Research paper

Atmospheric chemistry of hexanenitrile: Kinetics and products of the gas-phase reactions of CH$_3$(CH$_2$)$_4$CN with Cl atoms and OH radicals

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ABSTRACT

Smog chamber/Fourier transform infrared (FTIR) techniques were used to measure the kinetics of the reaction of CH$_3$(CH$_2$)$_4$CN, 1-cyanopentane, with Cl atoms and OH radicals: k(CH$_3$(CH$_2$)$_4$CN + Cl) = $(1.34 \pm 0.22) \times 10^{-10}$ and k(CH$_3$(CH$_2$)$_4$CN + OH) = $(2.84 \pm 0.66) \times 10^{-12}$ cm^3 molecules^{-1} s^{-1} at a total pressure of 700 Torr of air or N$_2$ diluents at 296 ± 2 K. The atmospheric oxidation of alkyl nitriles proceeds through hydrogen abstraction leading to several carbonyl containing primary oxidation products. Based on the OH radical rate constants the atmospheric lifetime of CH$_3$(CH$_2$)$_4$CN was estimated to be 4 days.

1. Introduction

There is a growing interest in halogenated nitriles as replacement compounds for compounds with higher climate impact [1,2]. Detailed knowledge of the atmospheric chemistry of nitriles is warranted to access their potential environmental impact, before any large-scale production and industrial use of these types of compounds. Previous studies of the atmospheric chemistry of nitriles have been limited to HCN, CH$_3$CN and CH$_2$=CHCN. Phillips was the first in 1979 to report a rate constant for the HCN + OH reaction at 298 K of 1.06×10^{-16} cm^3 molecule^{-1} s^{-1} [3]. In 1981 Harris et al. reported rate constants for the reaction of OH radicals with CH$_3$CN, C$_2$H$_5$CN and CH$_2$=CHCN [4]. The reaction of OH radicals with HCN proceeds via an HCN—OH adduct. Cicerone and Zellner speculated on the pathways of the HCN—OH adduct [5]. There has been two studies on the kinetics of the reaction of CH$_3$CN with OH radicals [6,7]. There is one products study of the Cl and OH radical initiated oxidation of CH$_3$CN [8] and a number of theoretical studies on reactions of OH radicals with different nitriles [9,10].

There are no previous studies of the atmospheric chemistry of long chain alkyl nitriles. In the present study, we investigated the reaction of 1-cyanopentane, CH$_3$(CH$_2$)$_4$CN, with Cl atoms or OH radicals at 296 ± 2 K.

2. Experimental method

The experiments were conducted in the CCAR (Copenhagen Center for Atmospheric Research) photoreactor. At the core of this setup is a 101 L quartz reactor interfaced with a Bruker IFS 66 v/s FTIR spectrometer. See Nilsson et al. [11] for details. All experiments in the present work were performed at 296 ± 2 K in 700 Torr of air or N$_2$ diluent. Using an analytical path length of 43.45 m, IR spectra were obtained by averaging 32 interferograms with a spectral resolution of 0.25 cm^{-1}. When analyzing the spectra, a process of spectral stripping was used in which scaled reference spectra were subtracted from the sample spectrum. Reactant and reference compounds were monitored using absorption features over the following wavenumber ranges: C$_2$H$_4$: 949 cm^{-1}; C$_2$H$_2$: 730 cm^{-1}; CH$_3$(CH$_2$)$_4$CN: 2900–3000 cm^{-1}.

The concentration of reactant and reference compounds was determined with a precision of ±1% of their initial concentrations. All reagents except CH$_3$ONO were obtained from commercial sources at purities >98%. CH$_3$(CH$_2$)$_4$CN had a purity of 98 %. CH$_3$-ONO was prepared using a well-established procedure [12]: H$_2$SO$_4$ was added drop-wise to a saturated solution of NaNO$_2$ in methanol and water, and was devoid of any detectable impurities using FTIR analysis. Experiments were performed using Cl atoms or

