−14.88	.36	11.40
	40	41.9	−3.99	−15.33	.46	11.80
	50	33.6	−4.19	−15.90	.61	12.32
	60	25.5	−4.40	−16.72	.85	13.17
35	0	74.9	−3.36	−13.68	.21	10.53
	10	66.1	−3.39	−13.98	.25	10.84
	20	57.5	−3.45	−14.33	.30	11.18
	30	49.5	−3.58	−14.72	.37	11.51
	40	40.8	−3.77	−15.18	.47	11.88
	50	32.6	−3.89	−15.74	.62	12.47
	60	24.8	−4.08	−16.45	.87	13.24

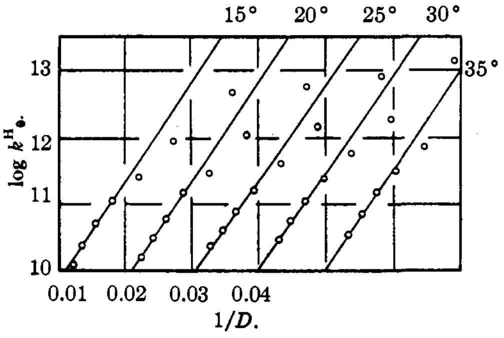

Fig. 3.—Log molar rate constants at zero ionic strength *vs.* $1/D$. Subtract 0.01 from abscissa for 20°, 0.02 for 25°, etc.

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[17] Amis and Potts, THIS JOURNAL, 63, 2883 (1941).

From the slopes of the lines of Fig. 3, the average value of $(r_A + r_B)$ is calculated to be 3.42 Å.

The Temperature Coefficient.—Values of log k_0^H were plotted *vs.* $1/T$, and in Table IV the values of $E_{exp.}/2.3\ RT$ obtained from the slopes are given; also values of log A of the Arrhenius equation

$$\log k_0^H = \log A - E_{exp.}/2.3\ RT \qquad (9)$$

For comparison a plot was made of log k_0^H *vs.* dielectric constant and interpolated values at $D = 75, 65, 55$ and 45 (for 25°) are given in Table V with the corresponding values of $E_{exp.}/2.3\ RT$ and log A. Finally $\Delta S^*/2.3\ R$ was calculated from the equation

$$\log A = \log eRT/Nh + \Delta S^*/2.3R \qquad (10)$$

and these values are also given in Tables IV and V.

TABLE IV

VALUES DERIVED FROM THE TEMPERATURE COEFFICIENTS IN ISO-COMPOSITION MEDIA AT 25°

$\log e\frac{RT}{Nh} = 15.01$ with the minute as time unit.

Dioxane, vol.%	$E_{exp.}/2.3RT$	log A	$\Delta S^*/2.3R$
0	7.49	17.83	2.82
10	7.49	18.08	3.07
20	7.38	18.26	3.25
30	7.16	18.36	3.35
40	6.82	18.43	3.42
50	7.27	19.43	4.42
60	7.61	20.53	5.52

TABLE V

VALUES DERIVED FROM THE TEMPERATURE COEFFICIENTS IN ISO-DIELECTRIC MEDIA AT 25°

D	log k_0^H	$E_{exp.}/2.3RT$	log A	$\Delta S^*/2.3R$
75	10.45	3.80	14.25	−0.76
65	10.77	3.80	14.57	− .44
55	11.14	3.47	14.61	− .40
45	11.61	3.35	14.96	− .05

The temperature coefficients in iso-dielectric media are shown in Fig. 4.

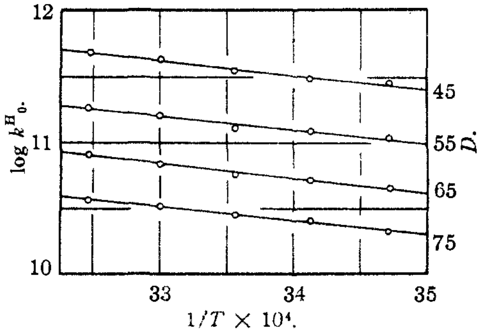

Fig. 4.—The temperature coefficient in iso-dielectric media.

