THE EFFECT OF SULPHUR DIOXIDE ON THE COMBUSTION OF SOME INORGANIC COMPOUNDS

PART 2.—THE NITRIC OXIDE+SULPHUR DIOXIDE+OXYGEN SYSTEM

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The nitric oxide+sulphur dioxide+oxygen system has been studied in the temperature range 20-570°C. The initial rate ρ_i of the oxidation of nitric oxide in a static system is approximately second order with respect to NO and first order with respect to O_2 at low pressures, but the dependence of the rate on the concentrations of both reactants become less at higher pressures. The reaction has a negative temperature coefficient, which can be expressed as an Arrhenius activation energy of $-1{\cdot}75$ kcal/mole. Nitrogen and sulphur dioxide have the same small retarding effect on the initial process, but at a slightly later stage the SO_2 takes part chemically in the reaction, the rate ρ_s of the second stage being directly proportional to the pressure of all three reactants, and the activation energy being 7·0 kcal/mole. Packing the vessel does not alter ρ_i nor ρ_s appreciably. The final product of the reaction was a white solid, probably at higher temperatures a mixture of SO_3 and $(SO_3)_2N_2O_3$.

It is suggested that the oxidation involves NO_3 radicals. These can react with either nitric oxide or sulphur dioxide to give NO_2 which, at temperatures above 200°C, may regenerate NO, thus enabling excess SO_2 to be oxidized.

Traces of nitrogen oxides are present in the exhaust fumes from internal combustion engines, and are thought to be the cause of certain unpleasant smog conditions in cities, e.g., Los Angeles, U.S.A.[1] This part presents the results of a study of the $NO+SO_2+O_2$ system.

There is still no agreement on the mechanism of the oxidation of nitric oxide to give nitrogen dioxide in the gas-phase. It has been suggested on the one hand that an intermediate compound is formed, and on the other that NO_2 is produced directly in termolecular collisions.[2] The reaction of sulphur dioxide with nitric oxide and nitrogen dioxide has been investigated by several workers.[3] Compounds such as $SO_3 . NO$ and $(SO_3)_2N_2O_3$ are formed.

EXPERIMENTAL

The static system described in part 1 was used, the reaction vessel being coated with boric acid. Oxygen, sulphur dioxide and nitrogen were purified as described. Nitric oxide was prepared by the action of cold dilute sulphuric acid on sodium nitrite. The red-brown mixture of nitrogen oxides, was condensed in a trap at −196°C. The temperature was raised to −78°C, and pure colourless nitric oxide was evolved and stored in a bulb. The infra-red spectrum of a sample showed only the two peaks at 5·2 and 5·4 μ corresponding to those for NO.

Sulphur dioxide in the mixture after reaction was estimated as described previously (part 1). It was not found possible to obtain accurate results when nitrogen dioxide was present, and other workers have had difficulty in analyzing SO_2+NO_2 mixtures. Oxygen was determined by adsorption in alkaline pyrogallol after the gas passing through the trap at −196°C had been collected in a gas-burette.

RESULTS

KINETIC

The reaction of nitric oxide and oxygen was accompanied by a very rapid initial pressure drop, which was followed after a short time by a much slower decrease (fig. 1*a*). The initial decrease in pressure became progressively smaller as the temperature increased from 20 to 580°C, but the " initial " and " secondary " rates of pressure change did not greatly alter. In the presence of sulphur dioxide there was again a rapid initial fall followed by a slower decrease, the rate of which now increased markedly with temperature above about 200°C (fig. 1*b*). Even at the highest temperatures, however, the pressure-time curves fell into two distinct parts (see fig. 2, the " break " coming at 1½-2 min), and the initial rate was at

