tion at 16,000 times gravity for 30 minutes. In addition, the uranium in these mixtures was completely dialyzable. This is good evidence that the uranium in all three mixtures was almost completely complexed.

Since the 1:1 and 1:8 mixtures gave *identical* absorption spectra, it is not likely there exist any complexes having a combining ratio, U/citrate, of less than unity. Since the absorption spectra given by the 1:1 and 1:8 mixtures differed from that given by the 2:1 mixture, the existence of a complex of combining ratio greater than one is suggested. Were the absorbance of the 2:1 solution due only to the presence of a 1:1 complex, some precipitation would have been observed because of the insufficiency of citrate. The existence of an ion of combining ratio, U/citrate, greater than two has not been ruled out. This seems an unlikely possibility, however. Such a complex, U_3R for example, would provide each uranyl ion with only *one* functional carboxyl group of a citrate molecule. A single carboxyl group does not provide for efficient complexing. For example, uranium in a ten-fold excess of acetate does not remain complexed but undergoes hydrolysis and precipitation as the *p*H is raised to *p*H 6.0.

Above *p*H 6.0, the spectra shift with time, the *p*H does not remain constant, and CO_2 absorption is a serious problem. Though the curves in Fig. 5 extend to the alkaline region, the data are not sufficiently accurate to permit an analysis and are included for reference purposes only. They do show that citrate is capable of preventing the precipitation of uranium even in basic solution.

Helpful discussions with Dr. Taft Y. Toribara and Mrs. Jean R. Havill are gratefully acknowledged.

ROCHESTER 20, N. Y. RECEIVED OCTOBER 28, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY]

The Crystal Structure of Sulfamic Acid[1]

BY FRANK A. KANDA AND ADEN J. KING

X-Ray studies show that sulfamic acid crystallizes in the orthorhombic system. The unit cell, comprised of eight molecules, has a_0 = 8.100 Å., b_0 = 8.049 Å., and c_0 = 9.228 Å., all ±0.002 Å. All atoms are in general positions of the space group $V_h^{15}-P_{bca}$. Analysis of diffraction intensity data by means of Patterson–Harker projections and Fourier refinements established the parameters. Hydrogen parameters were deduced to fit this structure. Interatomic distances within the molecule are: sulfur–nitrogen, 1.73 Å.; sulfur–oxygen (1), 1.49 Å.; sulfur–oxygen (2), 1.47 Å.; sulfur–oxygen (3), 1.48 Å. (all ±0.05 Å.). Bonding conditions are discussed resulting in the conclusion that the acid crystallizes as zwitterion molecules ($NH_3^+SO_3^-$) of a distorted tetrahedral form. Extensive hydrogen bonding of the type N–H· · ·O is shown to exist in the structure with each NH_3^+ group entering into five bridging systems. The hydrogen bond distances vary from 2.82–3.07 Å.

A survey of the literature discloses that sulfamic acid has been investigated from the standpoint of its chemical and physical properties, and its unit cell dimensions have been determined, but a complete analysis of its structure has never been made by X-ray diffraction methods. The structure of potassium sulfamate[2] and the Raman spectra[3] of the acid indicate that the ion is essentially tetrahedral, and infrared spectra[4] show N-H··O bonding in its crystalline condition. It has been suggested[5] that it may exist as a zwitterion, $^+H_3N·SO_3^-$, in the solid state. Although little evidence in support of this is available from its properties in aqueous solution, where it functions only as a relatively strong acid, its high melting point 206°, in contrast with other sulfonic acids, strongly favors this structure. An interesting analogy exists between sulfamic acid and glycine in that their melting points are both considerably higher than similarly constituted substances in which zwitterion formation is impossible. In Table I are listed for comparison the melting points of sulfamic acid, glycine and other closely related derivatives of sulfonic and acetic acids. It is evident that the lattice forces must be much stronger in the crystals of the $-NH_2$ derivatives of these acids than in their –OH or –Cl derivatives. The fact that glycine[6] has been shown to possess a zwitterion structure is at least indicative of a similar structure in sulfamic acid.

TABLE I

MELTING POINTS (°C.) OF SULFAMIC ACID, GLYCINE AND RELATED COMPOUNDS

H_2NSO_3H	206	H_2NCH_2COOH	233
$HOSO_3H$	10.49	$HOCH_2COOH$	63(α)
$ClSO_3H$	−80	$ClCH_2COOH$	63(α)

The following report gives the results of a study of sulfamic acid by X-ray diffraction methods with the objective of determining the types of bonding which exist in its crystalline form.

