UDC 547.138.7

ELECTROCHEMICAL DEGRADATION OF METHYL TERT-BUTYL ETHER

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A b s t r a c t

In this paper, we have examined the performance of PbO_2 anodes in the EC degradation of methyl tert-butyl ether (MTBE). It was shown that electrochemical oxidation of MTBE at lead dioxide anodes is effective method of anodic conversion of the organic pollutant to acetic acid as untoxic product. Proposed method is formally reagent treatment of water at the same time it does not need addition of any reagent in reaction media. All needed reagents formed directly from the solvent (water) due to electrochemical reactions. According to obtained data the main electrochemical stages of the process of anodic conversion of MTBE are formation of hydroxyl-radicals and molecular oxygen. Then formed compounds take part in stages of chemical MTBE oxidation and intermediate species that led to deeper oxidation to form acetic acid as the result. Proposed mechanism of MTBE electrochemical oxidation is in satisfactory agreement with experimental data. Dependence of MTBE conversion rate from the nature of micro-doped and composite lead dioxide anodes is explained by difference in hydroxyl-radical bond strength with an electrode surface that determined it reaction ability in secondary chemical reactions of organic compounds oxidation.

Keywords: methyl tert-butyl ether (MTBE), electrochemical oxidation, lead dioxide anode, degradation mechanism.

ЕЛЕКТРОХІМІЧНА РУЙНАЦІЯ МЕТИЛТРЕТ-БУТИЛОВОГО ЕТЕРУ

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А н о т а ц і я

Досліджено процес електрохімічного окиснення метилтрет-бутилового етеру (МТБЕ) на діоксидносвинцевих анодах, методом ГРХ визначено кінетичні параметри процесу електроокиснення МТБЕ на мікромодифікованих і композиційних діоксидносвинцевих електродах. Установлено, що основними електрохімічними стадіями процесу анодної конверсії МТБЕ є процеси окиснення води з утворенням гідроксил-радикалів і молекулярного кисню, які надалі беруть участь у стадіях електрохімічного окиснення МТБЕ та проміжних сполук до оцтової кислоти. Запропоновано механізм електрохімічного окиснення МТБЕ.

Ключові слова: метилтрет-бутиловий етер, електрохімічне окиснення, діоксидносвинцеві аноди, механізм руйнування.

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ЭЛЕКТРОХИМИЧЕСКОЕ РАЗРУШЕНИЕ МЕТИЛТРЕТ-БУТИЛОВОГО ЭФИРА

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Аннотация

Исследовано электрохимическое окисление метилтрет-бутилового эфира (МТБЭ) на микромодифицированных и композиционных диоксидносвинцовых анодах. Установлено, что данный метод является эффективным способом анодной конверсии МТБЭ с образованием малотоксичного продукта – уксусной кислоты. Основными электрохимическими стадиями процесса являются процессы окисления воды с образованием гидроксил-радикалов и молекулярного кислорода. Предложен возможный механизм электрохимического окисления МТБЭ.

Ключевые слова: метилтрет-бутиловый эфир (МТБЭ), электрохимическое окисление, диоксидносвинцовые аноды, механизм разрушения МТБЭ.

Introduction

Methyl tert-butyl ether (MTBE) is one of the most widely used motor fuel additives. Despite its success in the improvement of fuel combustion efficiency and air quality, numerous corrosion failures have caused it to leak from fuel storage tanks and now MTBE has been widely found in both groundwater and surface waters. Because MTBE is highly soluble and tends to resist to hydrolysis and biodegradation, this ether probably represent the most persistent and ultimately dangerous of all fuel additives and components. The presence of MTBE at levels as low as 5 μg/L can cause a substantial deterioration of taste and odor of drinking water. In addition to that, MTBE has been associated with toxic and carcinogenic effects [1; 2]. This necessitates the development of methods to remove MTBE from water. Technologies that currently are utilized to this purpose include air stripping, adsorption on activated carbon, biofiltration, membrane separations and reagent treatment methods (catalytic combustion in the gas phase, oxidation by ozone and oxygen-containing radicals that form in Fenton and radiolytic processes) [3–10]. In these methods, MTBE isolated from polluted water either needs to be disposed of post-treatment, or active reagents need to be continuously added to the water being treated to maintain adequately high reaction rates of MTBE degradation.