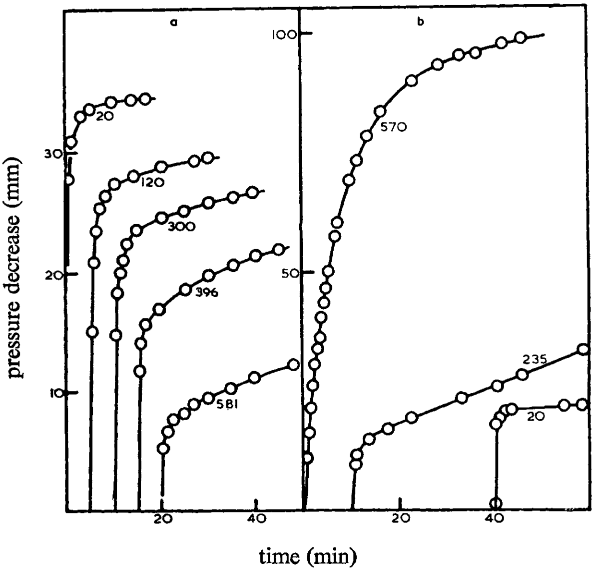

FIG. 1.—Typical pressure-time curves for the oxidation of nitric oxide in presence and absence of sulphur dioxide. NO and O_2 pressures, 100 mm: (*a*) no SO_2; (*b*) SO_2 pressure, 100 mm. Values of the temperature in °C are given on the curves.

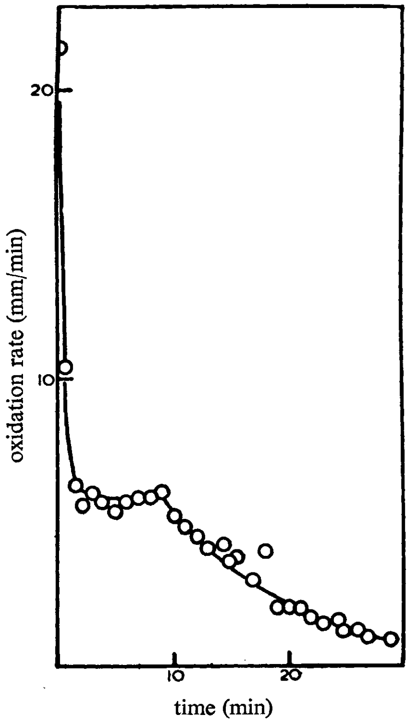

FIG. 2.—Variation of the rate of oxidation of a nitric oxide + sulphur dioxide + oxygen mixture with time at 540°C; NO, SO_2 and O_2 pressures, 50 mm.

least 8 times that of the secondary reaction, taken as the approximately flat part of the rate against time curves. Thus, the variation of the initial and secondary rates (ρ_i and ρ_s) with conditions was investigated.

The rates were reproducible to within ±10 %. Errors due to the " dead space " containing only oxygen were calculated to be small compared with the overall experimental error. When sulphur dioxide was present, solid tended to accumulate on the walls of the capillary tubes leading to the vessel, and then the secondary rates of subsequent oxidations of a standard mixture were slightly lower. This effect was eliminated by flaming the capillaries and then interposing a reaction of a standard $NO+O_2$ mixture between each experiment with SO_2 present. Packing the vessel (increasing the surface/volume ratio about 3 times) had little effect on ρ_i or ρ_s in the presence or absence of sulphur dioxide.

The variation of the rates with temperature is shown in fig. 3. The temperature coefficients can be expressed as an overall activation energy for ρ_i of about $-1{\cdot}75$ kcal/mole whether sulphur dioxide was present or not and for ρ_s of 7·0 kcal/mole with $NO+O_2+SO_2$ mixtures.

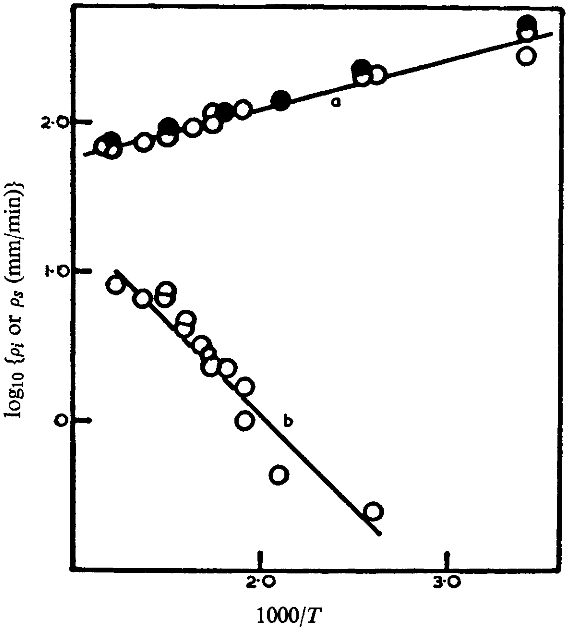

FIG. 3.—Variation of the initial and secondary oxidation rates (ρ_i and ρ_s) with temperature: (*a*) ρ_i; (*b*) ρ_s. Nitric oxide and oxygen pressures, 100 mm ● ; no SO_2 ; ○, SO_2 pressure, 100 mm.

