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The Kinetics of the Fast Gas-Phase Reaction between Nitryl Chloride and Nitric Oxide*

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The kinetics of the fast reaction between nitryl chloride and nitric oxide has been studied by absorptiometric methods in two systems of greatly different surface-to-volume ratio and over a temperature range from 1° to 71°. The pressure of each reactant has been varied from 0.1 mm to 18 mm and the total pressure from 0.2 mm to 384 mm. The reaction proceeds quantitatively according to the equation

$$ClNO_2+NO=NO_2+ClNO.$$

It is homogeneous and first order with respect to each reactant. The second-order rate constant is expressed by the equation

$$k=0.83\times 10^{12}\exp(-6900/RT)\text{cc mole}^{-1}\text{ sec}^{-1}.$$

An elementary bimolecular mechanism is proposed.

INTRODUCTION

In the thermal decomposition of nitrogen pentoxide there occurs a rapid reaction[1–3] which must have almost zero energy of activation[4]

$$NO_3+NO=2NO_2. \qquad (1)$$

Ogg and Weston[5] sought and found an analogue to this process in the fast reaction between nitryl chloride and nitric oxide

$$ClNO_2+NO=NO_2+ClNO. \qquad (2)$$

Ogg and Weston[5] also found that nitrogen pentoxide reacts with nitrosyl chloride to produce nitryl chloride and nitrogen dioxide

$$N_2O_5+ClNO=ClNO_2+2NO_2. \qquad (3)$$

This article reports the results of a kinetic study of the first of these reactions, Eq. (2). The nitryl chloride used in this investigation was prepared by way of the second reaction, Eq. (3).

EXPERIMENTAL

The rate of reaction was followed absorptiometrically in two systems of widely different surface-to-volume ratio.

The great majority of runs were carried out in the same low pressure apparatus that has been described by Johnston and Perrine.[6] A 22-liter, spherical Pyrex bulb, which served as the reaction vessel, was connected to two sets of pipets. Each set consisted of two pipets in series, one of which was one-hundredth and the other one-thousandth of the volume of the reaction bulb. Nitric oxide was introduced into one of these sets at a pressure measured directly with a mercury manometer. The pressure of nitryl chloride in the other set of pipets was determined with the aid of a Bourdon null gage. At zero time these reactants were passed together into the evacuated reaction bulb; the optical density of the mixture at 436 mμ was then followed by means of a 1P28 electron-multiplier photoelectric tube and an electronic voltmeter. Time was indicated by an electric metronome which gave both visible and audible signals every three seconds. The progress of the reaction was recorded at three-second intervals for some 39 sec and then at appropriately longer intervals until no further progress could be detected. Blank experiments indicated that the reactants came to temperature and pressure equilibrium in the reaction bulb in less than three seconds. The reaction cell and optical system were calibrated by Johnston and Perrine[6] by the introduction of nitrogen dioxide air mixtures into the reaction cell. The pipets could then be calibrated relative to the reaction cell by filling them to measured pressures of nitrogen dioxide, emptying their contents into the evacuated reaction cell, and determining the resulting pressure absorptiometrically.

A small number of runs were carried out in the intermediate pressure apparatus of Mills and Johnston.[3] In this apparatus reactants were mixed rapidly in a flow system, and a sample of the reacting mixture was isolated at constant volume and temperature. The transmission of 436 mμ radiation was followed on an oscilloscope by the method of Johnston and Yost.[7] The flow system of Mills and Johnston was modified by the introduction of a 66-cm pre-cooling coil of 6-mm glass tubing between the mixing chamber and the reaction cell. Advantage was taken of the nitrogen dioxide-nitrogen tetroxide equilibrium to establish absorptiometrically that the flowing gases came to thermal equilibrium with the surrounding water bath before entering

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TABLE I. Results of runs made in the low pressure apparatus at 27°C with unequal initial concentrations of the reactants.

Pressure of gases in mm NO	Pressure of gases in mm $ClNO_2$	$k\times10^{-7}$ cc mole^{-1} sec^{-1}
1.14	0.123	0.64
1.14	0.131	0.60
1.01	0.176	0.54
0.587	0.100	0.69
0.390	0.133	0.64
0.362	0.118	0.76
0.182	0.120	0.96
0.124	0.179	0.61
0.134	0.393	0.94
0.121	0.352	0.81
0.157	1.02	0.56
0.098	0.594	0.79
0.121	1.13	0.70
0.122	1.10	0.87

the reaction cell. The optical density was followed for a period of about two seconds during a typical run made in this system. The calibration of the reaction cell and optical system of the intermediate pressure apparatus was in principle identical to that for the low pressure apparatus. For convenience, however, only one quantitative mixture of air and nitrogen dioxide was made up, and successively lower concentrations of nitrogen dioxide were obtained by using this mixture at successively lower total pressures.

