Abstract

of the dissertation submitted by Smaiyl Madi Bekezhanuly for the degree of Doctor of Philosophy (PhD) in the educational program "8D05301 — Chemistry" on the topic: "Photocatalytic oxidation of volatile aromatic hydrocarbons in the gas phase"

General characteristics of the work.

The dissertation is devoted to the study of the features of photocatalytic oxidation of a gaseous mixture of aromatic hydrocarbons of the BTEX group (hereinafter benzene, toluene, ethylbenzene, and o-xylene) under conditions simulating indoor air purification. The relevance of the work is determined by the widespread occurrence of BTEX compounds in ambient air, their pronounced toxic and carcinogenic effects on humans, and the need to evaluate the efficiency of photocatalytic air purification technologies while taking into account the possible formation of oxidation by-products.

Relevance of the research topic. Atmospheric air pollution by volatile organic compounds (VOCs) formed as a result of anthropogenic activity is an urgent environmental problem. The presence of VOCs in air adversely affects human health, contributing to the development of respiratory and cardiovascular diseases and increasing the risk of cancer. In this regard, the development of efficient methods for air purification from organic pollutants remains an important task.

At present, various physicochemical methods are used to remove VOCs from air, including adsorption, thermal and catalytic oxidation, as well as plasma and photochemical technologies. However, many of the existing methods are characterized by high energy consumption, complex instrumentation, or the need for subsequent disposal of accumulated pollutants. A promising approach to air purification is photocatalytic oxidation, which is based on oxidation reactions proceeding under irradiation. The use of photocatalysts makes it possible to decompose organic compounds using renewable energy sources, in particular solar radiation.

At the same time, photocatalytic processes do not always lead to complete mineralization of the initial pollutants. During oxidation, intermediate compounds with pronounced toxicity may be formed, some of which are classified by the World Health Organization as carcinogenic substances.

Degree of prior research.

Modern studies on the photocatalytic oxidation of BTEX compounds and other common volatile organic compounds mainly focus on determining pollutant degradation rates under single-pollutant conditions and at high concentrations, as well as on comparative evaluation of the activity and stability of various modified photocatalysts. At the same time, studies carried out at low concentrations and in multicomponent systems remain limited, and therefore information on the composition of the intermediate products formed and their quantitative distribution is still insufficient.

In a study published in Applied Catalysis B: Environmental (2009, vol. 89, no. 3–4, pp. 570–576), proton-transfer-reaction mass spectrometry (PTR-MS) was used

to identify intermediate products of the photocatalytic oxidation of toluene, a probable mechanism of their formation was proposed, and the pathway of benzene formation from benzoic acid was demonstrated. Another study (Chemical Engineering Journal, 2022, vol. 427, p. 131536) the possible formation of benzene was included in the proposed transformation scheme of the products of photocatalytic oxidation of toluene. The reaction pathways proposed in the literature for benzene formation through the sequential transformation of the major oxygen-containing aromatic intermediates of toluene — benzyl alcohol, benzaldehyde, and benzoic acid — are predominantly mechanistic assumptions based on the simultaneous detection of these compounds during the photocatalytic oxidation of toluene. However, experimental data from separate gas-phase studies, in which each of the aforementioned compounds was used as an individual starting compound to investigate the possibility of benzene formation during photocatalytic oxidation, remain limited. Some publications report the formation of formaldehyde, one of the priority carcinogenic compounds, during the photocatalytic oxidation of various organic substances, including toluene, ethanol, methyl ethyl ketone, acetone, octane, and hexane. In some studies, attempts were made to assess the potential risk associated with the formation of intermediate products using various air quality indices. However, the regulatory criteria applied and the contribution of individual compounds to the total risk are often not analyzed, which substantially limits the interpretation of the obtained results.

Research objective:

To study the photocatalytic oxidation (PCO) of a BTEX mixture on commercial TiO_2 under air recirculation conditions at low initial concentrations of volatile aromatic hydrocarbons.

Research objectives:

To determine the kinetic parameters of the photocatalytic oxidation of the components of a BTEX gas mixture over commercial TiO_2 deposited on a volcanic glass support (hereinafter referred to as TiO_2/volcanic glass) in a test chamber with air recirculation at initial concentrations of about 1 ppmv.

To calculate air quality indices during the photocatalytic oxidation of the components of a BTEX gas mixture over a TiO_2/volcanic glass catalyst in a test chamber with air recirculation at initial concentrations of about 1 ppmv.

To determine the possibility of benzene formation during the photocatalytic oxidation of toluene and its major oxygen-containing aromatic intermediate products in the gas phase.

Objects of research: compounds of the BTEX group.

Subject of research: the process of photocatalytic oxidation of a BTEX gas mixture and its kinetic parameters.

Research methods: X-ray diffraction analysis (XRD), Fourier-transform infrared spectroscopy, thermal analysis (TG/DTA), and gas chromatography with mass spectrometric detection (GC–MS).

Scientific novelty of the work

For the first time, the specific features of the photocatalytic oxidation of BTEX mixture components under air recirculation conditions at low concentrations were

established, including differences in the kinetic behavior of individual compounds, and the role of benzene in contributing to the exceedance of the air quality index was identified.