The variation of the initial rate with the pressures of nitric oxide and oxide at three temperatures is shown in fig. 4 and 5. The order with respect to NO was about 2 at low pressures of the reactant but above 30-50 mm the variation became approximately linear. ρ_i was proportional to the oxygen pressure, at least if this was low, at any temperature, but the order became less than one at higher pressures especially at 540°C. Addition of nitrogen and sulphur dioxide reduced ρ_i to the same extent and this effect was greatest with low oxygen pressures and high temperatures, when the dependence on oxygen concentration was also altered, being greater than one. The effect of addition of these gases is also shown in fig. 6. The deviations from an order of two with respect to NO and of one with respect to O_2 are too marked to be accounted for by inaccurate measurement of the high rates.

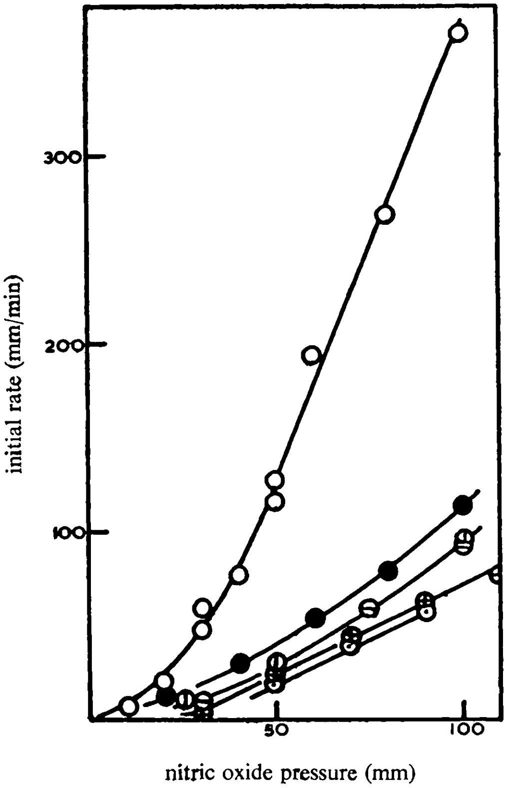

FIG. 4.—Variation of the initial oxidation rate with the pressure of nitric oxide. ○ oxygen pressure, 50 mm; temp. 20°C. ● oxygen pressure, 100 mm; temp. 300°C. ⦶ as for ●, but 100 mm nitrogen present. ⊖ as for ●, but 100 mm sulphur dioxide present. ⊕ (ord. × 0·5): oxygen pressure, 100 mm; temp. 570°C. ⊙ (ord. × 0·5) as for ⊕ but 100 mm nitrogen present.

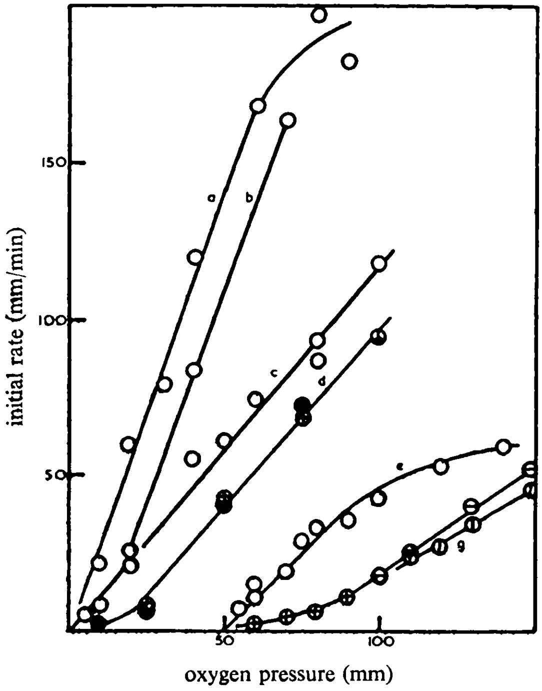

FIG. 5.—Variation of the initial oxidation rate with the oxygen pressure. (*a*) Nitric oxide pressure, 50 mm; temp. 20°C. (*b*) as for (*a*), but 100 mm nitrogen added. (*c*) nitric oxide pressure, 100 mm; temp. 300°C. (*d*) as for (*c*), but ● 100 mm nitrogen added, and ⊕ 100 mm sulphur dioxide added. (*e*) nitric oxide pressure, 100 mm; temp. 520°C. (*f*) as for (*e*), but 100 mm sulphur dioxide added. (*g*) as for (*e*), but 100 mm nitrogen added. (*e*), (*f*) and (*g*): abs. −50.