The Unit Cell and Space Group.—Measurements by goniometric methods and by Laue and oscillation photographs showed that sulfamic acid crystallizes in a primitive orthorhombic cell with a_0 = 8.100 Å., b_0 = 8.049 Å. and c_0 = 9.228 Å., all values correct to ±0.002 Å. These dimensions were calculated from back reflection diffrac-

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[1] Presented at the Symposium on Properties, Structure and Thermodynamics of Inorganic Substances sponsored by the Division of Physical and Inorganic Chemistry, A. C. S., at Syracuse, New York, June, 1948.

[2] C. J. Brown, F. G. Cox and F. J. Llewellyn, *J. Chem. Soc.*, 10 (1940).

[3] S. J. Gupta and A. K. Majumdar, *J. Indian Chem. Soc.*, **18**, 45 (1941).

[4] H. E. Cupery, *Ind. Eng. Chem.*, **30**, 526 (1938).

[5] P. Baumgarten, *Ber.*, **62B**, 820 (1939).

[6] G. Albrecht and R. Corey, THIS JOURNAL, **62**, 2758 (1940).

tions on a symmetrical rotation photograph taken in a camera with calibrated fiducial marks. They are in good agreement with those found by other investigators.[6a,7,8]

The fact that reflections from all orders of (*hkl*) were observed together with the systematic absence of all reflections of (0*kl*) and (0*k*0) having *k* odd, (*h*0*l*) and (00*l*) having *l* odd, and (*hk*0) and (*h*00) having *h* odd established the space group as $V_h^{15} - P_{bca}$. The observed density of 2.15 requires a cell containing eight molecules.

The oscillation photographs were taken by the multiple film technique[9] using filtered CuK_α radiation. Rods approximately 0.2 mm. in diameter with their long axes parallel to the axes of the crystal were prepared for these photographs. The intensities of the reflections were evaluated by visual comparison with the reflections on a series of standard films, and by means of a Knorr–Albers Speedomax densitometer. No corrections were made for extinction or absorption.

Determination of the Structure.—Since the unit cell contains eight molecules it is required that each of the atoms in H_2NSO_3H lies on a separate set of eight equivalent positions at: (x, y, z); $(1/2 + x, 1/2 - y, \bar{z})$; $(\bar{x}, 1/2 + y, 1/2 - z)$; $(1/2 - x, \bar{y}, 1/2 + z)$; $(\bar{x}, \bar{y}, \bar{z})$; $(1/2 - x, 1/2 + y, z)$, $(x, 1/2 - y, 1/2 + z)$; $(1/2 + x, y, 1/2 - z)$.

A complete solution of the structure necessitates the evaluation of twenty-four parameters. Nine of these are for hydrogens, and one can only speculate about them due to the low contribution of this element to the X-ray scattering. Distinction between the nitrogen and oxygen atoms was made difficult by the similarity of their bond radii and by the slight difference between their X-ray scattering factors.

One dimensional Patterson[10]–Harker[11] "F^2" projections were used to evaluate the parameters of sulfur and to obtain some indication of the positions of other atoms in the cell. With these as a guide, and with the aid of a model based on the structure of the sulfamate ion as found in potassium sulfamate,[2] various orientations were tested by the trial and error method. The trial structures were checked by comparison of the "F's" of (*h*00), (0*k*0) and (00*l*) calculated for these structures with those observed on the oscillation photographs.

A series of two dimensional Fourier projections on (*l*00), (0*l*0) and (00*l*) in combination with trial adjustments of the atomic positions resulted, after a number of refinements, in the parameters listed in Table II. The summations in the Fourier synthesis were carried out with the aid of Beevers and Lipson strips.[12]

The atomic positions in Table II do not deviate from those found in the final Fourier projections by more than ±0.003 of a parameter unit. Further adjustment of the atomic positions within this range failed to improve the agreement between calculated and observed "F's." Comparison of the observed "F's" with those calculated from these atomic positions is shown graphically in Figs. 1 and 2. The atomic scattering factors used in all calculations were taken from the "International Tables"[13] and were corrected with a Debye–Waller temperature factor using a value of $B = 2$.