On the other hand, electrochemical (EC) conversion and degradation of organic pollutants offers benefits such as potentially high efficiency, availability of convenient process control options (e.g., cell current, voltage and EC potential of working electrodes) and reagent-free operations that might result on lower costs of treatment. The EC degradation of MTBE and many other organic pollutants can take place *via* the transfer of oxygen atoms from water molecules to the target molecules and their breakdown products. These processes have been termed oxygen transfer reactions (OTR) [11]. In OTR, the degradation of the target species is caused by hydroxyl radicals that form at the anode of an EC reactor as a result of water oxidation. The efficiency of OTR is critically influenced by the choice of proper electrode materials that need to catalyze the release of hydroxyl radical. Transition metal oxide anodes, and most notably lead dioxide-based materials have been shown to exhibit high electrocatalytic activity in EC degradations of a number of recalcitrant organic pollutants, for instance 4-chlorophenol and 2,4-D and others [11; 12]. In this paper, we will examine the performance of PbO_2 anodes in the EC degradation of MTBE. It is also relevant to mention that information concerning EC oxidations of MTBE is practically absent.

Materials and Methods

Aqueous solutions of MTBE and acetone were used for EC experiments. They contained 0.5 M Na_2SO_4 and 0.03 M phosphate buffer to maintain pH at 6.7. The initial concentration of MTBE or acetone was $1.2 \cdot 10^{-2}$ M. All chemicals were of reagent grade. Doubly distilled water was used for all preparations.

Lead dioxide anodes were prepared by electrodeposition of that oxide on the platinized titanium substrate. The deposition was carried using 0.1 M $Pb(NO_3)_2$ + 0.1 M HNO_3 electrolyte. The deposition current density and time were 4 mA/cm² and 1 hour, respectively. To obtain PbO_2 films modified with Ni^{2+} ($3 \cdot 10^{-3}$ weight %), the corresponding weight amount of $Ni(NO_3)_2$ was added to the deposition electrolyte. To obtain Nafion®-containing PbO_2, the deposition was carried out from the

solution containing 5 % water/alcohol solution of Nafion®117 (Aldrich). The content of Nafion in the deposited PbO_2 film was 6.8 weight %.

Electrolysis was carried out in a cell with separated anodic and cathodic compartments. The volume of anolyte was 160 mL, anodic current density was 50 mA/cm². The surface area of both the anode and cathode was 2.5 cm². The chemical oxygen demand in EC treated solutions was determined using the standard dichromate method. Concentrations of species formed upon the EC oxidation of MTBE were determined using UV spectrophotometry and gas chromatography. A CHROM 5 gas chromatograph equipped with a SE-30 column and a flame ionization detector was used for relevant analyses.

Results and Discussion

Prior to EC treatment, solutions of MTBE exhibited little absorbance in the range of wavelengths below 220 nm (fig. 1). EC-treatment of MTBE was accompanied by the development of an intense absorbance band with a maximum at 260 nm (fig. 1)

For electrode materials used in the experiments, the intensity of that band increased for treatment time below 3 hours (fig. 2), after which it gradually diminished. The non-monotonic behavior of the absorbance indicated that the observed UV band was likely to be associated with the formation of unstable products of MTBE oxidation. The intensity of the absorbance at 260 nm was also observed to depend on the type of the anode materials. The maximum value of absorbance observed at a 3 hour electrolysis time decreases in the sequence PbO_2-Ni(II) > PbO_2-Nafion® > PbO_2.

The absorbance intensity also depended on the duration of time between sampling and actual measurements (fig. 3).