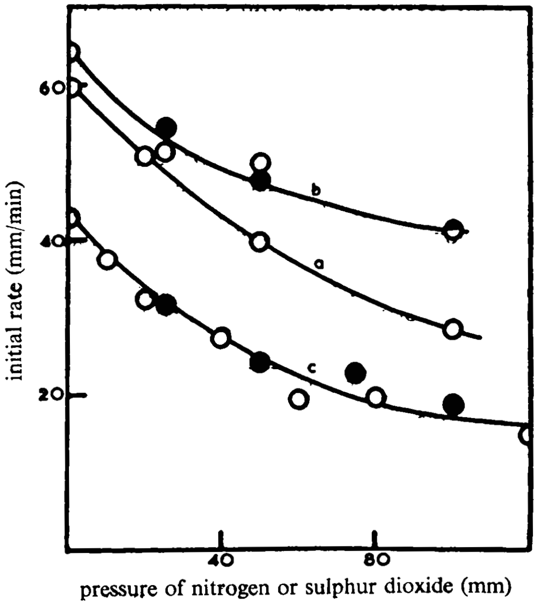

FIG. 6.—Effect of added nitrogen (○) or sulphur dioxide (●) on the initial oxidation rate. (*a*) nitric oxide pressure, 50 mm; oxygen pressure, 20 mm; temp. 20°C. (*b*) and (*c*) nitric oxide pressure, 100 mm; oxygen pressure 50 mm; temp. 300 and 570°C respectively.

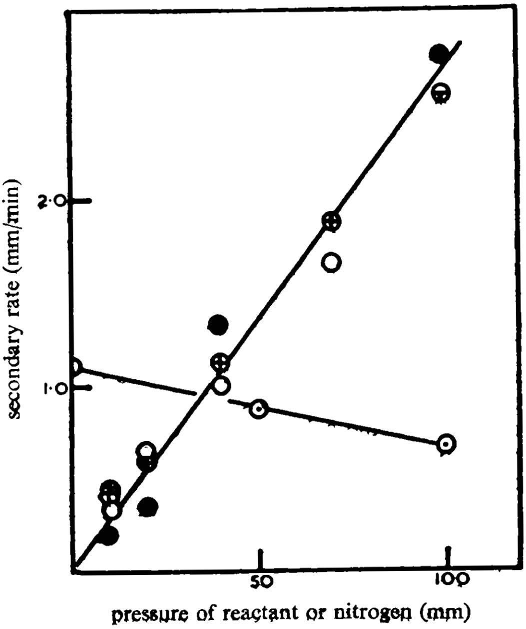

FIG. 7.—Variation of the secondary rate at 300°C with the pressures of nitric oxide, oxygen, sulphur dioxide and added nitrogen. ○ NO pressure varied; SO and O_2 pressures, 100 mm. ● O_2 pressure varied; NO and SO_2 pressures, 100 mm. ⊕ SO_2 pressure varied; NO and O_2 pressures, 100 mm. ○ N_2 pressure varied; NO, SO_2 and O_2 pressures, 50 mm.

The variation of the secondary rate with the pressures of nitric oxide, sulphur dioxide and oxygen is shown in fig. 7. ρ_s was proportional to the concentrations of all three reactants and was reduced slightly by the addition of nitrogen.

TOTAL PRESSURE CHANGE AND PRODUCTS

The total pressure decrease (ΔP_∞) became progressively larger as the amount of sulphur dioxide in the $NO+SO_2+O_2$ mixture was increased, but was not affected by increasing the pressure of oxygen provided this was in excess (table 1). Decreasing the concentration of nitric oxide reduced ΔP_∞ (table 1).

