



Photocatalytic degradation of methyl *tert*-butyl ether in the gas-phase: A kinetic study

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ABSTRACT

Methyl *tert*-butyl ether (MTBE) is the basic oxygenated motor fuel additive in Europe and is included in volatile organic compounds (VOCs), which can produce photochemical oxidants. In the present study the gas-phase photocatalytic oxidation (PCO) of MTBE over illuminated titanium dioxide was carried out at ambient temperature in a plug flow reactor. The intermediates detected are mainly *tert*-butyl formate and acetone, while the final products are CO₂ and water. The system was sensitive to the oxygen concentration, for concentrations up to 15% (v/v). Moisture had a positive effect on the reaction, obtaining an optimum value near 45% relative humidity for 200 ppmv MTBE initial concentration. A reaction scheme has been proposed for the interpretation of the experimental results and a kinetic study was conducted, using the Langmuir–Hinshelwood kinetics equation. The MTBE rate constant was $1.545 \times 10^{-6} \text{ M s}^{-1} \text{ g}_{\text{cat}}^{-1}$ for the reaction without moisture and $2.46 \times 10^{-6} \text{ M s}^{-1} \text{ g}_{\text{cat}}^{-1}$ for the reaction in the presence of moisture and the adsorption constant was $2.187 \times 10^5 \text{ M}^{-1}$ independent of humidity.

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1. Introduction

Volatile organic compounds (VOCs) are a significant class of air pollutants, which are considered as one of the most important pollutants of human origin generated in urban and industrial areas [1]. The Geneva Convention (1979) [2] on atmospheric pollution has defined VOCs as all organic substances of anthropogenic nature, other than methane, that are capable of producing oxidants by reactions with nitrogen oxides in the presence of sunlight. They are involved in photochemical reactions in the atmosphere forming tropospheric ozone or contributing to the depletion of the stratospheric ozone layer [3]. These compounds can also be directly harmful to human beings and induce odour pollution [4].

Oxygenated fuel additives, which are included in VOCs, are now increasingly used in order to enhance octane number and decrease pollution. The relative merits of them have sparked intense debate. Fugitive emissions form one facet of the controversy [5]. Methyl *tert*-butyl ether (MTBE) was the most widely used motor fuel additive in the USA until 1998 and is still the basic oxygenated additive nowadays in the rest of the world [6]. As a result of MTBE-containing gasoline, it is present in the troposphere, with concentrations of about 10 mg m^{-3} , which are expected to rise with increasing use [5].

It has been linked to human illness, having as a main disadvantage its potential for carcinogenicity.

The purpose of this study is to investigate the photocatalytic degradation of MTBE in the gas-phase using titanium dioxide as a catalyst.

Heterogeneous photocatalysis with TiO₂ is an attractive process. During the process the illuminated semiconductor adsorbs light and generates free radicals. TiO₂ has large band gap energy, and as a consequence it is able to absorb ultraviolet light (typically <380 nm). Alberici and Jardim [7] report that the major advantages of the process are: (a) TiO₂ is relatively inexpensive, (b) it dispenses with the use of other coadjutant reagents, (c) it shows efficient destruction of toxic contaminants, (d) it operates at ambient temperature and pressure and (e) the reaction products are usually CO₂ and H₂O, or HCl in the case of chlorinated organic compounds.

A limited number of studies have been carried out on gas-phase MTBE. Raupp and Junio [8] and Galanos et al. [9] have studied the PCO of MTBE without any kinetics analysis, while Idriss et al. [5] have investigated the fate of MTBE and ethanol on Ti and Fe oxides. Alberici and Jardim [7] examined the potential of the photocatalytic degradation of a mixture of VOCs, including MTBE, in regard only to the initial organic concentration, whereas Preis et al. [6] studied the transient PCO of MTBE and *tert*-butyl alcohol (TBA).

The present research deals with the continuous flow MTBE photocatalytic oxidation on a TiO₂ surface (P25). The effect of residence time, MTBE initial concentration, oxygen concentration and water vapour presence is investigated. Finally a reaction scheme is

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proposed for the heterogeneous gas–solid reaction and a kinetics analysis is conducted, taking into consideration both MTBE and the byproducts.