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OH radicals as reaction initiators. The Cl atoms were produced from the photolysis of Cl_2 (Waldmann F85/100 UV6 lamps, wavelength region 280–360 nm):

$$Cl_2 + h\nu \rightarrow 2Cl \qquad (1)$$
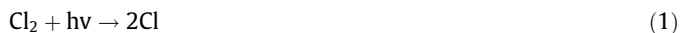
OH radicals were produced by photolysis of CH_3ONO in air in the presence of NO (Philips TUV 55 W HO, wavelength peak at 253.7 nm):

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \qquad (2)$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \qquad (3)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (4)$$

In smog chamber experiments unwanted loss of reactants, reference compounds and products via photolysis, chemistry occurring in the dark and heterogeneous reactions should be considered. Photolytic loss of $CH_3(CH_2)_4CN$, reference compounds or any of the observed degradation products is not expected to be a complication in the present work. Control experiments were performed in which reactant and product mixtures obtained after UV irradiation were allowed to stand in the dark in the chamber for 5 min. There was no observable (<2%) loss of reactants or products, which means that heterogeneous reactions, or dark chemistry are not a significant complication in the present experiments. The relative rate method was used to determine the kinetics of the reaction of $CH_3(CH_2)_4CN$ with Cl atoms and OH radicals using Eq. (1) [13] relative to the two reference compounds, C_2H_2 and C_2H_4.:
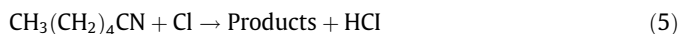
$$\ln\left(\frac{[\text{reactant}]_0}{[\text{reactant}]_t}\right) = \frac{k_{reactant}}{k_{reference}} \ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) \qquad (I)$$

where $[\text{reactant}]_0$, $[\text{reactant}]_t$, $[\text{reference}]_0$ and $[\text{reference}]_t$ are the concentrations of $CH_3(CH_2)_4CN$ and the reference compounds at times 0 and t. The rate constants for reactions of Cl atoms or OH radicals with $CH_3(CH_2)_4CN$ and the reference compounds are written as $k_{reactant}$ and $k_{reference}$. A plot of $\ln([\text{reactant}]_0/[\text{reactant}]_t)$ versus $\ln([\text{reference}]_0/[\text{reference}]_t)$ should be linear and with a slope of $k_{reactant}/k_{reference}$. The quoted uncertainties include two standard deviations of the linear least squares analysis and a 7.5% uncertainty range associated with the analysis of the IR bands.

3. Results and discussion

3.1. Relative rate study of $CH_3(CH_2)_4CN + Cl$

The rate of Reaction (5) was measured relative to Reactions (6) and (7). Experiments were performed both in N_2 and air.

$$CH_3(CH_2)_4CN + Cl \rightarrow Products + HCl \qquad (5)$$

$$C_2H_2 + Cl \rightarrow Products \qquad (6)$$

$$C_2H_4 + Cl \rightarrow Products \qquad (7)$$

Initial reaction mixtures were 13.0–15.5 mTorr $CH_3(CH_2)_4CN$, 0.730–2.92 mTorr C_2H_2 or C_2H_4 and 73.3–108 mTorr Cl_2 in a total pressure of 700 Torr of N_2 or air diluent. Total UV-B irradiation times were between 11 s in N_2 and 93 s in air.