The theoretical significance of the work lies in advancing the understanding of the reactivity of aromatic compounds under gas-phase photocatalytic oxidation at low concentrations. The established relationships between oxidation rate and the physicochemical characteristics of molecules contribute to understanding the factors governing photocatalytic processes. The obtained results refine existing concepts of the transformation mechanisms of aromatic compounds and the formation of by-products, including toxicologically significant compounds, and expand the theoretical basis of photocatalytic air purification. The findings also contribute to the development of gas-phase photocatalysis involving titanium dioxide, as well as to the photochemistry of VOCs.

Practical significance: the obtained results can be used for a scientifically grounded assessment of the applicability of photocatalytic technologies for the purification of air, including urban atmosphere and indoor air, from aromatic volatile organic compounds (BTEX). The identified kinetic limitations, the role of the secondary formation of toxic intermediates, and the assessment of the total hazard (HI) provide a basis for selecting operating conditions and efficiency criteria for photocatalytic systems aimed not only at the degree of removal of the initial pollutants but also at reducing the risk associated with the formation of secondary toxic products.

Main provisions submitted for defense:

1) The photocatalytic oxidation of o-xylene and ethylbenzene in a BTEX gas mixture in a test chamber (initial concentration of each component, $C_0 \approx 1$ ppmv; chamber volume, V = 300 L; relative humidity, $\varphi \approx 40\%$; catalyst, TiO_2/volcanic glass; UVA irradiation intensity, I = 15 mW/cm²) under air recirculation is described by apparent first-order kinetics, whereas the oxidation of toluene and benzene under the same conditions deviates from the first-order model.

2) An air quality index above unity (HI > 1), calculated for the BTEX components during 19 h of photocatalytic oxidation of a BTEX gas mixture in a test chamber ($C_0 \approx 1$ ppmv for each component, V = 300 L, $\varphi \approx 40\%$, catalyst — TiO_2/volcanic glass, I (UV-A) = 15 mW/cm^2) under air recirculation, is predominantly due to the presence of benzene.

3) The photocatalytic oxidation of benzaldehyde and benzoic acid in the gas phase ($\varphi \approx 50\%$, irradiation time = 30 min, I (UV-A) = 15 mW/cm^2) is accompanied by the formation of benzene.

The main results of the dissertation research were published in 2 scientific papers:

Smaiyl, M., Tulebekov, Y., Nurpeisov, N., Satybaldiyev, B., Snow, D. D., & Uralbekov, B. (2023). Human Health Risk Assessment of the Photocatalytic Oxidation of BTEX over TiO_2/Volcanic Glass. Molecules, 28(24), 8119. (WoS – Q2, Impact Factor 4.2; Scopus – Percentile 87%, CiteScore 8.6 according to 2024 data). Personal contribution of the doctoral candidate: conducting experimental

work on the photocatalytic oxidation of the compounds, conceptualization, methodology, investigation, and formal analysis.

Smaiyl, M., Satybaldiyev, B., Haghighat, F., Mamaghani, A. H., & Uralbekov, B. (2026). Photocatalytic Oxidation of VOCs: Assessing Health Risks and Mitigation Strategies for Safer Indoor Air Environment. Journal of Hazardous Materials Advances, 101024. (WoS – Q1, Impact Factor 7.7; Scopus – Percentile 87%, CiteScore 10.6 according to 2024 data). Personal contribution of the doctoral candidate: methodology, investigation, formal analysis, data curation, and conceptualization.

Based on the results of the dissertation research, the following conclusions were drawn:

The apparent reaction orders were determined using the differential method. For o-xylene and ethylbenzene, the corresponding values were $n_{app} = 1.01 \pm 0.11$ and $n_{app} = 1.01 \pm 0.09$, respectively. For toluene and benzene, the values obtained were $n_{app} = 0.72 \pm 0.08$ and $n_{app} = 0.68 \pm 0.11$, respectively.

The photocatalytic oxidation of toluene and selected major oxygen-containing aromatic intermediates is accompanied by the formation of benzene. This may be one of the reasons for the deviation of the oxidation kinetics of these compounds in the BTEX gas mixture from apparent pseudo-first-order behavior.

During the photocatalytic oxidation of the BTEX gas mixture, benzene remains the risk-determining component: its presence leads to the persistence of a hazard index (HI) above 1 and a carcinogenic risk above 1×10^{-4} throughout the process.

Assessment of the completeness of the accomplished objectives.

All tasks formulated to achieve the goals of this dissertation work were fully accomplished. The kinetic parameters of the photocatalytic oxidation of a BTEX gas mixture in a test chamber with air recirculation were determined. It was found that the reaction order for the oxidation of o-xylene and ethylbenzene was equal to one, whereas the concentration dependencies of benzene and toluene oxidation under the same conditions were not described by first-order kinetics. Air quality indices during the photocatalytic oxidation of a BTEX gas mixture over TiO_2 were calculated on the basis of permissible concentration limits for indoor environments. It was shown that benzene is the main hazardous compound in this mixture, and that the hazard index remains rather high throughout the oxidation process despite the almost complete disappearance of the other BTEX compounds. The possibility of benzene formation was studied for individual BTEX compounds as well as for the main oxygen-containing intermediate products of toluene oxidation (benzyl alcohol, benzaldehyde, and benzoic acid).

Compliance with the directions of scientific development or state programs. The dissertation work was carried out within the framework of the grant-funded project of the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan: AP09057924-OT-23 “Development of photocatalytic air purification technology for the removal of volatile organic compounds”.