

Short Communication

Photochemistry of condensed NO_2 and NO_2 -acetone mixtures

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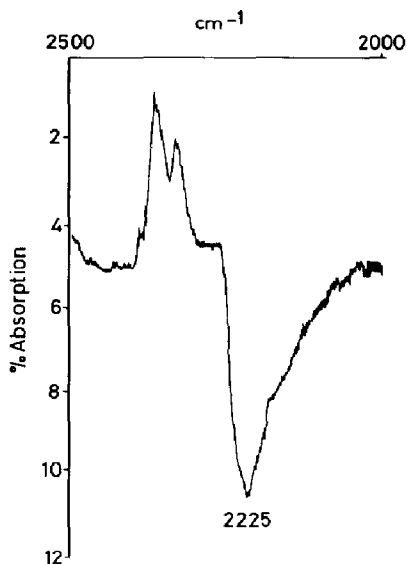
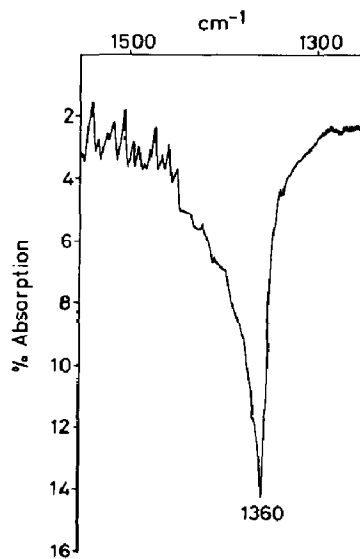
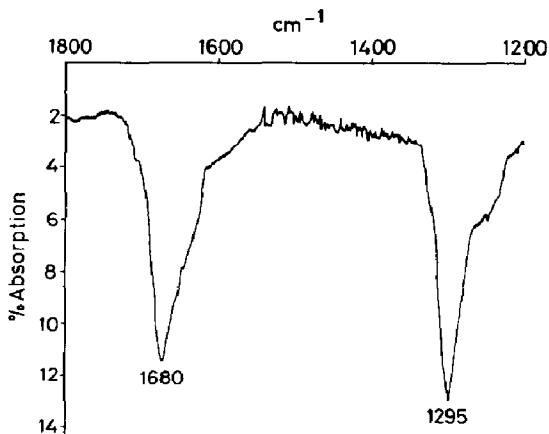
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Condensed phase photolysis of nitrogen dioxide on a NaCl substrate at 100 K gives evidence for a metastable intermediate, ONONO_2 , which reacts with the substrate to form NaNO_3 and NOCl . The production of oxygen atoms has been proved by the reaction with gaseous carbon monoxide. In the photolysis of nitrogen dioxide-acetone mixtures only carbon dioxide has been found as an additional reaction product.

The gas phase photochemistry of the oxides of nitrogen has been investigated to a large extent during the last few years. There is, however, very little information about the photochemistry of these gases in the condensed phase. Reaction possibilities may be markedly different from those in the gas phase not only due to the effect of temperature but also by the lack of translation and rotation. In this study, we report on some photoreactions of pure nitrogen dioxide and of mixtures of NO_2 and acetone condensed on a NaCl substrate.

The experiments were performed in a low temperature i.r. cell. Gases were condensed at 100 K onto the NaCl substrate and irradiated by a Hg-resonance lamp which could be introduced into the cell. Under our experimental conditions the quantum flux was about $10^{16} \text{ cm}^{-2}/\text{s}$, the intensity being mainly in the 254 nm line. Since the irradiation in some of the experiments lasted for 12 h the whole apparatus was built up in uhv-technique to avoid perturbations from the residual gas. Spectra were recorded in a Perkin-Elmer grating spectrograph (Model 457). The lower limit of detection was determined to be $6 \times 10^{16} \text{ molecules cm}^{-2}$ by measuring the CO_2 spectrum.

