Studies on Reactions of Ozone with Alkenes

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Abstract. In the last years, a continuous increase of the O3 concentration has been recorded in the lower atmospheric layers. Photochemical reactions with NOx, CO and organic compounds are the main sources of O3 in the troposphere. In this work, an attempt was made to determine the impact of alkenes on the O3 concentration in the troposphere. A study on the gas-phase reactions of O3 with 1-hexene, 1-heptene and 1-nonene was made. The reactions were carried out at room temperature under atmospheric pressure. Ozone was formed by the ultraviolet radiation emitted by a mercury lamp, in order to simulate the atmospheric conditions. The changes with time in the concentration of O3, 1-alkenes and formed aldehydes were investigated. Qualitative and quantitative analyses were done by means of the gas chromatography and colorimetry. The following products were identified: pentanal from 1-hexene; hexanal from 1-heptene; octanal from 1-nonene. For each of the reactions, HCHO was also determined as a product. The reaction rate constants were calculated and obtained in units of 10^{-17} cm^{-3} molecule^{-1} s^{-1}: 1.94-0.99 for 1-hexene, 5.34-4.51 for 1-heptene and 1.54-0.76 for 1-nonene. Based on the results obtained, an explanation of O3 concentration variations in the planetary boundary layer can be given. Last year a considerable increase of O3 concentration on the roads of Western Europe was recorded. This increase could have resulted from the decrease of alkene concentration in the air due to common use of the catalytic converters in cars. In Eastern Europe, where the amount of cars equipped with catalytic converters is smaller than in Western Europe, the alkene concentration has been recorded in the lower atmospheric layers. A study on the gas-phase reactions of O3 with 1-hexene, 1-heptene and 1-nonene was made. The unsaturated hydrocarbons rapidly oxidize on the catalyst. In Eastern Europe, where the amount of cars equipped with catalytic converters is smaller than in Western Europe, the alkene content in the exhaust fumes results in a decrease of the O3 concentration in the troposphere.

Keywords: Exhaust fumes; 1-heptene; 1-hexene; 1-nonene; ozone, tropospheric; ultraviolet radiation

Introduction

The atmosphere contains hundreds of organic compounds which participate in different chemical reactions. Large quantities of volatile organic compounds (VOCs) are emitted into the atmosphere from biogenic and anthropogenic sources. It is estimated, that world-wide emission results in about 100 million tons of VOCs per year from the anthropogenic sources and 1150 million tons per year from biogenic sources. Large quantities of organic compounds such as isoprene, monoterpenes, sesquiterpenes and oxygen-containing compounds are emitted to the troposphere by plants. VOCs emitted from diverse anthropogenic sources originate from the combustion processes, fuel storage and transport, solvents, paints and varnishes, industrial processes and the waste storage facilities. The level of VOC concentration in the air varies according to type and size of the source of pollution, distance from the source, weather and climate conditions, reactivity of particular compounds. Although the concentrations of VOCs depend on many factors, certain regularities in the distribution can be seen, particularly of the VOCs whose lifetimes exceed several days. The highest contents of VOCs in the air are observed above the northern hemisphere; while their contents decrease approaching the equator [1-9].

Ozone formation and decomposition is related to the photodecomposition of VOCs, which is a chain reaction process comprising three basic steps: initiating reaction of formation OH· and HO2· free radicals, reactions of the radical propagation and reaction of termination of the chain leading to the formation of stable products [10-12].

Ozone is mainly formed in the reaction (1):

\[ O + O_3 + M \rightarrow O_2 + M \]  

(1)

where: \( M = N_2 \) lub \( O_2 \)

NO participates in the chain propagation step, however, when its concentration exceeds that of \( O_3 \), which occurs over urban areas in the morning. The tropospheric ozone reacts with NO forming \( NO_2 \) as shown in the following reaction (2):

\[ NO + O_3 \rightarrow NO_2 + O_2 \]  

(2)

\[ NO_2 + hv \rightarrow NO + O \]  

(3)

\( NO_2 \) undergoes a photolysis reaction (3) producing \( O \), which reacts with \( O_3 \) in reaction (1). Accumulation of \( O_3 \) becomes significant, only when the \( NO \) concentration is substantially lower than that of \( O_3 \) and the \( NO_2 \) becomes the dominant component in the \( NO_2 \) mixture. Regeneration of \( NO_2 \) without \( O_3 \) consumption proceeds according to the reaction (4):

\[ RO_2^+ + NO \rightarrow NO_2 + RO^+ \]  

(4)

Another reaction sequence, using hydrocarbons, also leads to NO conversions into \( NO_2 \) without \( O_3 \) consumption:

\[ O_3 \rightarrow VOC + OH \rightarrow RO_2^+ + H_2O \]  

(5)

\[ RO_2^+ + NO \rightarrow NO_2 + RO^+ \]  

(6)

\[ RO^+ + O_2 \rightarrow R'CHO + HO_2^- \]  

(7)

\[ HO_2^- + NO \rightarrow NO_2 + OH^- \]  

(8)
The VOC reacts with the hydroxyl radical (OH) in the presence of oxygen, to produce a peroxy radical (RO$_2^\cdot$). The RO$_2^\cdot$ and HO$_2^\cdot$ radicals usually react with NO to produce NO$_3$ and a hydroxyl radical. Degradation of hydrocarbons in the atmosphere is initiated by OH radical attack, which causes H-atom abstraction from alkenes, or addition of the radical to alkenes and aromatic compounds. H-atom abstraction by OH$^-$ leads to an alkyl radical, to which O$_2$ is added rapidly to produce an alkyl peroxy radical, RO$_2^\cdot$. Similarly, the OH$^-$ addition to alkenes or aromatic compounds results in an alkyl hydroxy radical formation, which after a rapid reaction with O$_2$ produces an RO$_2^\cdot$ radical [3,4,10-12]. VOCs are the precursors of O$_3$ formation process. Reactions of VOCs and NO$_x$ with the OH$^-$ radical compete with each other. At high VOC to NO$_x$ concentration ratios, OH$^-$ will mainly react with VOCs; at low concentration ratios, the NO$_x$ reaction will predominate [11].

