FMN.[6] FAD-X is an intermediate in this process and under relatively mild conditions, such as exposure of FAD spots to ammonia vapor before paper chromatography, a quantitative conversion to FAD-X may be effected.

Treatment of FMN-X with intestinal phosphatase (Armour) yields a product which is chromatographically identical with riboflavin, thus excluding riboflavinyl glucoside.[7] Microbiological assays,[8] kindly performed by Dr. E. E. Snell, have shown that FAD-X contains riboflavin and not lyxoflavin.[9,10]

The above evidence supports the hypothesis that FAD-X is a flavin dinucleotide, isomeric with FAD, but having a *cyclic* phosphate structure. It cannot be stated at present whether FAD-X occurs naturally or is produced artificially during the isolation of FAD.

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THE MECHANISM OF THE REACTION BETWEEN OZONE AND NITROSYL CHLORIDE

Sir:

Schumacher and Sprenger[1] produced nitryl chloride by the reaction of ozone with nitrosyl chloride which they described as "rapid and complete"

$$NOCl + O_3 = NO_2Cl + O_2 \qquad (1)$$

This reaction is an interesting analog of the reaction between nitrogen dioxide and ozone,[2] and also it has an additional feature of interest in that it involves a forbidden electronic transition.[3] By following nitrosyl chloride by its absorption of the 405 mμ Hg line, we have followed this "rapid" reaction in a meter-long Pyrex tube by the same method used with nitrogen dioxide and ozone.[2] Our preliminary results were erratic, irreproducible, and partially heterogeneous. There was an induction period, followed by an increase in rate which went through a maximum and fell to zero as the reactants were consumed. We went to great lengths to remove all impurities from the reactants and used a cell with smaller surface to volume ratio. Under these conditions the reaction appeared to cease altogether. We finally concluded that the reaction as written above does not occur at all.

Ozone produced by an electric discharge contains traces of nitrogen pentoxide if the oxygen stream contains traces of nitrogen. Also nitrosyl chloride could be contaminated with nitric oxide or nitrogen dioxide, and ozone would rapidly convert either of these to nitrogen pentoxide. Therefore we deliberately added small amounts of nitrogen pentoxide to the ozone stream to examine the effect of a probable impurity. A fast homogeneous reaction set in with the stoichiometry of Eq. 1. With a large excess of ozone, the reaction in the presence of nitrogen pentoxide was found to be one-half order in nitrosyl chloride. By correcting for this dependence on nitrosyl chloride, rates were found to be one-half order in ozone, and all runs from start to finish were one-half order in each of the two reactants. When the log of these rate constants was plotted against the log of the catalyst concentration, the slope was very nearly one-half, indicating one-half order dependence on nitrogen pentoxide. Thus the empirical rate expression was

$$-d[NOCl]/dt = k[NOCl]^{1/2}[O_3]^{1/2}[N_2O_5]^{1/2} \qquad (2)$$

The following mechanism is proposed for this reaction

$$N_2O_5 \xrightarrow{k_1} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{k_2} N_2O_5$$

$$NO_2 + O_3 \xrightarrow{k_3} NO_3 + O_2$$

$$NOCl + NO_3 \xrightarrow{k_4} NO_2Cl + NO_2$$

By making the steady-state assumption for nitrogen dioxide and NO_3, the rate expression exactly derived from the mechanism is

$$\frac{-d[NOCl]}{dt} = \left(\frac{k_1k_3k_4}{k_2}\right)^{1/2}[NOCl]^{1/2}[O_3]^{1/2}[N_2O_5]^{1/2} \qquad (3)$$

which agrees with the observed rate function. The values of k_1/k_2 and k_3 are known,[4] and by substituting the values and the observed rate into Eq. (3) we find k_4 to be 0.7×10^8 cc. mole^{-1}sec.$^{-1}$ at 40°. If the pre-exponential factor is about 10^{12} cc. mole^{-1}sec.$^{-1}$, the energy of activation of k_4 is about 6 kcal.

It is interesting to notice that while Eq. (1) involves a forbidden electronic transition, no step in the proposed mechanism is forbidden. In the work of Schumacher and Sprenger there must certainly have been some unsuspected nitrogen pentoxide present. With initially pure reactants our work indicated heterogeneous catalysis for the equilibrium $2NOCl \rightleftarrows 2NO + Cl_2$ followed by rapid reaction of nitric oxide and ozone to produce nitrogen pentoxide, which then catalyzes reaction (1).

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