The decrease of the absorbance intensity in the absence of electrolysis appears to indicate that homogeneous decomposition of unstable products of MTBE degradation was taking place Gas chromatographic measurements showed that tert-butanol (TBA), acetone and acetic acid were main products of EC degradation of MTBE. The concentration of TBA reached a maximum after 1 hour of electrolysis, while the concentrations of acetone

Fig. 1. UV-Vis spectra of the solution 0.5 M Na_2SO_4 + buffer phosphate (pH 6.68) with initial content of MTBE $1,2\cdot10^{-2}$ M, after electrolysis:

a – at PbO_2-anodes at 50 mA/cm²; b – at composite anode PbO_2- Nafion® at 50 mA/cm²; c – at Ni^{2+}-doped PbO_2 at 50 mA/cm². Electrolysis time (h): 1 – 0; 2 – 0,5; 3 – 2,0; 4 – 3,0; 5 – 5,0; 6 – 7,0

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and acetic acid increased for treatment times up to 3 hours to reach the level of $5.5 \cdot 10^{-3}$ M. After 6 hours of electrolysis, only $2.0 \cdot 10^{-3}$ M of acetic acid was found.

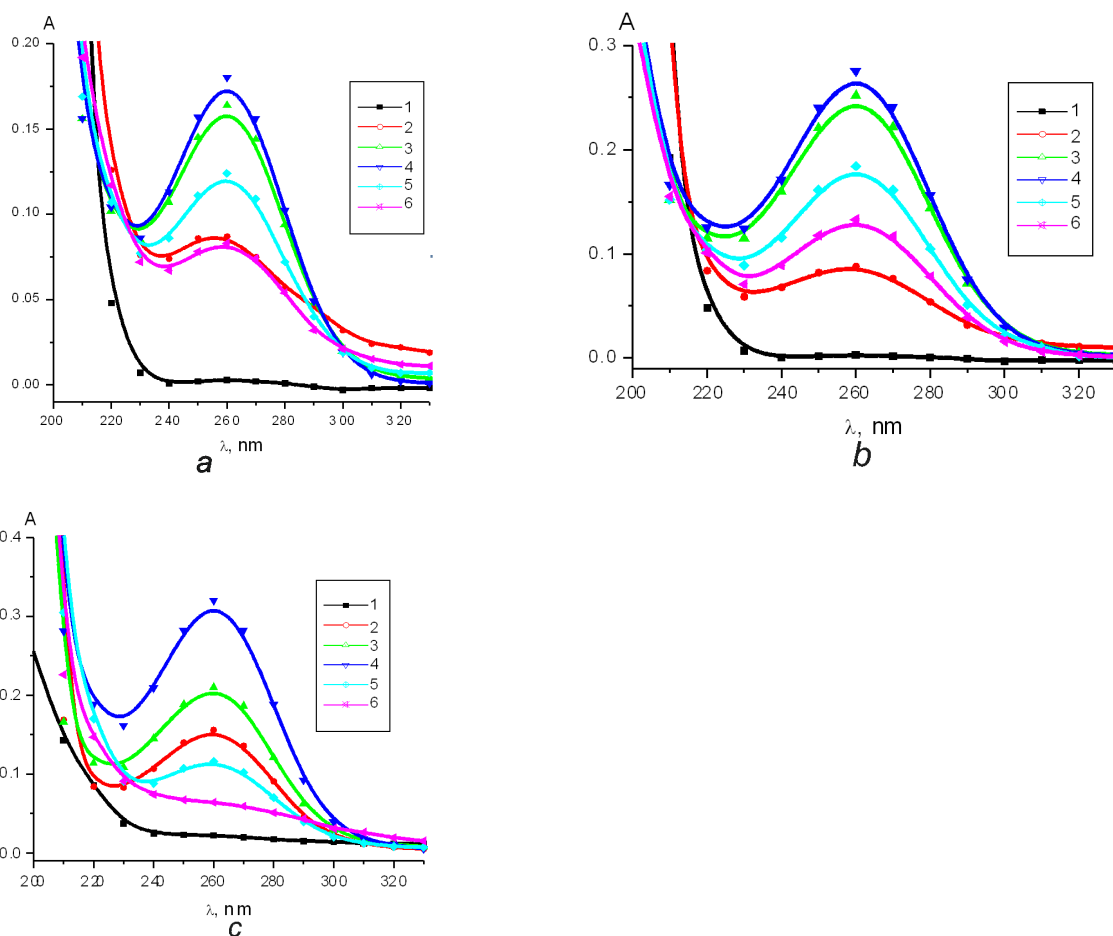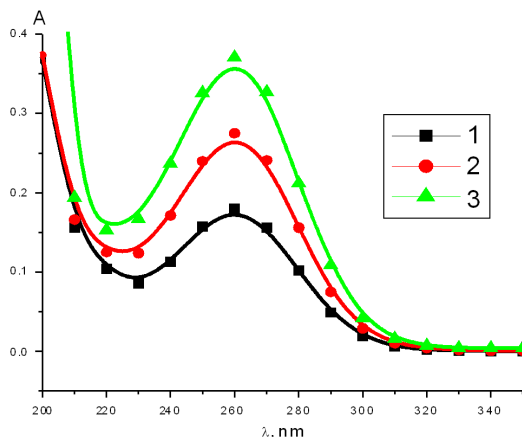**Fig.2. UV-Vis spectra of the solution 0.5 M Na_2SO_4 + buffer phosphate (pH 6.68) with initial content of MTBE $1.2 \cdot 10^{-2}$ M after electrolysis at 50 mA/cm^2 during 3 h at different anodes:**
1 – PbO_2; 2 – PbO_2-Nafion®; 3 – PbO_2-Ni^{2+}.

