

Microphotometer records of these have not been reproduced here since they make no new contribution to the absorption picture as presented for the vapor state. It is to be noted that the findings of Heyroth and Loofbourow² with respect to fine structure in pyrimidine have been confirmed.

Absorption maxima were found at the following wave lengths: for pyrimidine at 2326, 2375, 2427 and 2483 Å.; for pyrimidine-mercuric chloride compound at 2357, 2412 and 2475 Å.; for dichloropyrimidine a broad band covering approximately 2470-2630 Å. with its center at 2540 Å.; for trichloropyrimidine at 2575, 2633 and 2695 Å.; for tetrachloropyrimidine at 2690, 2760 and 2870 Å. Microphotometer traces of the spectrum plates resembled those obtained when the vapors of the corresponding substances were photographed. In case of the solutions, however, the curves were in general flatter, the major peaks less well differentiated, and the smaller peaks often absent. The sharp line-like bands seen in the pyrimidine vapor spectrum did not appear in the photographs of the solution; neither did the group of relatively sharp bands of tetrachloropyrimidine in the 2200-2500 Å. region.

The writers wish to express their indebtedness

to Dr. Victor R. Ells for assistance in the analysis of the Spekker plates for the solutions.

Summary

1. The ultraviolet absorption spectra of pyrimidine, dichloropyrimidine, trichloropyrimidine, and tetrachloropyrimidine have been photographed in the vapor state. All of these compounds exhibit a system of broad bands in the range 2300-2800 Å.

2. Pyrimidine shows some 125 sharp line-like bands in the 2700-3300 Å. region.

3. Molecular extinction coefficients in the range 2100-3000 Å. have been determined for solutions of pyrimidine, dichloropyrimidine, trichloropyrimidine, and tetrachloropyrimidine. Structure in the absorption bands, as observed in the vapor state, is still evident in solution, but is not so marked.

4. Absorption maxima shift progressively to longer wave lengths with successive increases in the number of chlorine atoms attached to the pyrimidine ring; corresponding increases in the magnitude of the molecular extinction coefficients also accompany the addition of successive chlorine atoms.

COLUMBIA, MO.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Catalytic Oxidation of Phosphorus Tribromide

BY C. R. JOHNSON AND L. G. NUNN, JR.

A number of methods are available for the preparation of phosphorus oxybromide, but none of them is particularly convenient or economical: it is perhaps significant that this compound is not found in most price lists of chemical reagents. The direct oxidation of phosphorus tribromide suggests itself as a convenient means of preparing the substance, but no reaction occurs when oxygen and the tribromide are mixed, at temperatures up to the boiling point of the latter. It has been stated that phosphorus oxybromide is formed by the action of oxygen on the tribromide at its boiling point.¹ This cannot be recommended as a method of preparation, as the reaction is not easy to control and sometimes goes explosively. Moreover, there seems to be some doubt whether

any appreciable amounts of POBr₃ are formed in the explosion, in which phosphorus pentoxide and bromine are also obtained.² Geuther and Michaelis³ attempted to prepare the bromine analog of P₂O₃Cl₄ by the action of gaseous N₂O₃ and N₂O₄ on well-cooled liquid PBr₃, and note briefly that they obtained POBr₃ and P₂O₅ in the reaction.

We have found that in the presence of nitrogen oxides and oxygen, over a somewhat limited range of conditions, phosphorus tribromide vapor may be oxidized smoothly and non-explosively. Enough phosphorus oxybromide has been isolated from the reaction products in trial experiments to warrant the hypothesis that it is the main product of the non-explosive oxidation, and that the

(1) Demole, *Bull. soc. chim.*, [2] **34**, 201 (1880).

(2) Christomanos, *Z. anorg. allgem. Chem.*, **41**, 276 (1904).

(3) Geuther and Michaelis, *Ber.*, **4**, 766 (1871).

formation of by-products can be minimized by choosing conditions favoring this reaction. To determine the optimum conditions for carrying out the reaction as a means of preparing phosphorus oxybromide, the effect of various factors on the velocity of the oxidation has been studied.