2. Experimental

The MTBE mixture in gas-phase was prepared in a sealed 1000 mL high pressure Parr vessel (model 4531 Parr Instrument Inc., USA) made of SS316 stainless steel. The desired amount of liquid MTBE was injected in it through an injection port and the vessel was filled with N_2 . The VOC-containing stream, finely controlled by a digital mass flow regulator, was diluted with N_2 and O_2 to deliver the desired MTBE and O_2 ratio to the reactor.

Humidity was introduced into the reactor by bubbling the stream of N_2 and O_2 through a water saturator. The water concentration is determined by adjusting the temperature of the saturator.

The PCO was conducted in an annular photocatalytic reactor in continuous gas-flow mode. The characteristics of the reactor are inner diameter 23.0 mm, outer diameter of the lamp 14.75 mm and effective volume 20 mL. A low-pressure Hg lamp of 12 W, which emits mainly (85–90%) ultraviolet light at 254.7 nm and 7–10% at 184.9 nm, was positioned coaxially in the reactor. The catalyst is immobilized in the internal surface of the cylindrical tube. The method used for immobilization is the one based on titania powder (Degussa P25) and proposed by Doll and Frimmel [10]. The TiO_2 density obtained was $3.5 \times 10^{-3} \text{ g cm}^{-2}$ as estimated by weighing the reactor before and after coating. The residence time was determined by the influent flow.

Illumination was initialized after steady-state conditions were established. Because of the direct contact of the treated stream with the lamp, the temperature of the reactor was 50°C . The evolution of the oxidation was attended quantitatively concerning both MTBE and intermediates, via gas chromatography, using a SHIMADZU GC-17A gas chromatograph with a HP1-MS column and a flame ionization detector (FID). The identification of the intermediates was achieved by gas chromatography–mass spectrometry (Hewlett Packard GC 6890–MS 5973, column HP1-MS). The samples were first concentrated by passing the reactor exhaust through a charcoal tube and subsequently extracting the adsorbed content with carbon disulfide, according to the ASTM D3687 procedure.

3. Results

3.1. MTBE PCO products—effect of MTBE initial concentration

It was established through preliminary experiments that the photodegradation of MTBE occurred only in the presence of titania catalyst, oxygen and near UV irradiation. Except from CO_2 and H_2O , which are the products of the total oxidation of MTBE and can only be detected by GC–MS, acetone, *tert*-butyl formate (TBF— $C_5H_{10}O_2$), isobutene and *tert*-butyl alcohol (TBA— $C_4H_{10}O$) are detected by both GC–FID and GC–MS. Because the production of isobutene and TBA was negligible, acetone and TBF were selected as intermediates to follow the variations of their concentrations.

These main byproducts are in accordance with the results of Galanos et al. [9], while Alberici and Jardim [7] detected TBA as the only intermediate of MTBE destruction on illuminated TiO_2 .

Fig. 1 shows the decrease in the concentration of MTBE and the increase in the concentrations of the organic byproducts for the experiment with 2100 ppmv MTBE initial concentration and 17.5% (v/v) O_2 concentration. The MTBE conversion increased rapidly and markedly by increasing the residence time from 10 to 60 s, reaching 97%. Above 60 s, the conversion changed slightly with varying the residence time, reaching 99.9% at residence time 77 s.

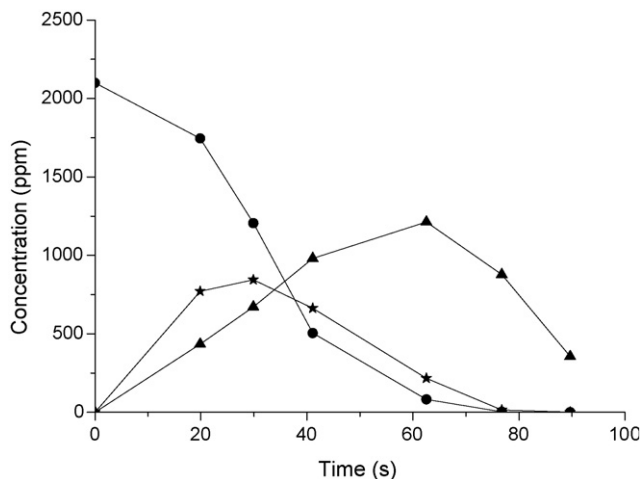


Fig. 1. Photodegradation of MTBE (2100 ppmv) (●) MTBE, (▲) acetone, (★) TBF.