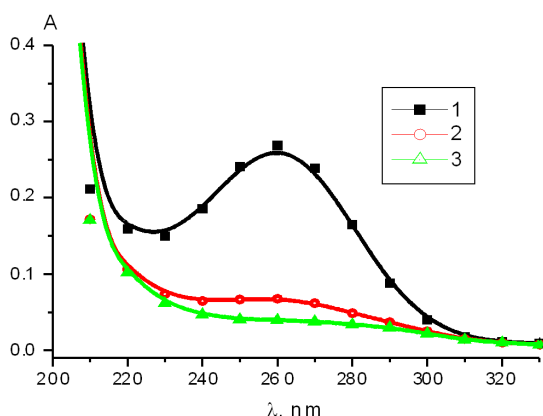**Fig. 3. UV-Vis spectra of the solution 0.5 M Na_2SO_4 + buffer phosphate (pH 6.68) with initial content of MTBE $1.2 \cdot 10^{-2}$ M after electrolysis at composite anode PbO_2-Nafion® at 50 mA/cm^2 during 4 h at different sampling time (min.): 1 – 5; 2 – 120; 3 – 300**

Because acetone was found to be one of the most important intermediate products of MTBE oxidation, its EC degradation was also examined. The relevant UV spectra (fig. 4, a) showed that the intensity of absorbance at 260 nm in the presence of this compound decreased as the duration of EC treatment increased, and the maximum of the absorbance band shifted from 265 to 260 nm. Similarly to the data for MTBE, a decrease of absorbance was observed for EC-treated MTBE solutions after electrolysis was stopped (fig. 4, b)

To determine the total concentration of organic species in EC treated MTBE solutions, corresponding COD values were measured at varying electrolysis time. As shown in Figure 5, the COD values decrease during the initial 3 hours of treatment by 5 to 10 times, depending on the type of anode used for EC treatment; 6 to 7 hours of EC treatment re-

sulted in COD values close to zero. This indicates the occurrence of a virtually complete EC incineration of MTBE.
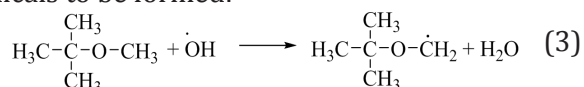
Mechanistically, the oxidation of MTBE with PbO_2-based anodes takes place at high anodic potentials and is accompanied by the evolution of oxygen and release of protons in the near-electrode solution volume [12]:

$$2\ H_2O - 4\ e^- \rightarrow O_2 + 4\ H^+ \qquad (1)$$
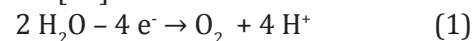
The acidification of the near-electrode solution provides conditions conducive for several types of homogeneous reactions that cause both MTBE and its intermediate degradation products to be oxidized. The above data support a hypothesis that the EC oxidation of MTBE occurs *via* a sequence of EC-mediated electron transfer reactions. Anodic water oxidation to form hydroxyl radicals and protons constitutes the first step in this reaction sequence [11; 12]:

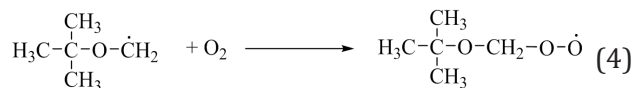$$H_2O - e^- \rightarrow \bullet OH + H^+ \qquad (2)$$
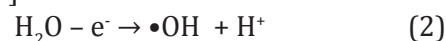
Hydroxyl radicals are extremely reactive and have been shown readily react with MTBE. At the same time, MTBE is virtually inert toward oxidation with ozone that can also be released *via* the oxidation of water with PbO_2 [4]. The oxidation of MTBE with OH$^\cdot$ was explored in the preceding studies of MTBE degradation in Fenton processes and γ-radiolysis [6; 7]. It was shown that interactions between MTBE and OH$^\cdot$ radical cause organic radicals to be formed:

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_3 + \overset{\cdot}{O}H \longrightarrow H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-\overset{\cdot}{C}H_2 + H_2O \quad (3)$$

The above radical can be stabilized by only cleaving a hydrogen atom from an α-carbon atom or other carbon atoms conjugated with that α-position [13]. According to the literature [7], the yield of the radical product of α-carbon cleavage in Reaction 3 is more than 70%.

The α-carbon radicals formed in Reaction 3 are likely to rapidly interact with oxygen to form corresponding peroxy radicals:

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-\overset{\cdot}{C}H_2 + O_2 \longrightarrow H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_2-O-\overset{\cdot}{O} \quad (4)$$