Since the equilibrium at 100 K is almost completely on the side of the dimeric nitrogen dioxide is present as a N_2O_4 layer. From X-ray measurements the stable configuration of N_2O_4 is known to be planar [1]. Two metastable configurations also have been observed, a non-planar structure showing a band at 1715 cm^{-1} [2] and at liquid helium temperatures

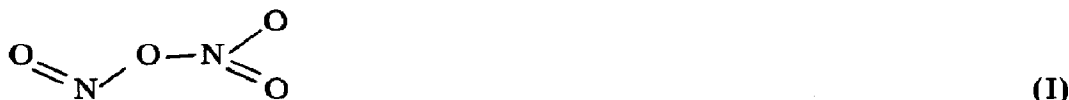
Fig. 1. Formation of NO⁺.Fig. 2. Formation of NO₃⁻.Fig. 3. NO₂Cl-bands.

a configuration which is linked over an oxygen atom [2]. An analysis of the products formed by the irradiation of N₂O₄ on NaCl, however, gives evidence for the occurrence of this structure as an intermediate even at 100 K. Figures 1 - 3 show the new bands appearing during the irradiation.

The band at 2225 cm⁻¹ can be attributed to the nitrosyl cation, NO⁺ [3]. The very broad band between 1400 cm⁻¹ and 1300 cm⁻¹ which becomes sharper during warm-up belongs to the NO₃⁻ ion.

By comparison with NaNO₃ in a KBr pellet the extinction coefficient at 1360 cm⁻¹ has been determined as $\epsilon_{1360} = 9 \times 10^4$ cm²/mol. The

appearance of the bands at 2225 and 1360 cm^{-1} indicates that N_2O_4 is not only present in the stable N-N bridged configuration but also in the metastable form:



The ONONO_2 formed by the irradiation partly reacts with the substrate to form NOCl and NaNO_3 :



Knowing the extinction coefficient ϵ_{1380} and the quantum flux of the light source the rate of formation for NaNO_3 can be estimated to be $3.5 \times 10^{13}\text{ s}^{-1}$ and the quantum efficiency to be about 10^{-3} .

The third band appearing very weakly at 1680 cm^{-1} together with another band at 1295 cm^{-1} belongs to NO_2Cl [4].

During warm-up the N_2O_4 - and NOCl -bands disappear at 180 K , the NO_2Cl bands at 210 K while the NaNO_3 band is still observable at room temperature.

Gas phase photolysis of NO_2 at 254 nm leads to the formation of $\text{NO}(^2\Pi)$ and $\text{O}(^3\text{P})$. Photolysis in a condensed layer should, if at all, be much less efficient than in the gas phase. However, atoms produced at the surface of the layer may be able to react with other molecules or radicals to form new products. In our experiment we passed a constant stream of carbon monoxide ($p = 6 \times 10^{-6}\text{ Torr}$) over the surface. The formation of carbon dioxide was monitored by recording the asymmetric stretching mode at 2350 cm^{-1} . The result is shown in Fig. 4.

After 6 h the absorption reaches a constant value of 3%, corresponding to approximately 50 CO_2 layers. The amount of carbon dioxide formed is independent of the thickness of the N_2O_4 layer. From the initial slope of the curve in Fig. 4 the rate of formation can be estimated to be $5 \times 10^{12}\text{ s}^{-1}$.

In another series of experiments mixtures of nitrogen dioxide and

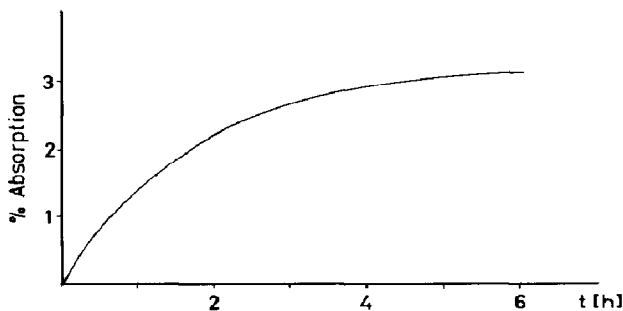


Fig. 4. Formation of CO_2 .

acetone in widely varying ratios were condensed and irradiated. While in gas phase photolysis involving methyl radicals and oxides of nitrogen nitromethane [5] is one of the major products only carbon dioxide has been found at 100 K beside the products of the N_2O_4 reaction. However, since CO_2 formation under the experimental conditions only can occur *via* a radical splitting of acetone it is probable that other products may be formed as well. These products are either volatile at 100 K or formed in amounts below the detection limit of our spectrometer. The possibility of direct photolysis of nitromethane by the 254 nm radiation was excluded by the use of Pyrex filters.

Acknowledgement

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