TBF and acetone profiles followed similar trends, exhibiting a strong dependence on residence time. For residence times up to 30 s, both of them were being produced, with TBF showing a higher production rate than acetone. For higher residence times TBF was further oxidized, while acetone started to oxidize for residence times over 60 s. At 90 s both MTBE and TBF were totally converted to products, whereas acetone was still present in the system. This striking effect of residence time on the byproducts has only been reported by Galanos et al. [9], who detected higher concentrations for acetone than TBF.

Experiments with initial concentrations of MTBE from 3200 to 50 ppmv were carried out for studying the influence of the feed concentration. Residence time was regulated from 4 to 90 s by varying the volumetric flow rate of the feed.

It is obvious from Fig. 2a and b that the reaction led to complete disappearance of MTBE in all cases except for the experiment with initial concentration 3200 ppmv. Increasing the concentration of MTBE at the reactor inlet severely inhibited the photodegradation, which resulted in increasing the reaction time needed for the total conversion of MTBE to products. The effect of MTBE initial concentration is related to the availability of adsorption sites on the photocatalyst surface, which depends on the experimental setup.

3.2. Effect of O_2 concentration

The effect of oxygen concentration at the reactor inlet on MTBE degradation is presented in Fig. 2c and d, for four different MTBE inlet concentrations (1850, 1080, 500 and 300 ppmv). As it is obvious, under fixed conditions, oxidation rates for MTBE increased with increasing O_2 concentration up to a certain point, beyond which the rates were becoming relatively insensitive. More specifically, for 300 and 500 ppmv the O_2 concentration affecting the system was less than 5% (v/v), whereas for 1080 ppmv was ~10% (v/v) and for 1850 ppmv ~15% (v/v). This saturation behavior is characteristic of Langmuir–Hinshelwood–Hougen–Watson kinetics observed in gas–solid heterogeneous reactions, but can also occur in complex gas–phase reactions which involve reactive intermediates [8], and can be attributed to the competition of MTBE and oxygen for TiO_2 active sites.

3.3. Effect of water vapor

The effect of water vapor in the reactor feed on MTBE PCO was examined by applying different relative humidity (0–68% RH) to a