TABLE II

ATOMIC POSITIONS[a] FOUND IN SULFAMIC ACID

	x	*y*	*z*
S	0.330	0.405	0.330
N	.445	.245	.405
O_1	.300	.310	.195
O_2	.445	.545	.325
O_3	.195	.420	.440

[a] These values were rounded off to the nearest 0.005 of a parameter unit.

The distribution of the eight sulfamic acid molecules in the unit cell is shown in Fig. 3. For convenience of interpretation the projection of each molecule is shown on the *x–y* plane.

Discussion of the Structure.—As mentioned earlier, the near equivalence of the scattering factors of oxygen and nitrogen made it impossible to identify these atoms unequivocally in the electron density plots. For this reason, the positions of the nitrogen and oxygens given in Table II were established through a consideration of the interatomic distances and the disposition of hydrogen bonds within the structure. The interatomic distances and angles calculated from these parameters are listed in Table III.

TABLE III

(A)	S–N	1.73 Å.	O_1–S–O_2	117°	N–S–O_1	92°
(B)	S–O_1	1.49	O_1–S–O_3	119	N–S–O_2	102
(C)	S–O_2	1.47	O_2–S–O_3	114	N–S–O_3	100
(D)	S–O_3	1.48				

The distance 1.73 Å., assigned to S–N in Table III, might be due either to the single S–OH bond, which, from the table of values for bond lengths should be 1.70 Å., or to the single S–N bond which should have a value close to 1.74 Å. Since two arrangements of the atoms in sulfamic acid are possible, $H_3{}^+N{\cdot}SO_3{}^-$ or $H_2N{\cdot}SO_3H$, where this distance could occur, identification of the atoms involved in this 1.73 Å. bond distance is essential to the correct solution of the structure.

The strong monobasic acid nature of sulfamic acid in water solution would suggest the existence of $H_2N{\cdot}SO_2{\cdot}OH$ molecules in the structure. Such a molecule would not be strongly heteropolar. Its lattice forces and consequently its melting point (206°) should therefore be of the same order as those of sulfuric acid whose melting point is only 10.49°.

The structures of most acids and acid salts where O–H··O bonding is possible show that the

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[6a] C. J. Brown and co-workers, a_0 = 8.06 Å., b_0 = 8.05 Å., c_0 = 9.22 Å.

[7] J. W. Hickman and D. Harker, private communication: a_0 = 8.02 Å., b_0 = 7.99 Å., c_0 = 9.18 Å. ± 0.02 Å.

[8] F. M. Jaeger, "Verslag. Akad. Wettenschappen," Amsterdam, **35**, 61 (1926). $a:b:c::1.006:1:1.146$.

[9] J. J. Delange, J. M. Robertson and I. Woodward, *Proc. Roy. Soc. (London)*, **A171**, 298 (1939).

[10] A. L. Patterson, *Z. Krist.*, **90**, 517 (1935).

[11] D. Harker, *J. Chem. Phys.*, **4**, 381 (1936).

[12] C. A. Beevers and H. Lipson, *Phys. Soc. London*, **48**, 772 (1936).

[13] "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntraeger, Berlin, Zweit. Band, p. 571.