TABLE 1.—VARIATION OF ΔP_∞ WITH PARTIAL PRESSURES OF NITRIC OXIDE, SULPHUR DIOXIDE AND OXYGEN, AND THE OVERALL LOSS OF O_2 AND SO_2

mixture				decrease in pressure			
NO (mm)	SO_2 (mm)	O_2 (mm)	temp. °C	ΔP_∞ (mm)	SO_2 (mm)	O_2 (mm)	ΔP_∞ calc.
50	—	100	20	35	—	—	
50	100	100	20	45	—	27	*
50	100	100	235	161	64	46	
50	—	100	570	37	—	—	
10	50	50	570	13	9	4·5	
50	50	50	570	126	—	—	
50	50	100	570	132	47·5	42·5	137·5 *
50	100	100	570	190	96	56	184 *
50	150	100	570	244	124	75	249 *

* represents the mean of several experiments.

Table 1 also shows the total loss of oxygen and sulphur dioxide in the system as determined by analysis. At 570°C if the ratio $SO_2:NO$ was 2 : 1, or 1 : 1, nearly all the sulphur dioxide was removed from the mixture during the reaction, and only when the ratio was 3 or above did an appreciable amount remain. In general at higher temperatures, more oxygen reacted than was required to oxidize the sulphur dioxide lost to sulphur trioxide, and the very large overall pressure decreases, greater even than the total loss of SO_2 and O_2, must have been partly due to condensation of a product or products.

At all temperatures the reaction of nitric oxide, sulphur dioxide and oxygen gave a white solid, deposited mainly in the capillaries leading to the vessel except at 20°C. It decomposed on heating or solution in water giving nitrogen dioxide. The solution contained sulphate ions. On passing air while heating the capillaries, white fumes of sulphuric acid mist were evolved. At 20°C the presence of nitrogen dioxide was noted throughout the reaction, whereas at 235°C it was only present at the beginning and could not be detected at all at 570°C.

If it is assumed that, at any rate at 570°C, the oxygen that was removed, other than that required to oxidize the sulphur dioxide lost to SO_3, reacted with the nitric oxide to give N_2O_3 and that both the SO_3 and N_2O_3 formed condense out (probably as a mixture of $(SO_3)_2N_2O_3$ and SO_3), then the calculated overall pressure decreases are given in the last column of table 1. The agreement with experiment is satisfactory in view of the experimental errors, and no other reasonable assumption as to the products enables the pressure changes to be explained. When the ratio $SO_2:NO$ was high (5 : 1), however, $\Delta P_\infty \approx \Delta P_{SO_2} + \Delta P_{O_2}$ and $\Delta P_{O_2} = \frac{1}{2}\Delta P_{SO_2}$, implying that little or no nitrogen oxides were present in the solid product.

DISCUSSION

Earlier workers [2] have found that the oxidation of nitric oxide at temperatures below 390°C was approximately of the third order (i.e., about second order with respect to NO and first order with respect to oxygen). Since the total pressures used were less than 50 mm, this is in agreement with the results presented here. Bodenstein[4] found that the temperature coefficient of the initial rate between 30 and 90°C was −0·92 per 10°C. This can be expressed as an overall activation energy of −1·7 kcal/mole, in good agreement with the value reported in the previous section. Bodenstein also considered that a moderate increase in surface/volume ratio had no effect on the oxidation rate, and it can be assumed that the rate-determining reactions in both the $NO+O_2$ and $NO+SO_2+O_2$ systems are homogeneous.

The kinetic results do not appear to be in agreement with the hypothesis that the oxidation of nitric oxide to nitrogen dioxide is a simple termolecular reaction, viz.,

$$2NO+O_2 = 2NO_2,$$

involving, in effect, triple collisions. For instance, as Treacy and Daniels[2] have pointed out, this would require the reaction to be strictly second and first order with respect to NO and O_2 respectively, and this appears to be so, if at all, only within a limited range of experimental conditions. Also, since the sulphur dioxide does not affect the initial oxidation rate of nitric oxide, except as an " inert " gas, in the second stage it must react with a product of the interaction of NO and O_2. Now the homogeneous reaction between sulphur dioxide and nitrogen dioxide, the rate of determining step of which is