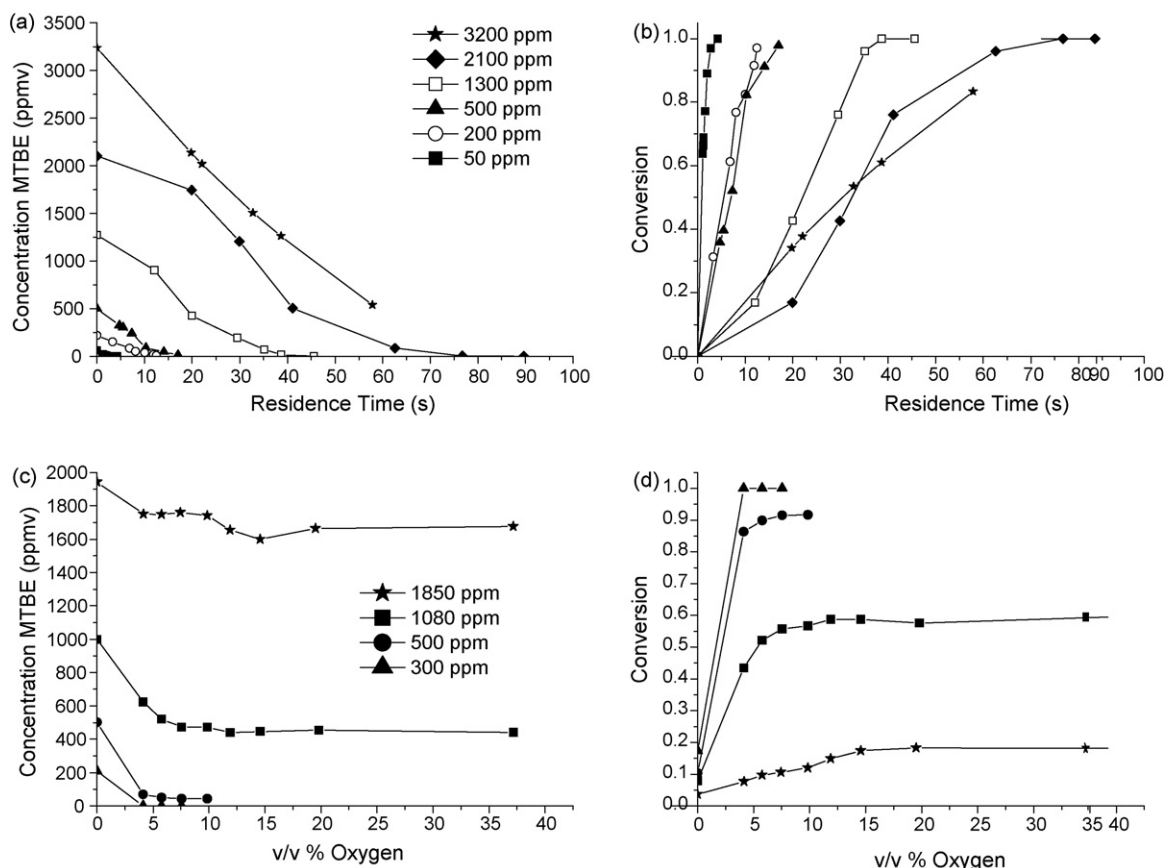


Fig. 2. MTBE degradation and conversion (a and b) versus residence time in the reactor for the effect of different initial MTBE concentrations and (c and d) versus the v/v% oxygen concentration for the effect of oxygen concentration.

fixed concentration of VOC. The concentration of MTBE and oxygen were 200 ppmv and 17.5% (v/v), respectively, while residence time was increased up to 14 s.

Fig. 3 shows the experimental results at certain residence times and different relative humidity. In all cases water enhanced the reaction rate to some extent. The rate increased with increasing relative humidity up to ~45%, when the positive influence started to decrease.

In the presence of water vapor, the hydroxyl radicals formed on the illuminated TiO_2 cannot only directly attack VOC molecules, but

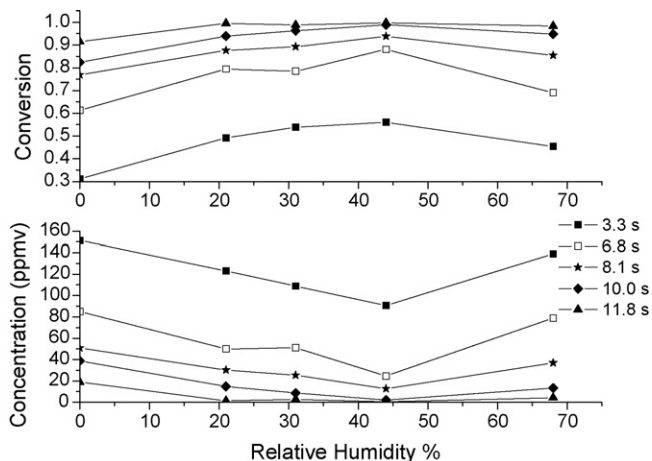


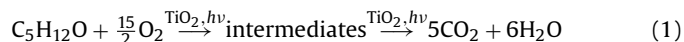
Fig. 3. MTBE degradation and conversion under different % relative humidity (200 ppmv MTBE, 17.4% (v/v) O_2 and different residence time).

also suppress the electron–hole recombination. Hydroxyl group or water molecules behave as a hole trap, forming surface adsorbed hydroxyl radicals [11,12]. However, higher concentrations of water vapor are inhibitory. This effect can be attributed firstly to the competition for adsorption between VOC and water vapor, secondly to the blocking of MTBE adsorption by the water vapor molecules and thirdly because an increased content of water vapor can destroy the equilibrium between consumption and adsorption of water in order to keep stable reaction rate, which results in lower reaction rates [1]. For MTBE the effect of water has been previously reported as totally reversible [5].

TBF and acetone formation was affected accordingly to MTBE. An increase in the concentration of the byproducts for higher concentration of water vapor present in the system is observed and can be attributed to the lower rates of their oxidation reactions.

