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OZONE AND NITROGEN DIOXIDE

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Kinetics of the Gas-Phase Reaction  
between Ozone and Nitrogen Dioxide\*

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The first measurement of the rate constant for the reaction of nitrogen dioxide and ozone



was reported in 1949 by Johnston and Yost<sup>1</sup>, who covered a narrow range of temperature, 286 to 302°K. Several other room temperature studies have been made; a summary of the work of various investigators was recently given by Wu, Morris, and Niki<sup>2</sup>. This reaction may be important in stratospheric photochemistry<sup>3</sup>; the present study reports measurements from 231 to 298°K.

This reaction was studied in a 45-liter gas cell equipped with multiple reflection mirrors. The cell consisted of a quartz tube 15 cm in diameter and 2 meters long, which was equipped with nickel-plated stainless-steel end-caps. The cell was enclosed in a thickly insulated box and cooled by circulated cold methanol; temperature was controlled by electrical heating wires, and the air space was stirred by a fan. Temperature was measured by thermocouples at 6 locations in the exterior air space and at one position in a thermocouple well inserted into the reaction vessel, and the temperature was uniform to  $\pm 0.1^\circ\text{C}$ . The preparation and purification of nitrogen dioxide has been described previously<sup>4</sup>. Oxygen was purified by passing through a silica

tube containing copper turnings at 900°K, a bed of 5% palladium on alumina at 650°K, and columns of ascarite and phosphoric pentoxide. Ozone, prepared by passing the purified oxygen through a silent electric discharge, was trapped on silica gel at 194°K and degassed as needed.

Gas pressures were measured with a Texas Instrument Model 145 quartz spiral manometer. The concentrations of nitrogen dioxide or ozone in the cell were followed by absorption spectrometry, using a chopped (400 hz) split beam from a Sylvania deuterium arc, a 1-meter McPherson 2051 monochromator, a photomultiplier and lock-in amplifier. Kinetic data were recorded and evaluated by a PDP-8/E computer interfaced with a Preston digital voltmeter. Both NO<sub>2</sub> and O<sub>3</sub> were calibrated at the temperatures used.

During experimental runs, the ratio of NO<sub>2</sub> to O<sub>3</sub> was varied from approximately 3 to 1/3 when NO<sub>2</sub> was followed and from 3 to 1 when O<sub>3</sub> was followed. Reaction times were from 200 to 1000 seconds with 1000 data points taken per reaction. The differential rate of change of reactants was calculated point-by-point, and the data were interpreted primarily in terms of differential rates between 20 and 60 per cent completion of reaction. Reaction stoichiometry was measured by switching back and forth between 255 nm (to measure O<sub>3</sub>) and 390 nm (to measure NO<sub>2</sub>).

From the balanced chemical equation, the stoichiometric ratio ( $\Delta\text{NO}_2/\Delta\text{O}_3$ ) is expected to be two, but the observed values were substantially less than two:  $1.89 \pm 0.08$  (standard deviation), independent of temperature, on the basis of 25 measurements. Rate constants were evaluated on the basis of the observed stoichiometry, and the results are given in

Table 1. A linear least squares fit gives the rate constant for reaction (1)

$$k_1 = (1.34 \pm 0.11) \times 10^{-13} \exp(-4900 \pm 60/RT) \quad (4)$$

where units are  $\text{cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1}$  and the uncertainties are the standard deviation. This activation energy is substantially less than the value of 7 kcal reported by Johnston and Yost<sup>1</sup>, and the pre-exponential factor is also less.

The reason for the low stoichiometry is not apparent. Wu, Morris, and Niki<sup>2</sup> found values between 1.65 and 2.00, and suggested that the low value came from the side reaction  $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{O}_2 + \text{NO}_2$  with loss of ozone as it reacts with nitric oxide. The reaction of NO with  $\text{O}_3$  is chemiluminescent<sup>5,6</sup>, and this mechanism was tested by looking for this chemiluminescence. The system was calibrated with 2 microns of NO, 20 microns of  $\text{O}_3$ , and 100 microns of argon. A strong chemiluminescent signal was observed. Nitrogen dioxide was substituted for the nitric oxide and no chemiluminescence was seen. From the sensitivity of the method, it appears that less than 0.2 percent of the  $\text{NO}_3$  reacted to give NO.

Table 1. Rate constants for the reaction  $\text{NO}_2 + \text{O}_3$ .

T °K	No. of runs	Ozone range, $\text{NO}_2$ range (in units of $10^{14}$ molecules $\text{cm}^{-3}$ )		$10^{17}$ k ( $\text{cm}^3$ molecule $^{-1}$ )
298.2	10	1.5-4.0	2.9-12.6	3.49
288.2	4	3.1-4.9	2.2-12.0	2.51
278.2	8	3.8-11.9	3.1-12.7	1.80
268.2	12	1.4-13.1	2.2-14.9	1.38
258.2	13	1.8-12.0	3.9-11.6	0.905
248.2	12	1.2-8.7	2.5-10.6	0.621
238.2	16	1.4-8.6	2.2-15.2	0.433
231.4	6	3.8-7.1	3.4-11.0	0.314

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