Measurement of Reaction Rates

In the Pyrex all-glass apparatus used in these studies the reactants were mixed in a 220-ml. system with an attached separatory funnel for adding the tribromide, and with separate inlets for oxygen and nitric oxide. The reaction bulb was surrounded by an electrically heated porcelain beaker furnace fitted with a tight asbestos cover. The lowest temperatures measured were probably significant to within 1°, the highest within 5°. The reaction bulb was joined by an inverted capillary U-tube to a 900 mm. mercury manometer. For measuring some of the slower reaction rates the manometer was filled with mineral oil, but in most cases mercury covered with a little oil was used.

Phosphorus tribromide samples were taken from two lots of Eastman material distilled between 169 and 172°, and from one control lot of known high purity, which had been repeatedly distilled in vacuum. Electrolytic tank oxygen was used directly after bubbling through wash bottles containing concentrated sulfuric acid and a tube containing cotton; analysis showed the gas to be 98 to 99% pure. Nitric oxide was prepared by the action of concentrated sulfuric acid on a 1:1 solution of sodium nitrite. The gas was washed with water to remove higher nitrogen oxides, dried in a tower containing anhydrous calcium chloride, and collected over mineral oil just before use. Numerous analyses of the nitric oxide by the physico-chemical method indicated in the following paragraph showed it to be free from any significant amounts of higher nitrogen oxides before it was mixed with oxygen in the reaction bulb.

The method of making the measurements varied somewhat, but the procedure finally adopted in most cases was as follows. The furnace was adjusted to the desired temperature and the reaction bulb was evacuated with a Hyvac pump. A measured amount of nitric oxide was introduced from an oil-filled gas buret with a capillary stopcock at the

top. The measured volume, two sets of temperature and pressure readings, and the known volume of the reaction system provided data for a check on the purity of the nitric oxide at this stage. Oxygen was then let in until the pressure in the reaction bulb was less than atmospheric by the anticipated increase due to subsequent addition of phosphorus tribromide. A 1.0 to 4.0 ml. volume of liquid tribromide was then added rapidly, and simultaneous readings of the time, temperature, and manometric height were recorded at suitable short intervals as the oxygen pressure decreased.

In other cases the phosphorus tribromide was added first. At temperatures between 40 and 165° subsequent addition of nitric oxide produced no measurable reaction. On adding oxygen to the mixture, reaction took place, sometimes at measurable velocities, either immediately or after an induction period, and sometimes explosively, depending on the temperature and initial concentrations of nitrogen oxides. When the reaction proceeded non-explosively, with tribromide in excess, only the oxygen appeared to be markedly depleted, since the initial pressure-time curve could generally be retraced to some extent by adding more oxygen. At high temperatures and high nitrogen dioxide concentrations bromine and nitrosyl bromide were formed. Whenever the reaction went explosively, phosphorus pentoxide and bromine were formed.

To calculate the various oxygen pressures, the partial pressures of the phosphorus tribromide and oxybromide were determined empirically; the partial pressures of the nitrogen dioxide and nitrogen tetroxide in the reaction system were calculated from the measured additions of nitric oxide, with the aid of data by E. and L. Natanson.⁴ The observation recorded in the preceding paragraph indicates that the partial pressures of these four constituents were maintained throughout the reaction—by regeneration in the case of the nitrogen oxides, and by volatilization in the case of the tribromide and oxybromide, the partial pressure of the latter reaching its equilibrium value in due time after the start of the reaction.

Summary of Results

Over the range of oxygen pressures from 700 mm. to about 150 mm. of mercury and for all temperatures and nitric oxide additions not producing explosive reaction, the rate of oxygen absorption, *i. e.*, the rate of oxidation of the tribromide, was proportional to the square root of the oxygen pressure:

$$-dp/dt = K\sqrt{p_{O_2}} \quad (1)$$

where p is in mm. of mercury and t is in seconds. For each set of data the velocity constant was evaluated graphically; the results of about sixty experiments are condensed in Fig. 1, which shows diagrammatically, yet with moderate precision, the variation of the velocity constant with temperature and amount of catalyst. Figure 1 rep-

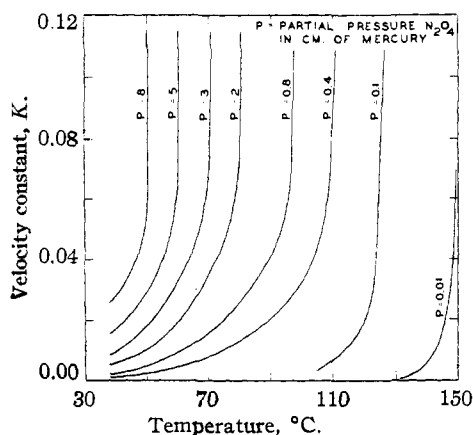


Fig. 1.—Variation of velocity constant with temperature and nitrogen tetroxide pressure.