3.4. Kinetics of the PCO of MTBE—mechanism aspects

The following expression presents the total photocatalytic oxidation process of MTBE:



Taking into account the photocatalytic properties of n-semiconductor TiO_2 , the initial reaction steps on UV-illuminated TiO_2 can be summarized in the following scheme [1]:





The band gap of TiO_2 is 3.2 eV and in order to excite the catalyst photons wavelengths shorter than 385 nm are required. When the photocatalyst is irradiated, conduction-band electron (e^-) and valence-band hole (h^+) pairs are formed. In the absence of electron and hole scavengers, most of them recombine with each other within a few nanoseconds. If the scavengers or surface defects are present to trap the electron or hole, e^-h^+ recombination can be prevented and the subsequent reactions caused by the electrons and holes may be dramatically enhanced [13].

The effect of the MTBE initial concentration, the oxygen concentration and the water vapour presented before, can be explained according to this initial reactions mechanism proposed by Shang et al. [1]. VOC molecules adsorbed on the surface play a significant role in the reaction with the holes, while the adsorbed oxygen in the reaction with electrons. The products of this electron transfer are O_2^- , O and O^- (reactions (3)–(5)) [1].

When a small amount of water vapor is introduced onto the photocatalyst, water is adsorbed on the surface of the photocatalyst, thus influencing severely the VOC oxidation rate. The adsorption of H_2O results in the formation of surface OH species by the reaction with the bridging-atoms, as well as OH radicals via the OH species under UV irradiation (reactions (6) and (7)). The oxidation reaction of MTBE is therefore enhanced. When water vapor was introduced in excess the effective adsorption sites were occupied completely by water molecules, which results in a decrease of OH radicals and the photo-induced uptake of oxygen [13].

The kinetics analysis was conducted for MTBE initial concentrations from 1300 to 100 ppmv. Various reaction schemes, based on the intermediates and final products detected in the experiments and the conclusions of the initial reaction steps proposed by Shang et al. [1], were tested and the kinetic expressions were solved (using MathCAD version 12 by Mathsoft) for the representation of the experimental results obtained. The procedure followed was:

- A possible reaction mechanism was suggested.
- The Langmuir–Hinshelwood rate expression was used for each reaction.
- The system of differential equations was postulated from mass balances.
- Initial values for concentrations and reaction rate coefficients were given.
- Nonlinear regression analysis (a fixed-step Runge–Kutta method) was used for the fitting of the experimental data to the system of differential equations.
- The objective function, the sum of squares of the differences between the experimental and the calculated values of concentrations, was minimized by the nonlinear Levenberg–Marquardt algorithm in order to determine the reaction rate coefficients.
- Finally the solution obtained was tested and compared to the experimental results (Fig. 4).

The following reaction scheme was found to be the best describing the experimental results:

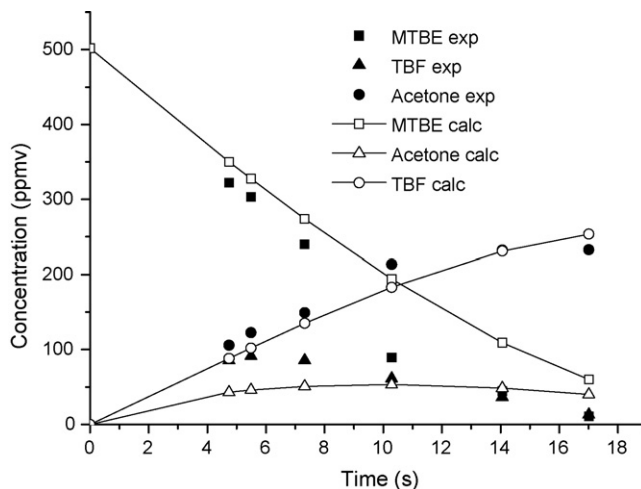
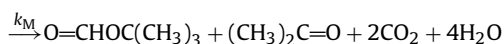
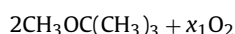
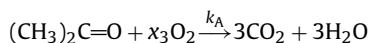
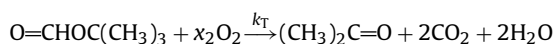


Fig. 4. Experimental and calculated values for initial MTBE concentration 500 ppmv.