Finally, in Table VI are given the corresponding values using "normalized" rate constants as suggested by Davis and LaMer,[4] using the water solution at 25° as the reference

TABLE VI

VALUES DERIVED FROM THE TEMPERATURE COEFFICIENTS USING "NORMALIZED" RATE CONSTANTS AT 25°

D	log ${}^Nk_0^H$	$E_{exp.}/2.3RT$	log A	$\Delta S^*/2.3R$
75	10.44	3.88	14.32	−0.69
65	10.69	3.73	14.42	− .59
55	11.05	3.88	14.93	− .08
45	11.42	3.88	15.30	+ .29

$${}^Nk_0^H = k_0^H \frac{\Sigma \text{ moles(solution)/liter}}{\Sigma \text{ moles(standard)/liter}} \qquad (11)$$

Discussion.—The nature of the reaction studied and the approximations in the calculations involved do not justify extensive conclusions concerning the theory. The low values of ΔS^* in iso-dielectric media—the largest (from Table V) being −3.5 e. u.—suggest that entropy of activation may really be small or negligible; negative values actually found could be due to a fractional "transmission coefficient" or other factors. The use of "normalized" or mole fraction rate constants makes comparatively little difference. The value of log Z of the collision theory is 15.31 in terms of moles, liters and minutes at 25° with $r_A + r_B = 3.42$ Å., making log P of equation (3) 0.3 unit smaller (or more negative) than $\Delta S^*/2.3$ R. Here, as in other cases,[6] agreement with the collision theory is not unreasonable, considering the uncertainties in the calculation of the rate constants and of Z.

Figure 4, as well as the similar plot for iso-composition media, shows that any variation of $E_{exp.}$ with temperature is within experimental error over the 20° range used. This does not mean, of course, that there is no such variation but only that it is small.

The estimation of k_0^H involves essentially a long and rather uncertain extrapolation to zero ionic strength as shown in Fig. 2. Rate measurements at lower ionic strength are difficult experimentally, and the contribution of the bivalent azodicarbonate ion to the ionic strength makes use of the Debye–Hückel "second approximation" equation somewhat uncertain, especially at lower dielectric constant. It is impossible to estimate the error introduced in this way, but it is probable that the errors are consistent throughout and do not greatly affect the conclusions.

The previous interpretation of the nature and mechanism of the reaction[12] seems fully confirmed, and the reaction is essentially unaltered in the dioxane mixtures. As shown in Table II the effect of dioxane is to diminish the observed rate greatly, but this is due to the decrease in water concentration, the water constant and the hydrogen ion concentration; the molar catalytic constant increases exactly as required by the theory. As expected, the exceedingly high molar rate constants are associated with low activation energies—*ca.* 5000 cal. in iso-dielectric media.

In conclusion, it may be said that the equations of Amis and Cook[18] and Amis and Potts[17] allow reasonably good calculation of the differences of log A in iso-composition and iso-dielectric media, and of the differences of $E_{\text{exp.}}$ in similar media. Also it should be mentioned that while the last term of equation (8) accounts reasonably for the variation in rate with dielectric constant it does not account for the variation with temperature. This situation has been studied in detail by Amis and Jaffe.[19]

Summary

The rate of decomposition of the azodicarbonate ion has been measured, in dilute sodium hydroxide in water and with addition of dioxane up to 60%, at five temperatures from 15 to 35°.

From these rates, molar hydrogen ion catalysis constants at zero ionic strength were calculated. Their variation with dielectric constant was found to agree satisfactorily with the predictions of electrostatic theory.

Temperature coefficients were determined for iso-composition and iso-dielectric solvents and energies and entropies of activation were calculated for comparison with the Eyring "absolute rate" and the collision rate theories. The results, especially in the isodielectric media, show agreement with theory quite comparable to that in other reactions reported in the literature.