Nitric oxide was prepared by using the same method and equipment that has been reported by Mills and Johnston.[3] Nitryl chloride was prepared according to the foregoing reaction (3) by condensing freshly distilled nitrosyl chloride upon a twofold excess of nitrogen pentoxide. When this reaction mixture was stored in a dry ice acetone bath under an atmosphere of nitrogen, the slow oxidation of nitrosyl chloride could be observed by the disappearance of its characteristic orange color. By hastening the reaction with frequent periods of agitation and gentle warming, there remained eventually only a white solid and a clear, colorless, supernatant liquid. The supernatant was separated and twice distilled from −78° to −196°, low and high boiling fractions being discarded with each distillation. An aerostatic balance of the type described by Stock and his co-workers[8] was used to determine the molecular weight of the purified product. A value of 81±3 was obtained while the theoretical value is 81.47. Although the distilled nitryl chloride invariably possessed a very pale straw-yellow coloration, the amount of impurity present was insufficient to permit detection by either the molecular weight determination or the quantitative conversion to nitrogen dioxide which will be described later.

RESULTS

The reaction was followed by the appearance of optical density at 436 mμ. Both products, nitrogen dioxide and nitrosyl chloride, absorb at this wavelength. At low temperatures nitrogen dioxide associates to form colorless nitrogen tetroxide. The association of nitric oxide with nitrogen dioxide was negligible under all conditions studied. If the trial assumption is made that the reaction goes according to Eq. (2) with no side reactions, then it follows from stoichiometric considerations that

$$[\mathrm{ClNO}]=[\mathrm{NO_2}]+2[\mathrm{N_2O_4}], \tag{4}$$

where the brackets refer to concentrations. These concentrations are related to the optical density D and the length of light path L by the equation

$$D/L=\epsilon[\mathrm{NO_2}]+\epsilon'[\mathrm{ClNO}], \tag{5}$$

where ϵ and ϵ' refer respectively to the molar extinction coefficients of nitrogen dioxide and nitrosyl chloride. Combination of these equations with the equilibrium expression

$$K=[\mathrm{NO_2}]^2/[\mathrm{N_2O_4}] \tag{6}$$

yields the relationship

$$[\mathrm{ClNO}]=\frac{D}{L\epsilon'}+\frac{K\epsilon(\epsilon+\epsilon')}{4(\epsilon')^2}\left\{1-\left[1+\frac{8D\epsilon'}{LK(\epsilon+\epsilon')^2}\right]^{\frac{1}{2}}\right\}. \tag{7}$$

Since this expression involves small differences between large numbers, it is expedient to make the definition

$$y=8D\epsilon'/LK(\epsilon+\epsilon')^2 \tag{8}$$

and expand Eq. (7) in a power series

$$[\mathrm{ClNO}]=\frac{D}{L(\epsilon+\epsilon')}\left[1+\frac{2\epsilon}{\epsilon'}\times\left(\frac{y}{8}-\frac{y^2}{16}+\frac{5y^3}{128}-\frac{7y^4}{256}+\cdots\right)\right]. \tag{9}$$

The factor enclosed in brackets serves to correct the optical density for the dimerization of nitrogen dioxide. In evaluating this factor all terms of the power series which contributed less than 0.05 percent of the total value of the factor were neglected. Thus, while it was necessary to include terms as high as the fourth power of y in applying Eq. (9) to runs made in the neighbor-

TABLE II. Results of runs made in the intermediate pressure apparatus using diluent nitrogen gas.