Primary and secondary peroxy radicals do not tend to participate in chain reactions, and their termination occurs with the formation of tetroxides that break down *via* a cyclical transient state [13]. The breakdown of the transient tetroxides will initially cause tert-butyl formate (TBF) and tert-butyl methanol (TBM) to be released, as was observed in the studies of MTBE ozonation [4]. These products are expected to hydrolyze easily to form TBA and formaldehyde as shown below:
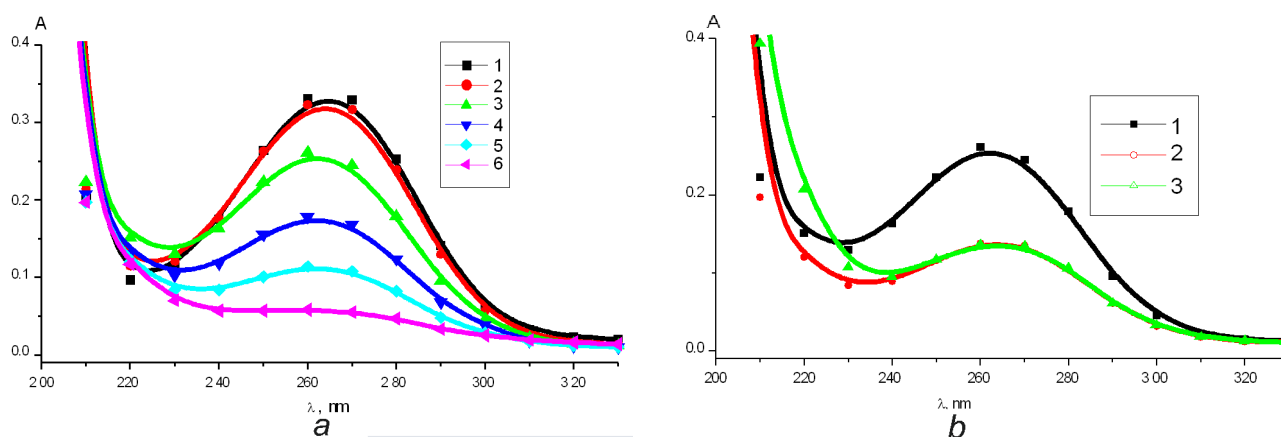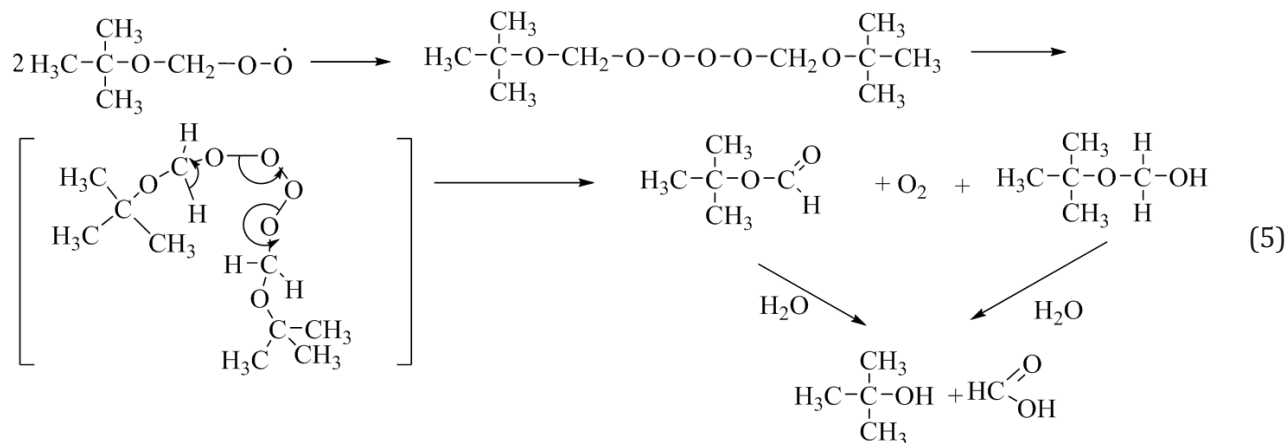
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$$2\,H_3C-\overset{\underset{\displaystyle CH_3}{|}}{\underset{\displaystyle |}{\overset{\displaystyle CH_3}{C}}}-O-CH_2-O-\dot{O} \longrightarrow H_3C-\overset{\underset{\displaystyle CH_3}{|}}{\underset{\displaystyle |}{\overset{\displaystyle CH_3}{C}}}-O-CH_2-O-O-O-O-CH_2O-\overset{\underset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_3}{C}}-CH_3 \longrightarrow$$

(5)

$$\longrightarrow H_3C-\overset{\underset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_3}{C}}-O-C\overset{O}{\underset{H}{\big<}} \; + O_2 \; + \; H_3C-\overset{\underset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_3}{C}}-O-\overset{\underset{\displaystyle H}{|}}{\overset{\displaystyle H}{C}}-OH$$

$$\overset{H_2O}{\searrow} \qquad \overset{H_2O}{\swarrow}$$

$$H_3C-\overset{\underset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_3}{C}}-OH \; + HC\overset{O}{\underset{OH}{\big<}}$$

Fig. 4. UV-Vis spectra of the solution 0.5 M Na_2SO_4 + buffer phosphate (pH 6.68) with initial content of acetone $1,2 \cdot 10^{-2}$ M after electrolysis at PbO_2-anodes at 50 mA/cm²:
a – electrolysis time(h): 1 – 0; 2 – 0,5; 3 – 3,0; 4 – 4,0; 5 – 5,0; 6 – 7,0; b – during 3 h at different sampling time (min.): 1 – 5; 2 – 60; 3 – 120
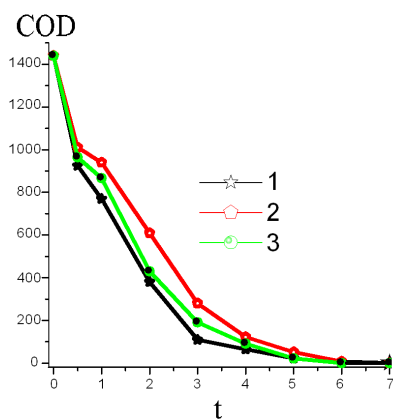

