Some new thermal data and interpretations for the system SO_2–NH_3–H_2O–O_2

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ABSTRACT

Thermal data have been obtained for gas-phase reactions in systems consisting of NH_3 and SO_2; of NH_3, SO_2 and O_2; of NH_3, SO_2, and H_2O (vapor); and of NH_3, SO_2, O_2 and H_2O (vapor). A special calorimeter was constructed with capability for rapid injection of gases, magnetically driven stirrer, and a fast-reacting thermocouple. Results yield reaction enthalpies of -30 kcal mole^{-1} for the anhydrous reaction of SO_2 with NH_3, with the presence of oxygen having no effect on that value. With water vapor present the enthalpy goes to -34 and -45 kcal mole^{-1} in the absence and presence of oxygen, respectively, indicating the importance of water to rapid oxidation in the system. The relationship of these results to other thermal information, together with implications for the atmospheric SO_2 cycle and particulate formation, is discussed.

Introduction

The major sink for atmospheric SO_2 has long been thought to be its oxidation to sulfate (Kellog et al., 1972), with subsequent removal of sulfate salts by precipitation processes. A good deal of study has gone into the oxidation rates of SO_2 by atmospheric oxygen under many conditions, including the effects of catalysts and pH, as well as of ultraviolet radiation (Bufalini, 1971). Ammonia has been recognized as having a role in the SO_2 removal process because of its effect in changing the pH of solution droplets in which oxidation takes place, as well as in supplying the cation for the product sulfate (Junge & Ryan, 1958). The reaction of anhydrous NH_3 and SO_2, followed by oxidation, has been suggested by Scott et al. (1969) as a possible mechanism in the formation of the stratospheric sulfate layer, although this layer would seem to have a large excess of sulfate over its stoichiometric equivalent in ammonium (Lazrus, 1971).

Formation of solid compounds by reaction of anhydrous NH_3 with SO_2 was first studied over a century ago by Döbereimer (1826). A good deal of classical chemical analysis has been done on the reaction products as well as on the materials formed by the hydrolysis of the reaction products, as summarized by, among others, Becke-Goehring (1960). The results indicate two initial compounds with molar ratios of 1:1 and 2:1 of NH_3 to SO_2, respectively, depending upon the relative concentrations of the two reacting gases. Hydrolysis of the material yields a large variety of products, including sulfite, sulfate, thio- and polythiosulfates, N_4S_4 and elemental sulfur, with the kinds and ratios of the hydrolysis products being dependent upon the temperature at which the material was made and stored (Goehring & Kalorimenos, 1950). Very little is known about the thermochemistry or kinetics of either the formation or hydrolysis reactions, except that the initial reaction is exothermic and fast. No direct measurements of reaction ethalpies have been made, although Scott & Lamb (1970) have calculated ΔH° values for the decomposition of $NH_3 \cdot SO_2$ and $(NH_3)_2 \cdot SO_2$ to be 32.2 and 62.2 kcal/mole, respectively. Their calculations were based on pressure measurements and the assumption of an ideal solid solution of the two solid compounds in equilibrium with a common vapor phase consisting only of SO_2 and NH_3. They also calculate ΔS° values of 84.8 and 174.8 cal mole^{-1} deg^{-1} for the two decomposition reactions, which permit calculation of the respective standard free energy values for the reaction-condensation process at 25°C: -6.9 and -10.1 cal mole^{-1} deg^{-1}, respectively. It is