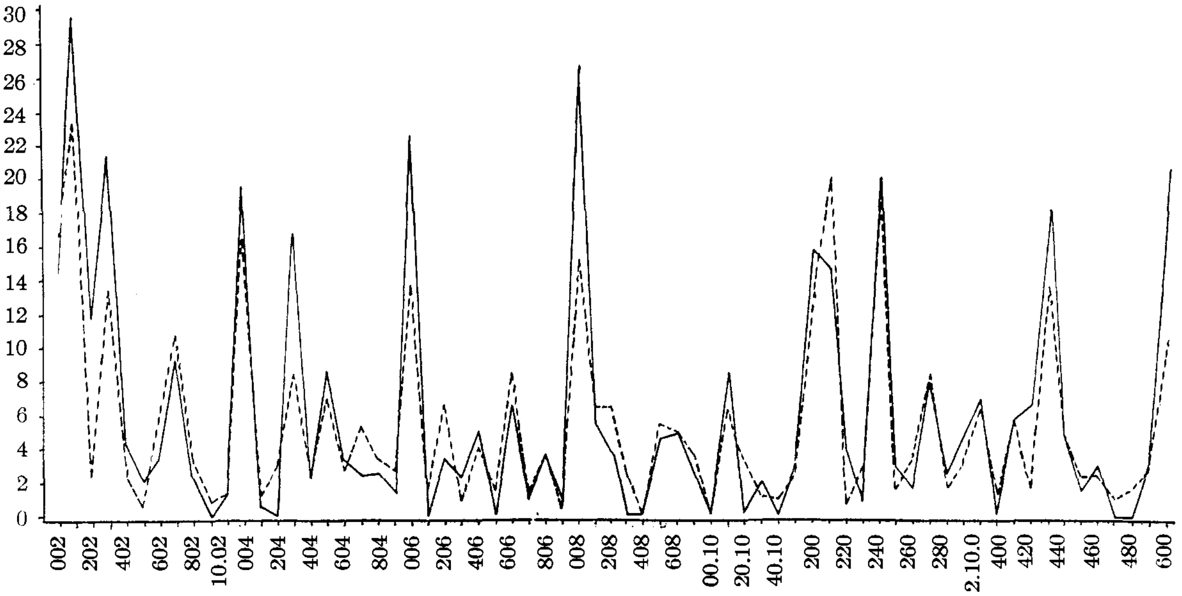

Fig. 1.—Comparison of observed —— and calculated — — — structure factors for sulfamic acid.

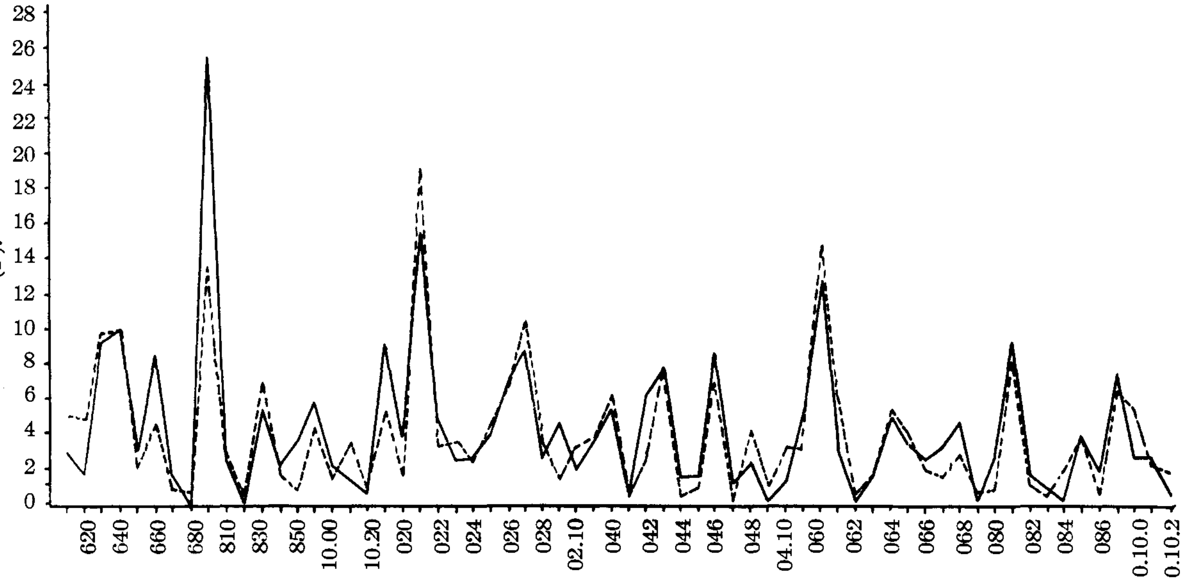

Fig. 2.—Comparison of observed —— and calculated — — — structure factors for sulfamic acid.

M–OH distance is usually closer to that of the double bond than to the single bond value. The presence of a S–OH bond in sulfamic acid would therefore not lead to a distance close to 1.73 Å., but to one which approaches the double bond distance of 1.49 Å. Furthermore, if the S–OH bond is associated with the 1.73 Å. distance, then one of the distances (B), (C) or (D) in Table III must be reassigned to the S–NH_2 bond. These are all too short, even for a S–N bond which is essentially double bond in character (1.56 Å.). The value for the S–N bond in potassium sulfamate[2] was found to be 1.57 Å. which is somewhat smaller than would be expected in sulfamic acid. It seems reasonable therefore to conclude that the 1.73 Å. distance found in sulfamic acid is due to a S–N bond, which is essentially a single covalent bond, and not to the S–OH bond. If the molecule possesses the zwitterion structure, the proton which is attached to the nitrogen at the fourth tetrahedral position would effectively block resonance in the S–N bond and limit its value essentially to that of the single bond distance (1.74 Å.). The S–O distances then, as observed in sulfamic acid, are necessarily equivalent and are, within the limits of error of the measurements, close to the values found in other substances of similar resonance structure.