Previous interpretation of the nature and mechanism of the reaction is substantiated.

WASHINGTON SQUARE COLLEGE
NEW YORK, N. Y.
RECEIVED JANUARY 14, 1944

(18) Amis and Cook, THIS JOURNAL, **63**, 2621 (1941).

(19) Amis and Jaffe, *J. Chem. Phys.*, **10**, 646 (1942).

[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR, BERKELEY, CALIFORNIA]

Heats of Formation of Solid and Liquid $Mn(NO_3)_2\cdot 6H_2O$[1]

BY C. HOWARD SHOMATE[2] AND FRANK E. YOUNG[2]

The heats of fusion of certain nitrates are important factors in thermal calculations pertaining to the nitrogen dioxide[3] process for extracting manganese from low-grade ores, now being studied by the Bureau of Mines. Available values for these nitrates antedate modern thermochemical methods and are of questionable accuracy. This paper presents new determinations of the heats of formation of solid and liquid manganous nitrate hexahydrate and of the heat of fusion of this compound. In a later paper, similar data will be reported for the nitrates of barium, calcium, and magnesium.

Method and Materials

The manganous nitrate hexahydrate used in this work was prepared by Dr. E. H. Huffman by dissolving electrolytic manganese (purity at least 99.9 per cent) in reagent-grade nitric acid. The manganese was added slowly to control the temperature until the acid had been largely used up. Finally, an excess of manganese was contacted until brown oxide of manganese just started to form, indicating virtually complete exhaustion of the acid. After filtration, a small amount of 30% hydrogen peroxide was added to clear up a slight discoloration remaining in the solution. The material then was evacuated with an oil pump and stored over a mixture of potassium hydroxide and calcium chloride. At this stage, the product was solid at room temperature, and analysis showed 4.13 moles of water per mole of manganous nitrate. Melting, with addition of enough water to bring the composition to the hexahydrate, yielded material with a melting point of 24.9°. Two fractional crystallizations produced crystals melting at 25.0°, which was not raised by further fractionation. The latter material constituted the final product. It analyzed 19.15% manganese (theoretical, 19.14%).

Heats of formation and the heat of fusion were determined by measuring the heat of solution of the salt in 1 N sulfuric acid in the apparatus described by Southard.[4] The 1.000 N sulfuric acid was prepared by dilution of reagent grade concentrated sulfuric acid and was standardized against sodium carbonate.

The calorimetric system was calibrated electrically, using a 100-ohm manganin heater. The heater current was measured by the potential drop across a 0.01-ohm standard resistance calibrated by the National Bureau of Standards. The usual heating period during a calibration was 600 seconds, which gave a temperature rise of about 400 μv. (about 0.36°). The temperature readings were estimated to 0.01 μv. from galvanometer deflections. All measurements were made with a White double potentiometer.

The results are expressed in defined calories (1 cal. = 4.1833 int. joules),[5] and all formula weights were calculated from the 1941 International Atomic Weights. All weights were corrected to a vacuum basis, using 1.8 for the density of solid manganous nitrate hexahydrate and 1.7 for the liquid.

Measurements and Results

The average sample weight of manganous nitrate hexahydrate (5.2895 g.) corresponds to the weight of manganese used in determinations of the heat of solution of manganese metal by Southard and Shomate,[6] whose value is adopted here. This sample weight corresponds to a dilution of 1 mole of anhydrous salt in $49.23H_2SO_4\cdot 5{,}355H_2O$.

The skeleton equations necessary to calculate the heats of formation of solid and liquid man-

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(2) Chemists, Western Region, Bureau of Mines.

(3) Dean, Fox and Back, Bureau of Mines, Rept. of Investigations 3626, 30 pp. (1942).

(4) Southard, *Ind. Eng. Chem.*, **32**, 442 (1940).

(5) Mueller and Rossini, *Am. J. Physics*, **12**, 1 (1944).

(6) Southard and Shomate, THIS JOURNAL, **64**, 1770 (1942).