The rate expressions used for each substance, respectively, were:

$$R_{\text{MTBE}} = -k_M \cdot \frac{C_{\text{MTBE}}}{1 + K_M \cdot C_{\text{MTBE}}} \cdot \frac{C_{\text{Oxyg}}}{1 + K_O \cdot C_{\text{Oxyg}}}$$

$$R_{\text{TBF}} = 0.5 \cdot k_M \cdot \frac{C_{\text{MTBE}}}{1 + K_M \cdot C_{\text{MTBE}}} \cdot \frac{C_{\text{Oxyg}}}{1 + K_O \cdot C_{\text{Oxyg}}} - k_T \cdot \frac{C_{\text{TBF}}}{1 + K_T \cdot C_{\text{TBF}}}$$

$$R_{\text{Acet}} = 0.5 \cdot k_M \cdot \frac{C_{\text{MTBE}}}{1 + K_M \cdot C_{\text{MTBE}}} \cdot \frac{C_{\text{Oxyg}}}{1 + K_O \cdot C_{\text{Oxyg}}} + k_T \cdot \frac{C_{\text{TBF}}}{1 + K_T \cdot C_{\text{TBF}}} - k_A \cdot \frac{C_{\text{Acet}}}{1 + K_A \cdot C_{\text{Acet}}}$$

In the presence of water vapour the rate expression for MTBE was:

$$R_{\text{MTBE}} = -k_{M,w} \cdot \frac{C_{\text{MTBE}}}{1 + K_M \cdot C_{\text{MTBE}}} \cdot \frac{C_{\text{Oxyg}}}{1 + K_O \cdot C_{\text{Oxyg}}} \cdot \frac{C_{\text{hum}}}{1 + K_{\text{hum}} \cdot C_{\text{hum}}}$$

The rate and adsorption constants obtained are presented in Table 1. The adsorption constant for MTBE was $2.19 \times 10^5 \text{ M}^{-1}$ and the rate constant for the reaction without moisture was $1.55 \times 10^{-6} \text{ M s}^{-1} \text{ g}_{\text{cat}}^{-1}$. Any comparison with the constants proposed in the references is not feasible, due to differences in the experimental set up and the conditions in which the reaction takes place. From the adsorption constants it is shown that the species are adsorbed on the catalyst in the following

Table 1
Langmuir–Hinshelwood parameters obtained in the photocatalytic degradation of MTBE

	Rate constant ($\text{mol}(\text{L s g}_{\text{cat}})^{-1}$)	Adsorption constant (M^{-1})
MTBE	$\frac{k_M}{K_M \cdot K_O} = 1.55 \times 10^{-6}$	K_M 2.19×10^5
O_2		K_O 1.92×10^5
Humidity	$\frac{k_{M,w}}{K_M \cdot K_O \cdot K_w} = 2.46 \times 10^{-6}$	K_w 1.09×10^4
TBF	$\frac{k_T}{K_T} = 1.19 \times 10^{-6}$	K_T 3.73×10^5
Acetone	$\frac{k_A}{K_A} = 6.71 \times 10^{-6}$	K_A 2.08×10^5

order: TBF < MTBE < Acetone < O₂ < Water. In addition the presence of moisture in the system increased the reaction rate by almost 60%. Finally MTBE has the highest oxidation rate, while acetone the lowest. The theoretical solution is compared to the experimental results as shown in Fig. 4.

4. Conclusions

The PCO oxidation proved to be very effective in the decontamination of MTBE-containing gas streams, obtaining conversions over 99%. TBF and acetone were the major intermediates, which are partially further photooxidized to the final products CO₂ and H₂O. The initial MTBE concentration was a decisive factor in the time needed for the total conversion of MTBE. Reactive oxygen species play an important role in the reaction, increasing the reaction rate up to a certain point, beyond which a saturation behaviour is observed. The presence of water vapour also affects the PCO of MTBE, enhancing the reaction rate up to an optimum relative humidity. The L–H kinetics model was used for expressing the reaction rate and the rate and adsorption constants were determined by a mathematical procedure. The results presented here suggest that the gas-phase photocatalytic oxidation can be considered in pollution control strategies concerning MTBE.

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