In Table IV are listed all distances between neighboring molecules which have been considered as either van der Waals contact distances or

TABLE IV

Hydrogen bond distances, Å.		van der Waals contact distances, Å.	
3N–$6O_1$	3.07	3N–$7O_2$	3.15
3N–$1O_2$	2.83	1N–5N	4.40
3N–$8O_3$	3.02	$1O_2$–$3O_1$	2.98
3N–$5O_1$	2.94		
3N–$4O_3$	2.82		

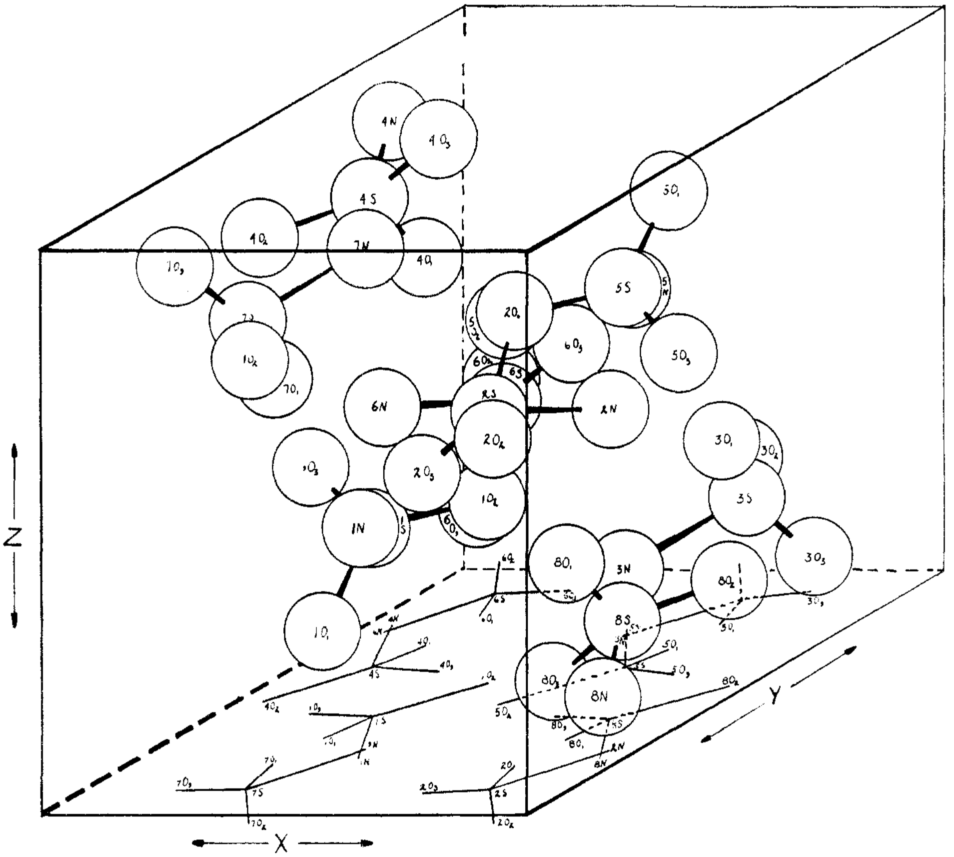

Fig. 3.—The arrangement of the eight molecules in the unit cell of sulfamic acid. Projections of the individual molecules are shown on the x-y plane.

hydrogen bonds. For convenience reference is made to atom pairs easily identified in Fig. 3.

Some of these distances involve atoms in two cells, *e. g.*, the $5O_1$ in the $3N–5O_1$ pair is in the cell below the one shown in Fig. 3.