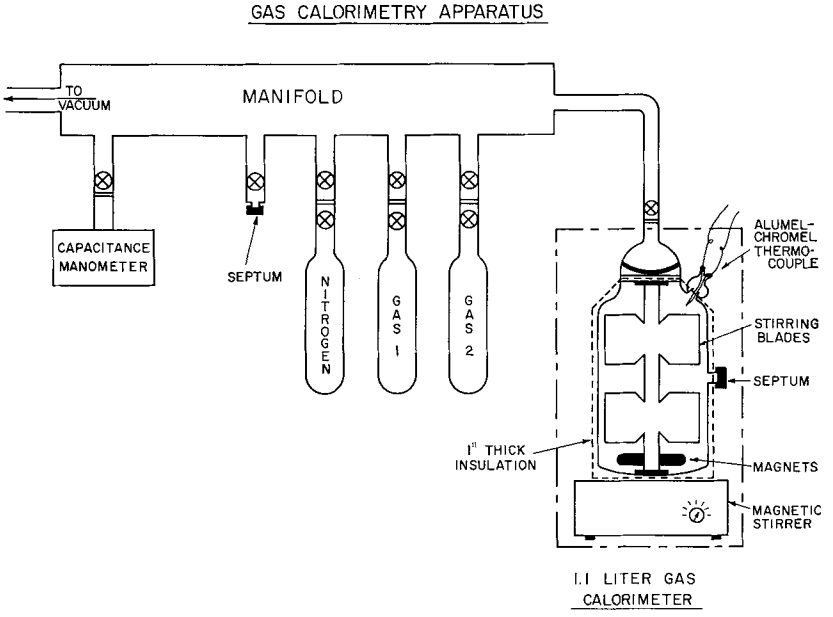

Fig. 1. Basic calorimetric system used for measuring heats of reaction in the SO_2–NH_3–H_2O–O_2 system.

thus predicted that at room temperature and 1 atm. total pressure the solid phases are stable, in accord with observations.

Because of their potential importance as sink reactions for SO_2 and source reactions for particulates in the atmosphere, we have undertaken calorimetric and kinetic measurements for the reactions, with preliminary results of the thermal measurements being reported here.

Experimental

The basic calorimetric system for these measurements is sketched in Fig. 1. The calorimeter itself was a large 1.1 liter Pyrex flask with built in magnetically driven stirrer, as illustrated. It was enshrouded with a fiberglass jacket for insulation, and was fitted with stopcocks and septum for gas injection, as well as a chromel-alumel thermocouple for temperature monitoring. The thermocouple output was fed into a digital voltmeter and then to a recorder. Standard vacuum line components and techniques were used throughout the experiments. Commercially available anhydrous gases were used in all experiments. Nitrogen, which was used as an inert atmosphere, was of high purity (99.998 % N_2).

The heat capacity of the calorimeter was determined by running analogous known gas reactions in the same manner as for NH_3 and SO_2. The calibration reactions were between NH_3 and HCl, and NH_3 and HBr.

In a typical experiment the calorimeter was filled to nearly one atmosphere with one of the reacting gases and with or without some combination of nitrogen, water and oxygen. A small measured quantity (about 15 ml) of the second reactive gas was then rapidly (over a period of about 1/2 second) injected into the calorimeter through the septum by means of a hypodermic syringe and needle. The temperature was continuously recorded during the pro-

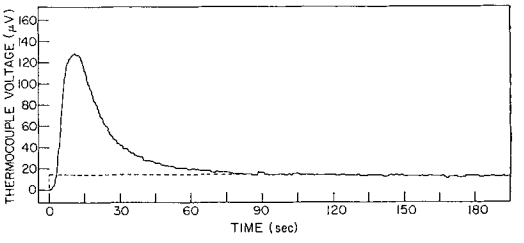

Fig. 2. Typical thermocouple recording indicating an increase in temperature of the system due to chemical reaction and subsequent heat loss to the calorimeter.

Table 1. *Summary of enthalpy calculations*

Initial gases	Pressure (Torr)	Gas added	No. of runs	Avg. ΔT (°C)	$-\Delta H_R$ Kcal mole^{-1}
NH_3	750	HCl	5	0.50	(Calibration)
NH_3	750	HCl	4	0.35	44.0 ± 2.2
NH_3	750	SO_2	4	0.35	29.9 ± 0.5
NH_3, H_2O	716, 24	SO_2	4	0.41	34.4 ± 1.1
NH_3, O_2	600, 150	SO_2	2	0.36	30.3 ± 1.1
NH_3, H_2O, O_2	576, 24, 150	SO_2	3	0.54	45.0 ± 1.1

cess. A typical record of this kind is shown in Fig. 2. All reactions were carried out at room temperature, 22 ± 1°C.

Experimental results

Temperature increases of the calorimeter at the time of reaction were obtained by backward extrapolation to the time of injection of the straight line portion of the curve representing the linear heat loss of the calorimeter, as shown in Fig. 2.

