

and anhydroanthramycin (14) follow from the interconversions which were discussed previously.¹

Anthramycin (1) possesses some structural features found in the actinomycins.^{1,2} A more pronounced relationship is apparent from the comparison of anthramycin with the 3-hydroxy-4-methylanthraniloyl peptides which are intermediates in the postulated biosynthesis of the actinomycins.^{1,3} Since the oxidative dimerization of these intermediates leads to the formation of actinomycins, conceivably anthramycin could be transformed *in vivo* to "actinomycin analogs" which actually may be responsible for the observed antitumor activity.^{1,4}

Acknowledgment. The authors sincerely wish to thank Professor G. Büchi for many stimulating discussions.

(11) The relative and absolute configurations of anthramycin are being investigated.

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(14) We have observed that anthramycin is easily oxidized by air under physiological conditions to products containing the actinomycin chromophore.

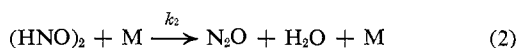
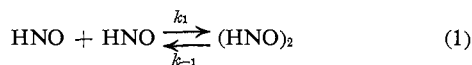
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Received October 27, 1965

On the Role of the Nitroxyl Molecule in the Reaction of Hydrogen Atoms with Nitric Oxide

Sir:

The suggestion that HNO is a reactive intermediate in the hydrogen atom-nitric oxide reaction has often been made on the basis of kinetic studies of stable product formation.¹⁻⁵ This suggestion has been confirmed by spectroscopic observation and study⁶⁻¹⁰ of a red emission from the reaction, which is attributable to excited nitroxyl molecules formed in a termolecular reaction.⁶⁻¹⁰ However, nitroxyl is not a stable product of the reaction¹⁻⁵ and, hence, must react further. In this regard, Strausz and Gunning⁵ have proposed that nitrous oxide and water are formed by the following mechanism.



We wish to report direct evidence of the correctness of this proposal⁵ and, in addition, an approximate lower limit to k_1 .

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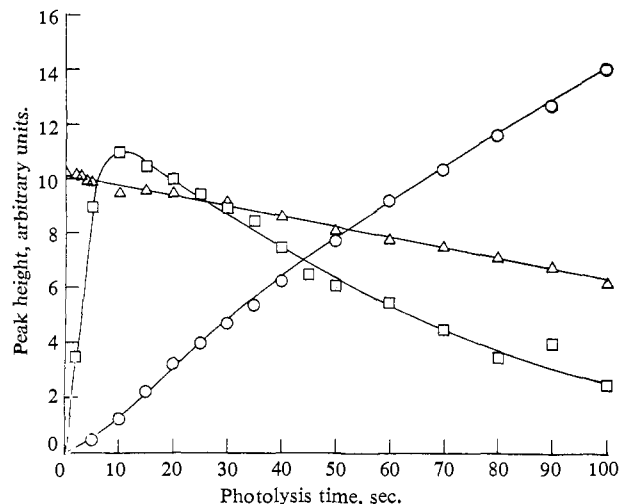


Figure 1. Formation of DNO and N₂O and depletion of NO during photolysis: Δ , m/e 30 (NO⁺); \square , m/e 32 (DNO⁺); \circ , m/e 44 (N₂O⁺).

We have studied the D + NO and H + NO reactions by mercury photosensitization (at 2537 Å.) of D₂-NO and H₂-NO mixtures in a cell containing a pinhole leak into a Bendix Model 14-101 time-of-flight mass spectrometer.^{11,12} We have observed nitrous oxide and water as stable products of the reaction, while nitroxyl is found as a transient intermediate. In addition, small amounts of hydroxylamine appear to be formed. We do not observe nitrogen, but this is as expected⁵ under our conditions of $P_{D_2}/P_{NO} \geq 138$. Masses higher than m/e 36 attributable to the dimer (HNO)₂ or to nitric acid were not observed.

The results of a typical reaction at $P_{D_2}/P_{NO} = 138$ and $P_{total} = 38$ torr are shown in Figures 1 and 2. Figure 1 shows the variation of m/e 30, 32, and 44 with photolysis time. These peaks are measures of the concentration of NO, DNO, and N₂O, respectively. However, since the peak base lines have been greatly suppressed to allow the measurement of small changes, the peak heights, as shown, are not proportional to concentrations. The rapid rise of m/e 32 to a maximum while the m/e 44 growth is accelerating, followed by the inflection point of m/e 44 close to the time of the m/e 32 maximum, indicates that N₂O arises from HNO. Actually, the rise of [DNO] is steeper and the fall less steep than shown by the time behavior of m/e 32. This is because [NO] decreases continually during photolysis and a significant part of m/e 32 is comprised of N¹⁴O¹⁸⁺. Identical behavior was observed for m/e 31, for the case of H₂-NO mixtures, including mass interference; but in this case the interference was from N¹⁵O¹⁶⁺. The growth curves of H₂O are similar to those of N₂O indicating their formation in a common reaction.