Fig. 5. COD of the solution 0.5 M Na_2SO_4 + buffer phosphate (pH 6.68) with initial content of MTBE $1,2 \cdot 10^{-2}$ M with different electrolysis time at anodic current density of 50 mA/cm²:
Anode materials: 1 - PbO_2-Nafion®; 2 - PbO_2; 3 - PbO_2-Ni^{2+}

Alternatively, the peroxy radicals formed in Reaction 4 can interact with OH˙ radical to form TBA and formaldehyde *via* a somewhat different mechanism [6]:
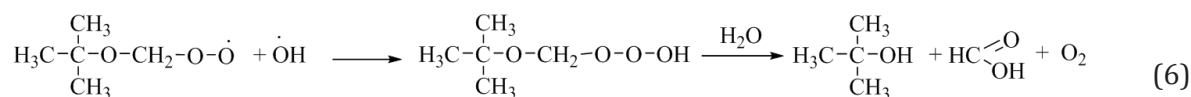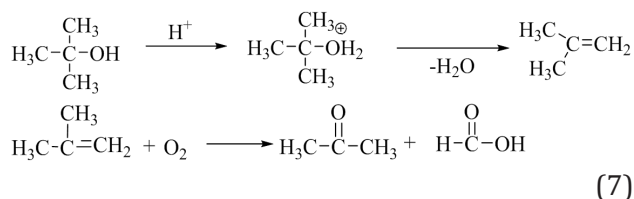
Since the breakdown of peroxy compounds is catalyzed in the presence of transition metal ions and their oxides [13], in EC oxidations the surface of PbO_2 is likely to act not only as a site of EC generation of O_2, O_3 and OH˙, but also a heterogeneous catalyst of the decomposition of organic radicals and their peroxo forms.

In contrast with the data for MTBE degradation with ozone, its EC oxidation was not accompanied by the release of noticeable amounts of TBM, TBF formaldehyde and formic acid, and TBA was the first stable degradation product released during the first hour of MTBE electrolysis. Formic acid and formaldehyde were likely to be rapidly oxidized to carbon dioxide [14] and water due to their low standard oxidation potential (-0.2 V for formic acid) while the actual potential of PbO_2 anodes were in range of +2.0 V.

The data also indicate that TBA formed because of MTBE oxidation in unstable on the conditions of EC treatment. For this compound, the homolysis of

$$H_3C-\overset{\underset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_3}{C}}-O-CH_2-O-\dot{O} \; + \dot{O}H \longrightarrow H_3C-\overset{\underset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_3}{C}}-O-CH_2-O-O-OH \overset{H_2O}{\longrightarrow} H_3C-\overset{\underset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_3}{C}}-OH \; + HC\overset{O}{\underset{OH}{\big<}} \; + O_2$$

(6)

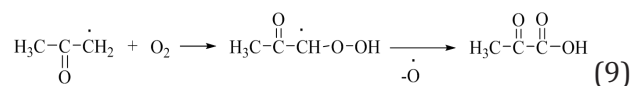Vìsnik Dnìpropetrovs'kogo unìversitetu. Serìâ hìmìâ 22 (2014), 1, 1-7

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the OH-bond at pH close to 7 does not take place [13] and the oxidation of TBA at the electrode surface is more likely to proceed *via* the cleavage of the C-O bond and ensuing degradation of the resulting alkene by oxygen to acetone [15]:
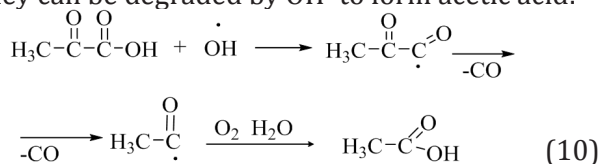
$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow{H^+} H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3\oplus}{|}}{C}}-OH_2 \xrightarrow{-H_2O} \underset{H_3C}{\overset{H_3C}{>}}C=CH_2$$

$$H_3C-\underset{\underset{CH_3}{|}}{C}=CH_2 + O_2 \longrightarrow H_3C-\overset{\overset{O}{\|}}{C}-CH_3 + H-\overset{\overset{O}{\|}}{C}-OH \tag{7}$$

