Investigation of N_2O formation in the NCO+NO reaction by Fourier-transform infrared spectroscopy

K.H. Becker, R. Kurtenbach and P. Wiesen

Physikalische Chemie/Fachbereich 9, Bergische Universität – Gesamthochschule Wuppertal,
Postfach 100127, W-5600 Wuppertal 1, Germany

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The NCO+NO reaction was investigated at room temperature in a static photoreactor using time-resolved Fourier-transform infrared spectroscopy. NCO radicals were generated by photolysing ClNCO diluted in argon at 254 nm. From the concentration–time profiles of the products CO, CO_2 and N_2O, the following branching ratios were determined: 0.35±0.06 for the product channel N_2O+CO, and 0.65±0.06 for the product channel N_2+CO_2.

1. Introduction

Interest in nitrous oxide (N_2O) in the earth's atmosphere has increased considerably over the past few years since N_2O contributes to the catalytic destruction of ozone in the stratosphere and because it is also an effective greenhouse gas. N_2O is produced by industrial and biological processes, however sources and sinks are not well established [1]. The atmospheric concentration of N_2O is known to be increasing at a rate of 0.2%–0.3% per year [2]. It has been proposed that the increase can be attributed to the use of fertilizers, combustion of fossil fuels, biomass burning and changes in land use in the tropics. From the estimated loss of N_2O in the stratosphere by photochemical reactions together with the observed increase in N_2O a total source strength between $(8\text{–}25)\times10^{12}$ g N_2O per year at the earth's surface has been calculated [3].

During the last ten years the contribution of fossil fuel combustion to total N_2O emissions has been overestimated because of inadequacies in the sampling method for N_2O [4]. During combustion N_2O can be formed both heterogeneously through different gas–solid phase interactions and homogeneously by gas-phase reactions. However, the relative importance of the different formation pathways is not clear yet. Kramlich et al. [5] suggested that N_2O appears in pulverized coal flames as a result of HCN oxidation beyond the flame front, namely by the homogeneous gas-phase reactions of NH, NH_2 and NCO radicals with NO. The reaction NCO+NO is probably the dominant homogeneous source for N_2O formation [6], however, there are insufficient data available concerning the products. According to Perry [7] the most likely reaction channel is the one leading to nitrous oxide. However, other channels are also thermodynamically accessible:

$$NCO+NO \rightarrow N_2O+CO\,,$$

$$NCO+NO \rightarrow N_2+CO_2\,,$$

$$NCO+NO \rightarrow N_2+CO+O\,.$$

Very recently the product branching ratios have been measured for this reaction by Cooper and Hershberger [8] by means of tunable diode laser spectroscopy. They found the reaction channel leading to N_2 and CO_2 to be dominant at room temperature.

In this Letter measurements of the product branching ratio of the title reaction are reported using the photolysis of ClNCO at 254 nm in a static photoreactor as a source for NCO radicals and following the concentration–time behaviour of the

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Correspondence to: P. Wiesen, Physikalische Chemie/Fachbereich 9, Bergische Universität – Gesamthochschule Wuppertal, Postfach 100127, W-5600 Wuppertal 1, Germany.

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products by Fourier-transform infrared (FTIR) spectroscopy.

2. Experimental

All experiments were carried out in a reaction chamber which has been described in detail previously [9]. The chamber consists of a 420 ℓ cylindrical glass tube (150 cm long, 60 cm in diameter) closed at both ends by Teflon-coated aluminium end flanges. The reactor is equipped with a quartz glass tube and 3 fluorescent lamps (Philips TUV, 60 W) and can be evacuated to less than 10^{-3} Torr with a 500 m^3/h roots pump and a 200 m^3/h forepump. A multireflection White mirror system (base path length 1.4 m) mounted in the reactor and coupled by an external mirror system to an FTIR spectrometer (Nicolet 7199, Globar light source, HgCdTe detector) allows in situ infrared spectroscopic monitoring of both reactants and products. Spectroscopic data were collected using 28 light traversals corresponding to a total pathlength of 39.4 m. A resolution of 1 cm^{-1} was used for rapid data collection. Typical time-resolved data were obtained by adding 64 scans per spectrum, a process taking approximately 2 min. Concentrations of both reactants and products were determined by computer-aided substraction of calibrated reference spectra of authentic samples of the compounds. A continuous stream of nitrogen was flushed through the FTIR spectrometer and the transfer optics in order to reduce the influence of CO_2 absorption in the background spectra.

All experiments were carried out at room temperature and 100 Torr total pressure argon. Typical mixtures for the experiments consisted of $(3.5–8.5)\times10^{13}$ molecules cm^{-3} ClNCO and $(1.5–3.4)\times10^{14}$ molecules cm^{-3} NO in 100 Torr argon. ClNCO was produced by thermal decomposition of $(ClNCO)_3$ [10] and purified by trap to trap distillation. It was stored in a 20 ℓ glass bulb diluted in argon by a ratio of 1/20. Fig. 1 shows an FTIR spectrum of the ν_2 band of pure ClNCO in the 2396–2000 cm^{-1} region.

Argon and nitric oxide were supplied by Messer Griesheim, with stated purities of 99.998% and 99.5%, respectively. NO was purified by trap to trap distillation in order to remove small impurities of NO_2 and N_2O. Argon was used without further purification.

3. Results and discussion

When the photolysis lamps were switched on ClNCO was rapidly photolyzed. Fig. 2 shows an example of the ClNCO concentration as a function of photolysis time. After a short induction period the ClNCO decayed exponentially with a decay constant K' of $(5.01\pm0.04)\times10^{-3}$ s^{-1}. Variation of the ini-

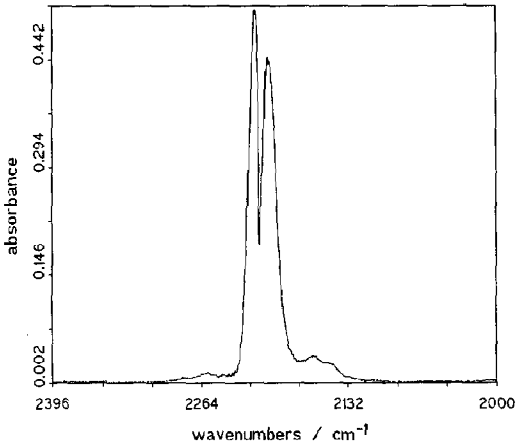

Fig. 1. Infrared absorption spectrum of the ν_2 band of ClNCO in 100 Torr argon.

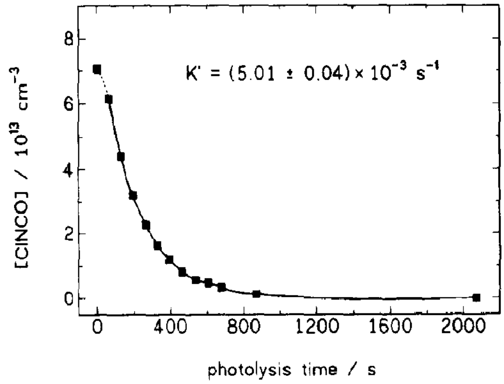

Fig. 2. Plot of [ClNCO] versus the photolysis time in the 420 ℓ photoreactor at 100 Torr total pressure argon; photolysis wavelength 254 nm; $[ClNCO]_0=(7.23\pm0.72)\times10^{13}$ cm^{-3}; $[NO]_0=(3.44\pm0.34)\times10^{14}$ cm^{-3}.

Hershberger [8] a third product channel which can lead to the formation of oxygen atoms was found to be negligible.

Further experiments are in progress in order to investigate the possible temperature dependence of the branching ratios.

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