Figure 2 depicts the logarithm of the relative peak heights of m/e 30, 32, and 44 as a function of time after the photolysis was stopped. The behavior shows quite conclusively that N₂O is formed by the dimerization of nitroxyl. In this flow apparatus, a stable product, A, which is neither being formed nor reacting, decays by a first-order leakage through the pinhole into the mass

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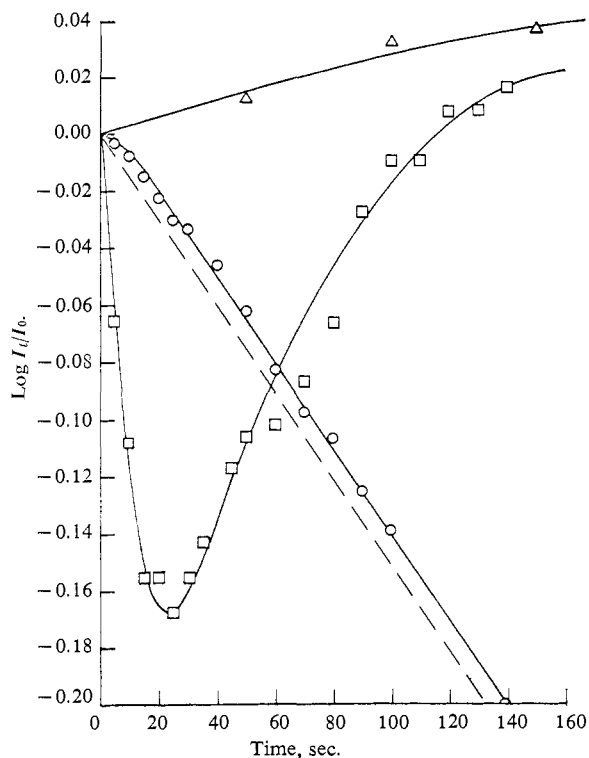


Figure 2. Decay curves of DNO, N₂O, and NO after photolysis: Δ , m/e 30 (NO⁺); \square , m/e 32 (DNO⁺); \circ , m/e 44 (N₂O⁺).

spectrometer.^{11,12} Hence, for this case

$$\log \frac{[A]}{[A]_0} = \frac{\lambda}{2.303} t \quad (3)$$

and the decay plot is as shown by the dotted line, where λ , the leak rate constant, was determined previously. The data for m/e 44 show, however, that for about the first 20 sec. N₂O is being formed, in addition to leaking through the pinhole. After this, the straight-line behavior characteristic of change solely by pinhole leakage is observed. The behavior of m/e 32 is quite different. It is apparent that DNO disappears by a process much more rapid than leakage through the pinhole. Furthermore, the minimum in the m/e 32 curve shows that DNO is essentially gone at $t \sim 20$ sec. when m/e 44 begins the normal pinhole leakage behavior. The minimum and subsequent rises of m/e 32 are due to the contribution to this peak of N¹⁴O¹⁸⁺. During photolysis [NO] is depleted, as shown in Figure 1. However, when the light is turned off diffusion of NO from the reservoir containing NO, H₂, and Hg occurs until [NO] is uniform throughout. This is shown by the rise of m/e 30 in Figure 2. This interpretation was confirmed by examination of the 32/30 peak height ratio over this time interval. This ratio at first fell very sharply, while DNO was reacting, but then subsequently rose and reached a constant value.

The behavior of m/e 32 and 44 in Figures 1 and 2 shows quite clearly that DNO is the precursor of N₂O. Moreover, a reasonably linear plot of the reciprocal of the peak height of m/e 32 vs. time (for $t < 20$ sec.) after the photolysis was stopped indicates the DNO disappears to form N₂O in a reaction that is second order in [DNO]. This is in agreement with the mech-

anism of Strausz and Gunning⁵ (eq. 1 and 2), which predicts

$$[\text{DNO}]^{-1} = [\text{DNO}]_0^{-1} + \frac{2k_1k_2[\text{H}_2]}{k_1 + k_2[\text{H}_2]} t \quad (4)$$

A peak height-concentration relationship is known for N₂O but not for DNO. However, if we assume that during the decay period, following the turning off of the light (Figure 2), the DNO reacts solely to form N₂O, we can use the stoichiometry to establish a relation between the change in peak height and concentration of DNO. With this admittedly crude calibration, we have constructed second-order plots according to (4); the slopes are pressure sensitive, in agreement with (4). We are at present studying this pressure dependency, but from our present results and the form of (4) we can state that $k_1 \geq 5.6 \times 10^{-15}$ cm.³ molecule⁻¹/sec.⁻¹.

Acknowledgment. This work was supported by Grant No. 833-A1 of the Petroleum Research Fund. Acknowledgment is also made to the Public Health Service for a fellowship (F. C. K.) and to the National Science Foundation for assisting in the purchase of the mass spectrometer.

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Received September 23, 1965

Measurement of the Inversion Rate of a Secondary Amine and Its N-Deuterio Analog by Nuclear Magnetic Resonance Spectroscopy¹

Sir:

2,2,3,3-Tetramethylaziridine (I) was first synthesized by Closs and Brois,² who reported that the n.m.r. spectrum of this compound "showed a single, sharp resonance line at 217 c.p.s. (relative to external benzene at 40 Mc.), thus revealing the equivalency of the four methyl groups."

Using the same method of preparation, we obtained I in pure form (as indicated by gas chromatography), having the same physical constants and infrared absorption bands as reported,² but showing in its n.m.r. spectrum two sharp peaks of equal intensities, at τ 8.88 and 8.72, respectively (at room temperature, in CCl₄, relative to internal tetramethylsilane at 60 Mc.). This separation of the chemical shifts of 6,6 methyl protons at room temperature was demonstrated in the spectra of solutions of I in several aprotic solvents as well as in the spectrum of the pure compound; however, it could be best studied in CCl₄ and DMF solutions at approximately 25% concentration of I. The compound is extremely hygroscopic; when its solution in CCl₄ was allowed to stand for a few minutes exposed to air, the two n.m.r. signals coalesced into a single, broader peak. This was obviously due to H₂O-catalyzed proton exchange. The same phenomenon was observed in the presence of trace amounts of alcohol or other substances having exchangeable hy-

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