$$NO_2+SO_2 = SO_3NO,$$

is of the first order with respect to both reactants, the activation energy being 26·5 kcal/mole,[3a] so that if this product was NO_2 it is difficult to explain the difference in the variation of ρ_i and ρ_s with reactant concentrations and the low activation energy for ρ_s (7·0 kcal/mole). Thus, it seems probable that SO_2 reacts almost exclusively with a complex of NO and O_2 rather than with NO_2 itself. The hypothesis that the oxidation of nitric oxide proceeds via the formation of an intermediate complex has been suggested by a number of workers.[2] This complex is usually considered to be nitrogen trioxide, and there is considerable evidence for the participation of this radical in various reactions involving nitrogen oxides.[5] It has been pointed out that, since NO and O_2 are both paramagnetic and therefore possess some free radical properties, their union to form NO_3 seems very probable.[6] Also, since nitric oxide does not react with sulphur dioxide below 400°C,[3b] it seems unlikely that the complex is $(NO)_2$.

Although some oxidation of sulphur dioxide probably occurs at low temperatures (table 1), the rate of the secondary reaction and the removal of amounts of SO_2 in excess of those of nitric oxide does not become appreciable until above 200°C when the thermal decomposition of nitrogen dioxide is becoming rapid. Thus the following mechanism, which is an extension of that proposed by Treacy and Daniels[2] for nitric oxide oxidation, is suggested.

$$NO+O_2 \rightleftharpoons NO_3 \tag{1}$$
$$NO_3+NO \rightleftharpoons NO_3.NO \tag{2}$$
$$NO_3.NO \rightarrow 2NO_2 \tag{3}$$
$$NO_3.NO+N_2(SO_2) \rightarrow 2NO+O_2+N_2(SO_2) \tag{4}$$
$$NO_3+SO_2 \rightarrow NO_3.SO_2 \rightarrow NO_2+SO_3 \tag{5}$$
$$NO_3.SO_2+N_2 \rightarrow NO_3+SO_2+N_2 \tag{6}$$
$$2NO_2 \rightarrow 2NO+O_2 \tag{7}$$
$$SO_2+NO_2 \rightarrow SO_3NO \tag{8}$$
$$SO_3NO+NO_2+SO_3 \rightarrow (SO_3)_2N_2O_3. \tag{9}$$

If the first two equilibria are very rapidly attained and reaction (3) is the rate-determining step, then the initial rate depends on the square of the nitric oxide pressure and on the first power of the oxygen pressure. The effect of nitrogen or sulphur dioxide on ρ_i is due to reaction (4). When the pressures of oxygen or nitric oxide are " high " these reactants may possibly act as the third body in (4), reducing the dependence on their concentrations as found experimentally. If reaction (5) is relatively slow the chemical effect of sulphur dioxide will become appreciable only after a short time. Above 200°C, since SO_3, unlike NO_2, cannot be converted to the lower oxide, there will be an overall loss of oxygen and thus a pressure decrease due to this reaction, and ρ_s will be directly proportional to the pressure of all three reactants as found. The activation energy of 7·0 kcal/mole may thus refer to reaction (5). Reaction (6) accounts for the slight reduction in the secondary rate on adding nitrogen. Reactions (8) and (9) will be very slow and thus nitric oxide will be reformed by (7) enabling excess sulphur dioxide to be oxidized. In time, however, sulphur trioxide and nitrogen oxides will condense out and the reaction come to a halt.

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[1] Hanst, Stephens and Scott, paper presented at meeting of Amer. Petroleum Inst., 1955.

[2] see Treacy and Daniels, *J. Amer. Chem. Soc.*, 1955, **77**, 2033.

[3] (*a*) Boreskov and Illarianov, *Z. Fiz. Khim.*, 1940, **14**, 1428. (*b*) Terres and Constantinescu, *Z. angew. Chem.*, 1934, **47**, 468.

[4] Bodenstein, *Z. Elektrochem.*, 1918, **24**, 183.

[5] Lewis and von Elbe, *J. Amer. Chem. Soc.*, 1937, **59**, 2022; 1939, **61**, 1350. Smith and Daniels, *J. Amer. Chem. Soc.*, 1947, **69**, 1735. Johnston and Yost, *J. Chem. Physics*, 1949, **17**, 386. Johnston and Leighton, *J. Amer. Chem. Soc.*, 1953, **75**, 3612. Ashmore and Levitt, *Research*, 1956, **9**, S25. Davidson and Schott, *J. Chem. Physics*, 1957, **27**, 317.

[6] Gerschinowitz and Eyring, *J. Amer. Chem. Soc.*, 1935, **57**, 985.