Temperature °C	Pressures of gases in mm NO	Pressures of gases in mm $ClNO_2$	Pressures of gases in mm Total	$k\times10^{-7}$ cc mole^{-1} sec^{-1}
4.1	18.7	18.8	384	0.35
1.4	14.2	14.2	290	0.33
1.8	13.7	13.7	280	0.26
4.1	6.68	6.70	137	0.26
27.1	4.69	4.70	95	0.69
27.0	4.11	4.12	84	0.59
27.3	3.28	3.29	67	0.64
29.5	3.05	3.06	62	0.95
28.6	2.78	2.79	57	0.67

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hood of 0°, at 27° and above no more than the first-order term had to be evaluated. ϵ was obtained from the data of Dixon,[9] ϵ' from the data of Goodeve and Katz,[10] and K was evaluated from the results of Verhoek and Daniels.[11]

The purity of nitryl chloride was established by determining its molecular weight. A further check on the purity of either reactant was obtained by comparing the absorptiometrically observed pressure of nitrosyl chloride at the completion of a run with that expected from manometer readings and pipet volumes when the reaction was carried out in the presence of an excess of the other reagent. The results of 9 runs carried out with an excess of nitryl chloride yield a value of 1.008 ± 0.009 for the ratio of observed-to-expected pressure, while the results of 7 runs made with nitric oxide in excess yield a ratio of 1.01 ± 0.01. Each reagent was, therefore, 99 ± 1 percent pure. This agreement indicates further that side reactions, if they exist, are negligible.

A sensitive test which shows the reaction to be complete was an attempt to follow the reverse reaction. A mixture of nitrogen dioxide and nitrosyl chloride was followed absorptiometrically for 48 minutes without detection of decrease in optical density. Under the conditions of the experiment this indicated that the reaction between nitryl chloride and nitric oxide is at least 99 percent complete. Combined with the qualitative observations of substantial amounts of nitrosyl chloride in the reaction products, these results establish that the reaction proceeds quantitatively according to Eq. (2). Thus the rate of the reaction is equal to the rate of formation of nitrosyl chloride and can be determined from the appearance of optical density as indicated previously.

The rate of reaction for any given run was found to fit the appropriate form of the integrated rate expression for a second-order reaction. The ratio of initial concentrations was varied from about 1:10 to 10:1, and the second-order rate constants obtained are given in Table I. The mean is 0.72×10^{7} cc mole^{-1} sec^{-1} and the standard deviation 0.14×10^{7} cc mole^{-1} sec^{-1}. There is no significant trend in the rate constants, and thus the reaction is second order and first order in each reactant.

The runs made in the 6-mm diameter cell of the intermediate pressure apparatus are shown in Table II. The temperatures were measured rather than controlled, and therefore they vary from run to run. A comparison of the individual values of the rate constants from studies made in this apparatus at temperatures near 27° with those made at 27° in the large bulb shows that the reaction is homogeneous. In spite of a 40-fold change of surface-to-volume ratio, the second-order rate constants are the same in each apparatus. In Table II the results of a few runs made between 1° and 4° are also given.

TABLE III. Results of runs made in the low pressure apparatus using equal concentrations of the reactants.

Temperature °C	Number of runs	$k_{Av}\times10^{-7}$ cc mole^{-1} sec^{-1}	Standard error of mean $\times10^{-7}$ cc mole^{-1} sec^{-1}
27	28	0.79	0.02
38	20	1.25	0.04
50	9	1.64	0.06
61	16	2.56	0.05
71	25	3.4	0.1

In order to determine the activation energy 98 runs were made in the low pressure apparatus using equal initial concentrations of reactants. These runs covered a temperature range from 27° to 71°. The results are summarized in Table III. All runs in Tables I, II, and III were fitted to the Arrhenius equation by the method of least squares. The rate constant may be expressed as

$$k=0.83\times10^{12}e^{-E/RT}\ \text{cc mole}^{-1}\ \text{sec}^{-1},$$

where the energy of activation is 6.9 kcal and twice its standard error of estimate is 0.3 kcal.

DISCUSSION

This investigation has shown that the reaction between nitryl chloride and nitric oxide is given quantitatively by Eq. (2), and it is fast, homogeneous, and first order in each reactant. There is no indication that the reaction is complex; and since the energy of activation is less than any bond energy in either reactant, it is not unimolecular. Thus it is proposed that this is an elementary bimolecular reaction.

Even if this mechanism is correct, it still leaves open an interesting ambiguity of path. Nitryl chloride could pass either an oxygen atom or a chlorine atom to nitric oxide with the same chemical result. The following experiment might clarify this question: Label nitryl chloride with isotopic nitrogen N*; make a series of studies to see if the reactants and products undergo exchange; and if the exchange rates can be neglected, carry out this reaction to see which path it takes:

$$ClN^{*}O_2+NO=N^{*}O_2+ClNO$$

$$ClN^{*}O_2+NO=NO_2+ClN^{*}O.$$

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