These distances indicate the presence of five N-H··O bonds in the structure with values 2.82 –3.07 Å. which are in agreement with those found in glycine,[6] diketopiperazine,[14] urea[15] and glycylglycine.[16] These five hydrogen bonds can be accounted for only by postulating that two of the three hydrogens are involved in bifurcated bond systems in which each is offered equally by the nitrogen to two oxygen atoms. Figure 4 shows the bonding about the nitrogen of molecule (3). The bifurcated hydrogen bond systems involving 3N are: $1O_2\cdots H_2\cdots 8O_3$ and $4O_3\cdots H_3\cdots 6O_1$ with the single bond being: $5O_1\cdots H_1$. The molecules to which the S–O pairs belong in Fig. 4 are (going clockwise and starting on the right side of nitrogen): 5, 8, 1, 4 and 6. A structure such as this would impose certain restrictions on the positions which can be occupied by the hydrogen atoms. Considering the disposition of the oxygens about the nitrogen these restrictions are met with a fair degree of approximation by the hydrogen parameters proposed in Table V. With these values the hydrogens lie at 1.0 Å. from the nitrogen, all are tetrahedrally disposed with respect to sulfur and nitrogen, the S–O··H angles are close to 120°, and the $\text{N-H}\!:\!\begin{matrix}\cdot\text{O}\\ \cdot\text{O}\end{matrix}$ system is essentially coplanar.

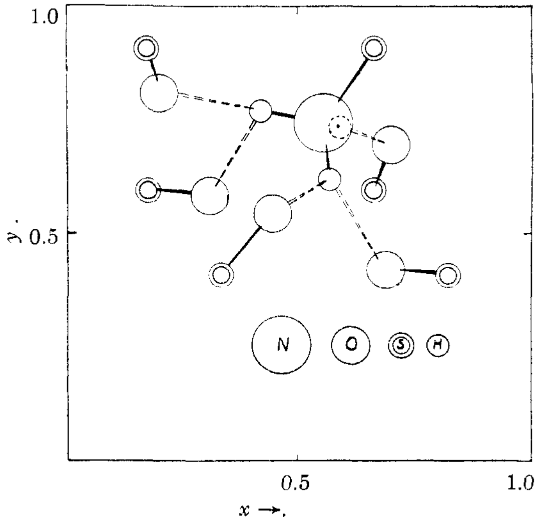

Fig. 4.—The hydrogen bonding involving 3N. Dashed bonds represent hydrogen bonds.

Table V

Postulated Hydrogen Parameters on 1 N

	x	y	z
H_1	0.41	0.23	0.50
H_2	.43	.12	.34
H_3	.58	.27	.42

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(14) R. Corey, This Journal, **60**, 1598 (1938).

(15) R. W. G. Wyckoff and R. Corey, *Z. Krist.*, **89**, 462 (1934).

(16) E. W. Hughes and W. J. Moore, This Journal, **71**, 2618 (1949).

The deviation of the N–S–O and the O–S–O bond angles from the normal tetrahedral value is significant and probably due to a combined effect of the mutual repulsion of the negatively charged oxygen atoms, and the attractive forces between these and the positively charged ammonia ion. This distortion results in a molecule which is nearly tetrahedral, except that the three oxygen atoms are drawn more closely into the plane of the central sulfur atom.

The hydrogen bonds are so disposed throughout the structure that no well defined cleavage was found in any direction in the crystal.

SYRACUSE 10, N. Y. RECEIVED NOVEMBER 1, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, AND THE M. W. KELLOGG COMPANY]

The Kinetics of the Thermal Decomposition of Nitric Acid Vapor

BY HAROLD S. JOHNSTON, LOUISE FOERING, YU-SHENG TAO AND G. H. MESSERLY

The thermal decomposition of nitric acid vapor was studied in two glass cells of considerably different surface-to-volume ratio from 100 to 465°. The rate was followed colorimetrically as the appearance of nitrogen dioxide. The decomposition is a heterogeneous reaction at low temperatures and predominantly a fast homogeneous first-order reaction above 400°. The heterogeneous reaction is initially first order, but its rate is reduced by water or nitrogen dioxide on the surface. It has a very low energy of activation, about 5 kcal. The homogeneous rate is independent of reaction products; its energy of activation is 40 kcal. or higher. A partial mechanism is proposed whereby nitric acid decomposes to hydroxyl radical and nitrogen dioxide.

The equilibrium constants for the reaction

$$2HNO_3 = 2NO_2 + H_2O + {}^1/_2O_2 \qquad (1)$$

were established by Forsythe and Giauque,[1] but the reaction as written has not been given a kinetic study over a wide range of conditions. Part of the reason for neglect of this reaction is probably that it is very fast in the temperature region of greatest interest. Thus the colorimetric and oscillographic method of following fast reactions[2] at constant temperature and constant volume was used for this investigation.