VOCs can undergo photolysis, reactions with the OH$^-$ radical, reactions with the NO$_3^-$ radical and reactions with O$_3$. Knowledge of the mechanisms and products of the degradation reactions of VOCs in the troposphere is essential in understanding the impact of emissions on the Earth's ecosystem. The effects of this process are very serious: deposition of the VOC reaction products (including of acidic compounds), formation of toxic air contaminants in the troposphere, stratospheric ozone depletion and the potential for global warming [3,4]. Hence, the great interest in research on the kinetics of the reactions of ozone with hydrocarbons, which will help in better understanding of the reaction mechanisms and estimating the level of concentration of these compounds in the troposphere. A lot of kinetic data and methods of the determination of VOCs is available [13-24], but the results of many authors are considerably different. The discrepancies are probably connected to differences in measuring techniques and research conditions.

In this work, the course of reactions of 1-alkenes with O$_3$ with time and the products formed were studied. The gas-phase reactions were carried out at the room temperature under atmospheric pressure. Afterwards, the rate constants for O$_3$ reactions with 1-hexene, 1-heptene and 1-nonene were determined.

1 Experimental Section

Experiments were carried out in a measuring set prepared especially for this purpose. The basic part of the set was a generator, in which O$_3$ was produced using ultraviolet radiation emitted by a mercury lamp placed in a 12.0 L glass container. Air was supplied to the container from a steel pressure bottle with a constant flow rate (30 L/h), which was controlled by a rotameter. The temperature inside the generator was measured by a thermocouple. The air containing ozone was supplied from the generator into a 5.8 L dark glass container, where reactions of O$_3$ with the 1-alkenes were conducted. After a constant O$_3$ concentration in the container (5.8 L) was reached, a corresponding amount of 1-alkenes was introduced. In the assumed time intervals, the concentration of O$_3$, 1-alkenes and aldehydes formed were determined. For this purpose, the air samples were aspirated with a volumetric micropump through a washer with a porous plate of Vašak type, containing an absorbent solution. The 1-alkenes and aldehydes (other than HCHO) were determined by gas chromatography. The air pressure inside the 5.8 L container was compensated after sampling by feeding the air through a drier containing the silica gel and molecular sieves 4A.

Tests of the O$_3$ reactions with alkenes were carried out under atmospheric pressure at room temperature. Several series of measurements have been performed for each particular 1-alkene.

Determination of 1-alkenes and aldehydes. The analysis was carried out using a gas chromatograph GCHF 18.3 with a flame ionization detector. Steel columns with the following packings were used: column I - 7% SE 30 + 0.21% Carbowax 20M on Chromosorb W NAW (60-80 mesh), column II - 8% XE 60 + 0.24% Carbowax 20M on Chromosorb W NAW (60-80 mesh).

The qualitative and quantitative analyses of 1-alkenes and the aldehydes formed were carried out directly from the dark glass container (5.8 L). The gas samples were introduced into the chromatographic column through a dosage valve with a 1 cm$^3$ stainless steel loop. The identification of substrates and reaction products was done for a comparison of the retention times of samples on both columns with the retention times of standards. The quantitative analysis was carried out based on the calibration performed on the measuring set employed to investigate O$_3$ reactions with 1-alkenes. Known amounts of particular standards in an air stream were introduced into the 5.8 L dark glass container. Next, the air samples were drawn and dosed into the gas chromatograph. – The initial reactant concentrations were: 1-hexene, $3.25 \times 10^{14}$; 1-heptene, $3.71 \times 10^{14}$; 1-nonene, $13.85 \times 10^{14}$ molecule cm$^{-3}$.

Determination of ozone. Ozone was determined by spectrophotometry using a method according to [25]. The method depends on the parallel absorbing of air samples into two washers containing an absorbent solution. Before one of the washers, a cotton wool filter was installed for the O$_3$ destruction. The ozone content was estimated on the basis of the difference of iodine amount evolved in the washer without a filter and in the washer with a filter. This eliminates the effect of nitric oxides on the result. The ozone content in the washers was measured at a 350 nm wavelength. – The initial concentrations of ozone were: $(3.82-15.06) \times 10^{14}$ molecule cm$^{-3}$.

Determination of formaldehyde. Formaldehyde was determined by spectrophotometry as a complex with 1,8-dihydroxynaphthalendisulfonic acid [26].

Chemicals. In this work, the following reagents were used: 1-hexene (98%) and 1-heptene (99%), Fluka AG; 1-nonene (97%), Koch-Light Laboratories Ltd. The O$_3$ was produced by a 400 Q ultraviolet lamp of Polish production.

2 Results and Discussion

In these studies, the 12.0 L glass container for O$_3$ formation and the 5.8 L glass container for observation of the course of the O$_3$ reactions with 1-alkenes were used. Atkinson et