(4) Natanson and Natanson, *Wied. Ann.*, **24**, 454 (1885); **27**, 606 (1886).

resents our best present estimate of the conditions under which the reaction becomes explosive; data given in the figure may be used in conjunction with equation (1) in designing apparatus and determining suitable conditions for the smooth, non-explosive oxidation of phosphorus tribromide.

In addition to the results summarized in Fig. 1, other evidence bearing on the mechanism of the reaction may be drawn from our data. It appears that the oxidation of phosphorus tribromide (to oxybromide) is catalyzed by nitrogen tetroxide but not by nitrogen dioxide. Even at high temperatures and fairly high nitrogen dioxide pressures the non-explosive oxidation goes only slowly when little or no tetroxide is present. Under these conditions induction periods ranging from 140 to 1100 seconds were observed. When the velocity constants were plotted against temperature (Fig. 1) the points representing different nitrogen tetroxide pressures fell on regularly spaced isobars; the points representing different nitrogen dioxide pressures did not seem to fit into any pattern. The rate of the mild oxidation is thus

more or less independent of the nitrogen dioxide pressure; at high temperatures and high nitrogen dioxide pressures, of course, other reactions involving the dioxide do take place. Further analysis of the curves in Fig. 1 indicates that at constant temperature, at least up to 100°, the velocity constants are directly proportional to the nitrogen tetroxide pressures. The oxybromide probably acts only as a diluent, except above the temperature at which dissociation begins.

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Summary

Over a limited range of conditions, in the presence of nitrogen oxides and oxygen, phosphorus tribromide vapor is oxidized rapidly yet non-explosively to the oxybromide. The effect of various factors on the velocity of the oxidation has been studied, and the conditions under which the reaction can be controlled have been outlined.

AUSTIN, TEXAS

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Heats of Organic Reactions. X. Heats of Bromination of Cyclic Olefins

BY M. W. LISTER¹

Studies of the heats of hydrogenation and bromination of unsaturated organic compounds published in recent years from this Laboratory² have established certain regular relations between these quantities and the structures of the molecules investigated. The previous work was limited to gas phase reactions, and the study of brominations in particular was confined to the simplest molecules because of the low vapor pressures of the products. The present experiments are an extension to reactions in the liquid phase. The brominations of a series of cyclic olefins have been investigated, and the results throw further light on the causes of the regularities previously noted.

Experimental

The calorimeter was designed for general utility in measuring heat changes in liquid phase reactions. It is an

(1) Commonwealth Fellow.

(2) Kistiakowsky, *et al.*, *THIS JOURNAL*, **61**, 1868 (1939), and earlier.

improvement on an apparatus developed by R. B. Williams in this Laboratory but not yet described in the literature.

It consisted of a long-necked spherical Dewar flask of 500-cc. capacity, with the bottom of the inside of the neck ground into a conical joint. Into this fitted a platinum cup from which tubes, closed at the bottom and open at the top, dipped into the body of the flask. These contained (i) a platinum resistance thermometer, (ii) a constantan wire resistance, both occupying only lower parts of the tubes so that they were completely below the level of the liquid in the flask. A brass cup was soldered into the platinum cup to strengthen it. The leads to the thermometer and to the resistance were brought out through thin stainless steel tubes, soldered into the brass cup. This design ensured (i) low heat exchange with the outside, (ii) that no vapor from the liquid in the flask could diffuse into the neck, and there condense.

In order that the reaction to be measured could be started at any given time, one of the reagents (usually bromine) was placed in a sealed glass ampoule which could be broken during the operation of the calorimeter. This ampoule was held in a platinum basket slung from hooks on the underside of the platinum cup, and was broken by striking down a thin platinum rod fitting closely in a stainless steel tube soldered to a short and narrow platinum