Experimental

Apparatus.—The flowmeters, saturator for nitric acid, mixing chamber, stop-gate, photoelectric tube, oscilloscope, light chopper and camera were essentially the same as those described by Johnston and Yost.[2] The light source was a mercury arc filtered to give the 436 mμ line. The reaction cells were quite different and will be described in detail. (a) Small glass reaction cell. Flat Pyrex windows were fused to the end of a glass tube 6 mm. i.d. and 10 cm. long. About one mm. from each window side arms led off as entrance and exit tubes. The entrance tube was 50 cm. long and formed into a flat coil. The exit tube led straight out. The coil, reaction cell and exit tube were tightly and heavily wound with copper foil to equalize the temperature. Over the foil was wrapped asbestos paper and then a 1000 watt heating coil of chromel wire. Over the heating elements was molded a three inch thickness of plumbers magnesia insulation. A 500-degree thermometer was inserted into the copper foil, and a calibrated platinum-platinum rhodium thermocouple was inserted down the exit tube so that its junction just entered the reaction cell. The entry hole for the thermocouple was sealed with a cement made of water glass and talc. Thus the gases were mixed at room temperature or slightly higher (leads from the saturator were wrapped with heating wires to keep the temperature at 60°), brought through the stop-gate into the furnace, heated up as they flowed, brought into the reaction cell and out the exit tube through the stop-gate. When the stop-gate was closed, the reactants were isolated at constant volume, and flowrates were chosen such that it was also at constant temperature. The thermometer outside the reaction cell and the thermocouple inside gave the same temperatures to within ±3°. Some reaction occurred as the gases were heated up, but this did not usually offer any complication to interpreting the results. (b) Large glass cell. Flat Pyrex windows were fused to a glass tube 25 mm. i.d. and 10 cm. long. About 3 mm. from each window a side arm led off as in the case of the small cell. The thermocouple was inserted into the reaction tube about 8 mm. The cell was wrapped in copper, asbestos, heating coil and insulation as in the other case.

Materials.—Commercial sources of compressed gases were: nitrogen and oxygen, Linde; carbon dioxide, Pure Carbonic; nitrogen dioxide, Matheson. These gases were dried by passing through traps at Dry Ice temperature, and not otherwise purified except for nitrogen dioxide which was vacuum fractionated. Anhydrous nitric acid was prepared by vacuum distillation from concentrated sulfuric acid and sodium nitrate at room temperature to −30°. The nitric acid was condensed directly into an all-glass saturator and was completely colorless. All stopcocks were greased with chloro-trifluorocarbon stopcock grease. This grease is poor for continual vacuum work, but it is inert to nitric acid and very useful for flowmeter work and short periods of vacuum.

Taking of Data.—The flow-rate of dry nitrogen was given by manometer readings and calibration curve for the flowmeters. Concentration of nitric acid was found by freezing out nitric acid from the carrier nitrogen stream with liquid nitrogen. The acid was slowly thawed, dissolved and titrated with standard base. The apparent vapor pressure was always less than the true vapor pressure,[1] and so analyses had to be made as a part of every series of runs. The reaction cells were calibrated for nitrogen dioxide by passing streams of known concentration through them. The light intensity before (I_0) and with nitrogen dioxide (I) gave the optical density log I_0/I which is proportional to concentration of nitrogen dioxide. The calibration curve was found to be constant from room temperature to 450° provided that concentration of nitrogen dioxide and not its pressure is considered. For a run the following light intensity readings were taken: I_0 with only nitrogen flowing, I at zero time with nitrogen and nitric acid flowing, and after the stop-gate closed a series of readings I at regular time intervals as the reaction progressed. At the end of each run the cell was swept out, and another value of I_0 taken. At low temperatures the readings were made visually at clocked intervals, and at high temperatures they were recorded photographically as the beam of the oscilloscope swept once across the screen. From values of I_0/I the concentration of nitrogen dioxide was found as a function of time.

Results

1. Rate.—The equilibrium of the reaction given by Equation (1) lies well to the right under all conditions reported here. The quantity measured is the concentration of nitrogen dioxide. The initial concentration of nitric acid is known

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[1] W. R. Forsythe and W. H. Giauque, THIS JOURNAL, **64**, 48 (1942).

[2] Harold S. Johnston and Don M. Yost, *J. Chem. Phys.*, **17**, 386 (1949).