The formation of acetone was confirmed in this study by gas chromatographic measurements, and it was also seen in the studies of MTBE ozonation The molecules of acetone released as a result of the degradation of TBA (7) can be readily oxidized by $OH^{\cdot}$ radicals to form yet another organic:

$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3 + \overset{\cdot}{O}H \longrightarrow H_3C-\overset{\overset{O}{\|}}{C}-\overset{\cdot}{C}H_2 \tag{8}$$
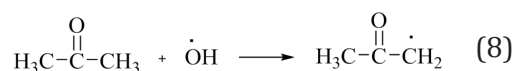
Reactions of that radical with dissolved oxygen will lead to the formation of pyruvic acid [16]:

$$H_3C-\underset{\underset{O}{\|}}{\overset{\cdot}{C}}H_2 + O_2 \longrightarrow H_3C-\overset{\overset{O}{\|}}{C}-\overset{\cdot}{C}H-O-OH \xrightarrow{\cdot O} H_3C-\overset{\overset{O\ O}{\|\ }}{C}-C-OH \tag{9}$$

2-oxycarboxylic acids can be either directly EC oxidized either at potentials above +1 V [17], or they can be degraded by $OH^{\cdot}$ to form acetic acid:

$$H_3C-\overset{\overset{O\ O}{\|\ \|}}{C}-C-OH + \overset{\cdot}{O}H \longrightarrow H_3C-\overset{\overset{O}{\|}}{C}-\overset{\cdot}{C}\overset{\nearrow O}{} \xrightarrow{-CO}$$

$$\xrightarrow{-CO} H_3C-\overset{\overset{O}{\|}}{\underset{\cdot}{C}} \xrightarrow{O_2\ H_2O} H_3C-C\overset{\nearrow O}{\underset{OH}{}} \tag{10}$$

The suggested mechanism of EC degradation of MTBE is in adequate agreement with the data of this study and also with the results of studies of MTBE degradation by ozone or in advanced oxidation processes (AOP). Essentially all processes described above are mediated by the action of $OH^{\cdot}$ radicals as well as those ozone and oxygen formed upon the EC oxidation of water. It also appears that effects of PbO_2 modification are relatively secondary and do not cause changes in the mechanism of MTBE degradation although they affect its rate, as was also seen for the degradation of chlorophenols with PbO_2 modified with Ni^{2+} or Nafion [12]. As has been shown in prior literature [11], modification of PbO_2 with Ni^{2+} causes the strength of bonds between the oxide surface and oxygen-containing intermediates formed upon the EC oxidation of water to decrease. This indicates that the use of electrode materials (for instance, PbO_2 modified with either transition metals or organic polymers) characterized by high yields of such reactive species will help further increase the efficiency of EC degradation of MTBE.

Conclusions

Electrochemical oxidation of MTBE at lead dioxide anodes is effective method of anodic conversion of the organic pollutant to acetic acid as untoxic product. Proposed method is formally reagent treatment of water at the same time it does not need addition of any reagent in reaction media. All needed reagents formed directly from the solvent (water) thanks to electrochemical reactions.

According to obtained data the main electrochemical stages of the process of anodic conversion of MTBE are formation of hydroxyl-radicals and molecular oxygen. Then formed compounds take part in stages of chemical MTBE oxidation and intermediate species that led to deeper oxidation to form acetic acid as the result. Proposed mechanism of MTBE electrochemical oxidation is in satisfactory agreement with experimental data. Dependence of MTBE conversion rate from the nature of micro-doped and composite lead dioxide anodes is explained by difference in hydroxyl-radical bond strength with an electrode surface that determined it reaction ability in secondary chemical reactions of organic compounds oxidation.

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