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The influence of reaction conditions on the photooxidation of diisopropyl ether

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Abstract

The hydroxyl radical initiated oxidation of diisopropyl ether has been studied in the large-volume outdoor European Photoreactor (EUPHORE) and in a small, laboratory-based reactor system. The product distributions determined from the experiments were found to be significantly dependent on the reaction conditions and provide strong evidence for the existence of three distinct regimes within the reaction system. In the presence of NO_x, the peroxy radicals react with NO to produce chemically activated $(CH_3)_2CHOC(O)(CH_3)_2$ alkoxy radicals which undergo decomposition by C─C bond scission to yield isopropyl acetate and formaldehyde as the major products. Under conditions where the self-reaction of peroxy radicals dominates, thermoneutral $(CH_3)_2CHOC(O)(CH_3)_2$ radicals are produced, which appear to undergo two reaction pathways; C─C bond scission to yield isopropyl acetate and formaldehyde and isomerisation to form acetone, acetic acid and formaldehyde. Under conditions where the reaction between peroxy and hydroperoxy radicals dominates, unstable hydroperoxides are produced which decompose to yield acetone as the only major reaction product. The results of our study are used to construct chemical mechanisms for the gas-phase photooxidation of diisopropyl ether under various tropospheric conditions.

Keywords: Oxygenated fuel additives; Diisopropyl ether; Atmospheric chemistry; Alkoxy radicals

1. Introduction

Ethers are widely used as fuels additives and solvents. Methyl *tert*-butyl ether (MTBE) is the most common oxygenated fuel additive but other branched ethers, such as ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME) and diisopropyl ether (DIPE), are also present in certain formulations. The emission of these volatile organic compounds into the atmosphere is an important issue since their oxidation may affect tropospheric ozone levels and also lead to the formation of other secondary pollutants [1]. In order to fully assess the environmental impact of the use of ethers as fuel additives, a detailed understanding of their atmospheric degradation is required. The main atmospheric fate of saturated ethers is gas-phase reaction with hydroxyl radicals [1]. Detailed mechanistic studies on the photooxidation of a range of ethers have been reported in the literature [2] and provide important information on the decomposition pathways available to oxygenated alkoxy radicals.

In this study, the OH radical initiated oxidation of diisopropyl ether (DIPE) has been investigated in the presence and absence of NO_x at the large-volume outdoor European Photoreactor (EUPHORE) [3]. The product distributions in the experiments were found to be significantly dependent on the NO_x concentration thus suggesting the existence of different reaction pathways in the presence and absence of NO_x. Additional experiments have been performed in a laboratory-based reactor under a variety of conditions to elucidate further mechanistic details. The

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results of our study are used to construct chemical mechanisms for the gas-phase photooxidation of DIPE under various tropospheric conditions.

2. Experimental

The photooxidation of DIPE was investigated under simulated tropospheric conditions at EUPHORE and also in a small reactor system.

2.1. EUPHORE

The European Photoreactor comprises two large-volume outdoor atmospheric simulation chambers located at the Centro de Estudios Ambientales del Mediterraneo (CEAM) in Valencia, Spain. A detailed description of the installation can be found in the literature [3–7]. The photooxidation of DIPE was performed in a 195 m^3 hemispherical chamber made of Teflon FEP foil and surrounded by a retractable steel housing that is used to control the time of exposure to sunlight. Experiments performed in the presence of NO_x relied upon the in situ production and photolysis of HONO as the source of hydroxyl radicals. For experiments performed in the absence of NO_x, photolysis of hydrogen peroxide was used as the source of hydroxyl radicals. Nitric oxide (Aldrich, 98.5%) and DIPE (Aldrich, 98%) were introduced into the chamber via a stream of purified air, whilst H_2O_2 (Merck, 35 wt.% solution in water) was added to the chamber using a nebuliser.

