

information concerning gases and low boiling liquids produced in large quantities by industry.

This paper presents some preliminary results of the photolysis of C_2H_5Cl (Freon 160) at 147 nm. The extinction coefficient at this wavelength is of the order of $10^{31} \text{ mol}^{-1} \text{ cm}^{-1}$ and the molecule readily photolyzes to give C_2H_4 and $1,4-C_4H_8Cl_2$ as the two major products at conversions of $< 1\%$. Other photolysis products observed, in decreasing order of yield relative to C_2H_4 , were: C_2H_6 , $n-C_4H_{10}$, $1-C_4H_9Cl$, C_2H_3Cl , C_3H_8 , C_3H_6 , C_2H_2 , CH_4 , $1-C_4H_8$, *cis* $2-C_4H_8$, *trans* $2-C_4H_8$ and CH_3Cl . The yields, relative to C_2H_4 , of $n-C_4H_{10}$, C_2H_6 , C_2H_2 and CH_4 did not vary with photolysis time at a fixed pressure of ethyl chloride. In the presence of nitric oxide, ethane was no longer observed and the relative yield of $n-C_4H_{10}$ was significantly suppressed as were the relative yields of most of the other minor products.

The results are interpreted in terms of primary processes where molecular elimination is not a major contributor. The principal reaction pathway appears to be carbon-chlorine bond fission from an electronically excited state of ethyl chloride, followed by rapid decomposition of the highly energized $C_2H_5^{**}$ radical to C_2H_4 . Subsequent hot atom and radical reactions account for the majority of the remaining observed products.

A comparison of these results with those obtained in the 147 nm photolysis of C_2H_5F suggests different modes of excitation and reaction channels in C_2H_5Cl and C_2H_5F . In the case of ethyl fluoride the observed major products were C_2H_3F and C_2H_2 and it was concluded that molecular eliminations were the major primary processes. Molecular orbital calculations have now been carried out and the molecular orbital descriptions of the first electronic excited states for both halides were found to be antibonding with respect to the carbon-halogen bond ($\sigma^* \text{ c-x}$). This should lead to carbon-halogen bond fission in both cases at 147 nm which is observed in the case of C_2H_5Cl , but does not occur to any significant extent in the case of C_2H_5F . It would therefore seem that

C_2H_5F undergoes an internal conversion to a highly vibrationally excited ground electronic state prior to decomposition.

It is apparent that the C_2 -Freons exhibit a spectral specificity of photodecomposition which is not readily predicted.

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Experimental Study of the $NO^+ + e \rightarrow N + O$ Recombination in the Vacuum UV Flash Photolysis of Nitric Oxide

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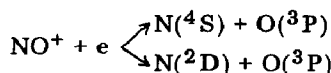
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The main result from this study is the first experimental determination of the $N(^2D)$ branching ratio $f = [N(^2D)] / \{[N(^2D)] + [N(^4S)]\}$ in a laboratory experiment.

Nitric oxide was irradiated with a fast flash lamp ($t = 10 \mu\text{s}$), separated by a LiF-window from the reaction chamber. The type of flash lamp used has been described earlier [1]. In short, it consisted of a $0.5 \mu\text{F}$ capacitor, charged to 25 kV. The discharge took place between copper electrodes 15 mm apart in nitrogen at atmospheric pressure. The reaction chamber was a stainless steel tank of approximately 50 l volume. The flash lamp light entering the chamber at one side of the tank was focused by a large concave mirror to the center of the tank yielding a very high photon flux density in a volume of about 1 cm^3 . NO, typically at densities of about $10^{14} / \text{cm}^3$, mixed with argon or nitrogen at a total pressure of 10 Torr was continuously pumped through the chamber.

Nitrogen atoms in either 4S or 2D state, the products of the photolysis and ion-electron recombination were detected by resonance absorption with a calibrated resonance lamp, shining through the tank's focal plane, dispersed by a vacuum UV monochromator and recorded on a multi-channel analyzer.