Calculations

The heat capacity of the calorimeter was calculated from the temperature increases in the calibration runs, and was found to be 49.6 ± 0.5 cal deg^{-1}. Enthalpies for the reactions of interest were then calculated in the usual manner. Results of the calculations for the various experiments are listed in Table 1. No corrections were made for the differences in heat capacities of the different gaseous reactants or solid products. Such differences would be very small, compared to the total heat capacity of the calorimeter, because of the similarity of the gaseous systems and small amounts of solid products involved.

Discussion of the results

From Table 1 it is seen that the ΔH values for the reaction of anhydrous SO_2 with NH_3 is close to -30 kcal mole^{-1}. This is consistent, and in relatively close quantitative agreement with the enthalpy value 32.2 kcal mole^{-1} calculated by Scott & Lamb (1970) for the reverse process. It is also reasonably consistent with the results of a calculation based on an empirical method shown by Drago et al. (1971) to predict the enthalpies of many polar adduct species. The calculation by Drago's method yields a value of -4.05 kcal mole^{-1} for the formation of molecular (gas phase) $NH_3 \cdot SO_2$ from its two constituent gases. If one assumes that the molecules are largely held together in the solid form by an average of three hydrogen bonds per molecule, a lattice energy of about 25 kcal mole^{-1} is not unreasonable, making up the total of 29–30 kcal mole^{-1} total energy measured. These values are in turn consistent with the observed direct formation of solid products from gaseous reactants, and with the model on which Scott & Lamb's (1970) calculations were based.

Some preliminary results from similar measurements using a smaller calorimeter indicate in some cases a ΔH value of about double that found when using the large calorimeter. This seems to indicate the possibility of the 2:1 compound, $(NH_3)_2 \cdot SO_2$, being formed under certain conditions, although the exact differences in conditions between the two experiments, which give rise to the different products, are as yet not clear.

Our results for the heat of reaction of NH_3 and SO_2 in the presence of oxygen, but with no water present, indicate no significant change from those of the system without oxygen. The addition of water vapor, however, did cause a notable increase in ΔH, especially when oxygen was present. This clearly indicates the importance of water in the overall reaction process which, in addition to the initial association of SO_2 with NH_3, may include oxidation. Additional data are necessary for precise interpretation as to likely reaction routes and final products.

From the pattern and magnitudes of the results reported here, it appears that initial

association of NH_3 and SO_2 is followed quite rapidly, in the presence of water and oxygen, by subsequent reactions of oxidation and disproportionation. Since atmospheric conditions, especially in polluted regions, provide suitable situations for these specific reactions, it is indeed possible that they do serve as SO_2 sinks and particulate sources. We are continuing to study the thermodynamics and kinetics of the system, with great attention being given to the problem of identification of intermediate and final products, as well as to measurements at much lower concentrations and temperatures. With respect to identification of final products and the probability of disproportionation reactions, we have already clearly identified elemental sulfur in our samples (Yencha et. al., to be published). It should be of interest and value for others who are analyzing samples of atmospheric particulates to look for elemental sulfur. It could be an important end product in the atmospheric sulfur cycle.

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НЕКОТОРЫЕ НОВЫЕ ТЕРМИЧЕСКИЕ ДАННЫЕ И ВЫВОДЫ ДЛЯ СИСТЕМЫ SO_2—NH_3—H_2O—O_2

Получены термические данные для реакций в газовой фазе в системах, состоящих из NH_3 и SO_2; NH_3, SO_2 и O_2; NH_3, SO_2 и H_2O (пар); NH_3, SO_2, O_2 и H_2O (пар). Был построен специальный калориметр с быстрым вводом газа, смесителем, приводимым в действие магнитным полем и с термопарой с малой постоянной времени. Для ангидридной реакции SO_2 с NH_3 получено значение энтальпии — 30 ккал/моль, причем присутствие кислорода не влияет на эту величину. Если имеется водяной пар, то энтальпия принимает значения — 34 и — 45 ккал/моль в отсутствии и присутствии кислорода, соответственно, что указывает на важность воды для быстрого окисления в системе. Обсуждается связь этих результатов с другой термической информацией и делаются выводы относительно цикла превращений SO_2 в атмосфере и образования твердых частиц.