The loss of reactants and formation of products was monitored using a Nicolet Magna 550 FT-IR spectrometer equipped with a mercury cadmium telluride (MCT) detector. Infrared spectra were obtained by in situ long-path absorption, and were derived from the co-addition of 550 scans recorded using a path length of 553.5 m and a resolution of 1 cm^{-1}. The reactants and products were quantified using calibrated reference spectra which were obtained by introducing known volumes of materials into the chamber. Additional chemical detection was provided by a gas chromatograph (Fisons 8000) equipped with flame ionisation and photoionisation detectors (FID and PID). The chromatograph was operated using a 30 m DB-624 fused silica capillary column (J&W Scientific, 0.32 mm i.d., 1.8 μm film). Air was sampled from the chamber into a 2 cm^3 sampling loop and then injected onto the column. A trace gas analyser (TGA, Fisons), which incorporated a cryogenic enrichment trap coupled to a flame ionisation detector, was also used for chemical analysis of reactants and products. Air samples (200 cm^3) were collected in a sampling loop at 120 °C and passed to a Tenax micro-trap cooled to -120 °C with liquid nitrogen. Injection onto the 30 m DB-1 chromatographic column (J&W Scientific, 0.25 mm i.d., 1.0 μm film) was achieved by rapid heating of the micro-trap to 240 °C.

The concentration of reactants and products decreased through chemical processes and also due to leakage from the chamber. The leak rate in each experiment was determined by adding an unreactive tracer gas (SF_6) to the chamber and measuring its loss by FT-IR spectroscopy. The temperature inside the chamber was continuously monitored using three PT-100 thermocouples and was 303 ± 2 K for all experiments. The intensity of sunlight was measured using two $J(NO_2)$ filter radiometers; the first of which measured direct sunlight and the second faced downwards to measure reflected light from the floor panels. Ozone and NO_x concentrations were continuously monitored using chemiluminescent analysers (Monitor Labs Model 9810A and Eco Physics Model CLD 770 AL, respectively).

2.2. Small reactor

Experiments were performed at 298 ± 2 K and 760 ± 10 Torr of purified air in a collapsible 50 L Teflon reaction vessel [8]. The photooxidation of DIPE was carried out in the absence of NO_x using the photolysis (10 Philips TUV 15 W lamps with an intensity maximum at 254 nm) of H_2O_2 or ozone/water mixtures as the hydroxyl radical source. Measured amounts of reactants were flushed from calibrated Pyrex bulbs into the reaction vessel by a stream of ultra-pure air and the chamber was then filled to its full volume with air. The reactants were allowed to mix for at least 30 min prior to the start of photolysis.

Throughout the course of the reactions, samples of the reaction mixtures were expanded into an evacuable 5 L Teflon coated multipath cell mounted in the sample compartment of an FT-IR spectrometer (Mattson RS series). Infrared spectra were derived from the co-addition of 128 scans recorded using a path length of 9.75 m over the range 500–4000 cm^{-1} with a resolution of 2 cm^{-1}. Products and reactants were identified by comparison of the infrared spectra with those of authentic samples. The possible loss of reactants and products in the dark was measured but found to be negligible over the timescale of the experiments. Reference spectra and calibration curves for reactants and products were obtained by expanding measured pressures of the pure compounds into the IR cell. Complex spectra were analysed by successively subtracting the absorption features of known compounds with the use of calibration spectra.

3. Results

3.1. EUPHORE

A series of experiments was performed at EUPHORE on the photooxidation of DIPE in the presence and absence of NO_x. Data from three of the experiments are presented here and summarised in Table 1. The first experiment was carried out under “classic NO_x” conditions where the initial NO concentration was about one tenth that of the hydrocarbon concentration. In the initial stages of the reaction, the major products detected by FT-IR spectroscopy were isopropyl acetate (IPAc) and formaldehyde. IPAc was also detected and quantified by GC-PID. In the latter stages of the reaction acetone was detected as the major reaction product by GC-PID. Acetone is a relatively weak infrared absorber and was difficult to measure quantitatively using FT-IR spectroscopy. The concentration–time profile and product yield plots are shown in Fig. 1 and clearly indicate that a significant change in product distribution is observed as the NO concentration is depleted during the course of the reaction. In the early stages of the experiment, whilst NO was present