At wavelengths shortward of 1340 Å, nitric oxide is photodissociated and photoionized. The products of the ion-electron recombination



are nitrogen atoms in the ^4S and/or ^2D configuration and ground state oxygen atoms.

The knowledge of the $\text{N}(^2\text{D})$ branching ratio is essential for the understanding of the ionospheric nitric oxide balance.

- 1 D. Kley, F. Stuhl and K. H. Welge,
Z. Naturforsch., 18a (1963) 906.

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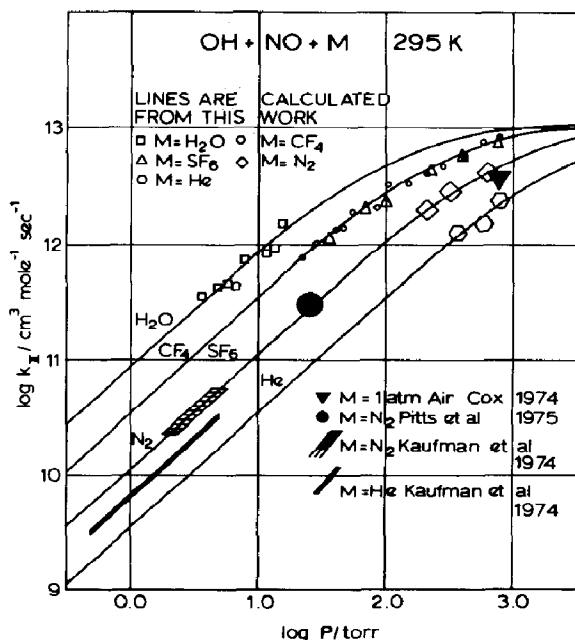
Hydroxyl Radical Combination with Nitric Oxide.



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The technique of flash photolysis of water vapour to produce hydroxyl radicals, coupled with resonance absorption ($\text{OH}^2\Sigma^+ \leftarrow \text{X}^2\Pi$ transition) detection of the transient hydroxyl decay has been used to study the reaction of hydroxyl with nitric oxide at 295 K. The reaction is termolecular and over the pressure range 50 - 760 Torr, changes from 3rd order to 2nd order kinetics.



Using gases assumed to be efficient third bodies (CF_4 and SF_6) the bimolecular reaction rate (k_{II}) dependence on the pressure of M was followed. The results when plotted in the Lindemann Hinshelwood form

$$1/k_{\text{II}} = 1/k_{\text{II}\infty} + \text{const}/P$$

yielded good linear plots which by extrapolation gave $k_{\text{II}\infty}$ at infinite pressure as $1.1 \pm 0.1 \cdot 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$. The experimental value is very close to the value $1.2 \cdot 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ predicted by Tsang (1973) from RRKM theory.

By suitable fitting of the data obtained for other gases as M the relative efficiencies (collision adjusted) are $\text{H}_2\text{O} = 1.0$, $\text{CF}_4 = 0.41$, $\text{SF}_6 = 0.37$, $\text{N}_2 = 0.12$, $\text{He} = 0.02$.

The fitted curves and the data obtained in this study are plotted on the attached figure. The points displayed for nitrogen and helium are those at high pressure. Data were obtained over the entire pressure range, but the lower pressures require adjustment for the effect of water vapour and are not shown.

The agreement between this work and that of different sources is also shown on the attached figure for nitrogen.

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Nitric Oxides in the Stratosphere -- A Two Dimensional Atmospheric Model

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The global distribution of nitric oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) in the stratosphere (10 - 50 km) is investigated using an oxygen-hydrogen-nitrogen photochemical scheme and a parameterized two-dimensional transport model. The following assumptions are made to predict the distribution of NO_x : (1) The distribution of N_2O , which is assumed the main source of NO_x are not considered at this time. (2) The detailed treatment of the photodissociation processes in the O_2 -Schuman-Runge band region, especially the NO photodissociation in the δ -bands,