Linear least squares analysis of the data in Fig. 1 give rate constant ratios of $k_5/k_6 = 2.57 \pm 0.33$ and $k_5/k_7 = 1.49 \pm 0.14$. The rate constant of $CH_3(CH_2)_4CN + Cl$ is determined to be $k_5(CH_3(CH_2)_4CN + Cl) = (1.30 \pm 0.18) \times 10^{-10}$ and $(1.38 \pm 0.15) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, using $k_6(C_2H_2 + Cl) = (5.07 \pm 0.34) \times 10^{-11}$ [14] and $k_7(C_2H_4 + Cl) = (9.29 \pm 0.51) \times 10^{-11}$, respectively [14]. We cite a final value for k_5 that is the average of the two individually determined rate constants for $CH_3(CH_2)_4CN + Cl$, which
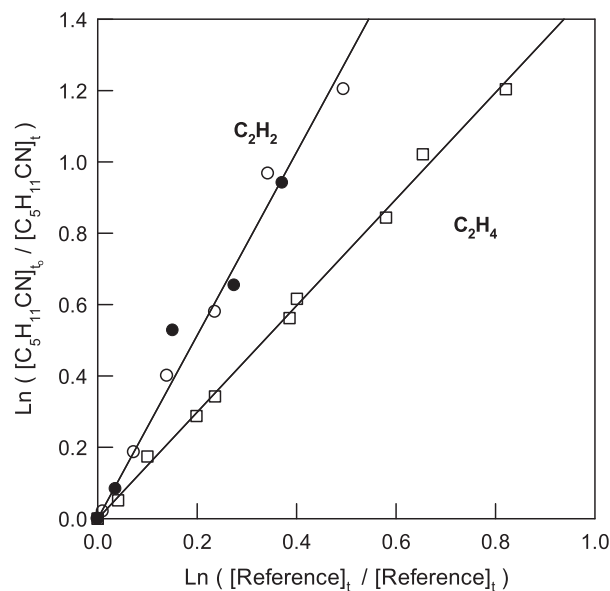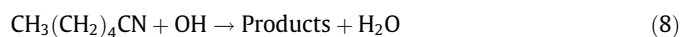

Fig. 1. Kinetic data for reaction of Cl atoms with $CH_3(CH_2)_4CN$ in 700 Torr of either N_2 (solid symbols) or air (open symbols), 296 ± 2 K.

gives $k_5(CH_3(CH_2)_4CN + Cl) = (1.34 \pm 0.22) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The uncertainty on the average rate constant accounts for the extremes of the uncertainties on the individual determinations.

3.2. Relative rate study of $CH_3(CH_2)_4CN + OH$

The rate of Reaction (8) was measured relative to Reactions (9) and (10):

$$CH_3(CH_2)_4CN + OH \rightarrow Products + H_2O \qquad (8)$$

$$C_2H_2 + OH \rightarrow Products \qquad (9)$$

$$C_2H_4 + OH \rightarrow Products \qquad (10)$$

Initial reaction mixtures consisted of 13.0–13.3 mTorr $CH_3(CH_2)_4CN$, 92.8–97.9 mTorr CH_3ONO and 0.730–3.13 mTorr of either C_2H_2 or C_2H_4 in a total pressure of 700 Torr of air. The mixtures were irradiated with UV-B light for 630–720 s.

Linear least squares analysis of the data in Fig. 2 gives rate constant ratios of $k_8/k_9 = 3.20 \pm 0.40$ and $k_8/k_{10} = 0.349 \pm 0.037$. Using $k_9(C_2H_2 + OH) = (8.45 \pm 0.85) \times 10^{-13}$ [15] and $k_{10}(C_2H_4 + OH) = (8.52 \pm 1.28) \times 10^{-12}$ [16], the rate constant for the reaction of $CH_3(CH_2)_4CN$ with OH is determined to be $k_8(CH_3(CH_2)_4CN + OH) = (2.70 \pm 0.43) \times 10^{-12}$ and $(2.97 \pm 0.53) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively. We cite a final rate constant for the reaction of $CH_3(CH_2)_4CN$ with OH radicals of $k_8(CH_3(CH_2)_4CN + OH) = (2.84 \pm 0.66) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The uncertainty in the average rate constant reflects the extremes of the uncertainties on the individual determinations. There are no previous literature values for this rate constant. However, the rate constant for the $CH_3(CH_2)_4CN + OH$ reaction is approximately 50% smaller than that for the reaction of OH radicals with $CH_3(CH_2)_4CH_3$ 5.27×10^{-12} cm^3 molecule^{-1} s^{-1} [16]), which is expected due to the presence of the deactivating, electronegative CN functional group. It is also interesting to compare the rate constant for the reaction of OH radicals with $CH_3(CH_2)_4CN = (2.84 \pm 0.66) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, with that of *n*-pentane, 3.96×10^{-12} cm^3 molecule^{-1} s^{-1}. The —CN group has an expected deactivating effect on the rate constant compared to the —CH_3 group, but the effect does not extend a long way into the C_5 alkyl chain.