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Relationships between the efficiency of cyclohexane oxidation and the electrochemical parameters of the reaction solution

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ABSTRACT

Vanadyl(IV)-acetylacetonate-catalyzed oxidation of cyclohexane with H_2O_2, at 40 °C under air atmosphere, has been studied in the presence of small quantities of oxalic acid. The process efficiency is increased by this additive and depends on the nature of the solvent ($MeCN \geq MeOH > Me_2CO \geq$ 2-PrOH > EtOH). The relationships between the results (conversion, yield) and the electrochemical characteristics of the reaction solution (relative permittivity, redox-potential) are highlighted and discussed.

1. Introduction

The oxidative functionalization of hydrocarbons is important from both practical and fundamental points of view. Cyclohexane oxidation is the basic process of the industrial-scale production of cyclohexanol and cyclohexanone [1,2] – these compounds being the precursors for Nylon-6 and Nylon-66 manufacturing [3,4]. The commercial homogeneous Co(II)-based process, which occurs at 160–180 °C, 1.3–1.5 MPa of air, leads to low (4–6%) conversions and moderate (75–80%) selectivities. Therefore, the elaboration of better protocols remains a challenge and their achievement can afford valuable information to carry out oxidative transformation of other hydrocarbons.

Previously, we disclosed that the efficiency of C_6H_{12} oxidation into $C_6H_{11}OH$, $C_6H_{10}O$, and $C_6H_{11}OOH$, at 40 °C and 0.1 MPa, using H_2O_2 as oxidant, $VO(acac)_2$ (**1**) as catalyst, and MeCN as the solvent is noticeably increased by addition of small amounts of glyoxal [5] and oxalic acid ($H_2C_2O_4$) (**2**) [6]. As appeared, the exchange of MeCN by EtOH was detrimental to this process [6]. Therefore, we assumed that this effect can be, among others, referred to the electrochemical parameters of the reaction solution (e.g., relative permittivity ε_r). Such an assumption is in agreement with literature data [7]. Nevertheless, in all previous reports, the kinetics of oxidation was studied exclusively in connection with ε_r values inherent to pure solvents. The possible modification of ε_r and the redox-potential of the reaction mixture by catalyst and additives has not been studied. Using low-frequency (10–10^5 Hz) dielectric spectroscopy (DS) [8,9] and cyclic voltammetry (CV) [10] techniques, we have tried to estimate the impact of the catalyst and additives on ε_r and the redox-potentials of the solutions, and to determine plausible relationships between these parameters and the reaction efficiency. These two methods have emerged as the most powerful noninvasive electrochemical tools to investigate the mechanism of oxidation processes [11,12]. The solvents for the oxidation, CV, and DS experiments have been chosen according to their various relative permittivity values as well as to their ability to be inert under the experimental conditions and to dissolve reagents and products. MeCN, MeOH, Me_2CO, 2-PrOH, and EtOH agree with these requirements.

2. Experimental

2.1. Chemicals

The commercial aqueous solutions of hydrogen peroxide (35 wt.%, Fluka) have been concentrated by vacuum distillation at 45 °C/10 mm Hg to 70 wt.% (caution: risk of explosion. All glassware has to be thoroughly rinsed by distilled water to remove traces

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of any heavy metals). As the commercially available vanadyl(IV)-acetylacetonate (Aldrich) is of ca. 95% purity only, the crude $VO(acac)_2$ was dissolved in MeCN to give a saturated solution, which was then filtrated through a micro-porous paper filter. The filtrate was evaporated at 40 °C under reduced pressure, and the resulting solid was dried under vacuum at 20 °C for 48 h, leading to dark-green tiny (0.5–1 mm) crystals which were used in the oxidation experiments. Cyclohexane, acetonitrile, methanol, ethanol, 2-propanol, acetone, triphenylphosphane, and tetra-n-butyl ammonium perchlorate (all from Aldrich) were used as purchased.

2.2. *Experimental installation and oxidation reactions*

The catalytic experiments were carried out in 25-mL round-bottom glass flasks equipped with reflux condenser and magnetic stirrer. In a typical experiment, 3.36 g (40 mmol, 1.8 mol L^{-1}) of cyclohexane were dissolved in 15 mL of MeCN containing 0.0032 g (0.012 mmol, 5×10^{-4} mol L^{-1}) $VO(acac)_2$ and 0.038 g (0.3 mmol, 0.014 mol L^{-1}) oxalic acid. The mixture was heated at 40 °C for 5 min before 1.34 g (40 mmol, 1.8 mol L^{-1}) of H_2O_2 were added. This moment corresponds to the beginning of the oxidation reaction. Usually, the reaction has been carried out for 5 h under atmospheric pressure.

The values of relative permittivities (ε_r) of the reaction solution have been obtained by dielectric spectroscopy (DS) measurements [8]. The dielectric response of any medium is characterized by the spectral shape of the real (in-phase) $\varepsilon_1(\omega)$ and imaginary (quadrature) $\varepsilon_2(\omega)$ components of the dielectric complex constant $\varepsilon^*(\omega) = \varepsilon_1(\omega) – j\varepsilon_2(\omega)$ or by the corresponding complex capacitance $C^*(\omega) = C_1(\omega) - jC_2(\omega)$, where j is the imaginary unit and ω is the angular frequency; $C_1(\omega)$ and $C_2(\omega)$ are the real and imaginary components of the complex capacitance, respectively. Complex capacity and complex ε_r are connected via the constant factor S/d by the equation: $\varepsilon_r^* = C * /d(\varepsilon_0 S)$, where S is the area of contacts of the plane capacitor, m^2; d the thickness of polarization region, m; ε_0 the relative permittivity of vacuum (8.85×10^{-12} F m^{-1}) [8,9]. In some cases the use of complex capacity instead of complex dielectric constant have some advantages, particularly, when electrode or double layer polarization effects dominate on the spectra. Dielectric spectra in the frequency range of 10–10^5 Hz have been measured by transducing the complex capacity into sinusoidal voltage on the basis of operational amplifier [8]. This method eliminates the influence of stray capacitors of connecting cables. Sinusoidal voltage 100 mV rms was applied to the measuring cell. Phase shifts were measured using a digital phase-meter. Calibration of the equipment using etalon elements permits to exclude the constant bias errors. A 10-mL glass vial equipped with two parallel stainless steel electrodes (1 mm × 10 mm × 20 mm) with fixed 2 mm inter-electrode distance has been used as the measuring cell. Usually, the total volume of reaction mixture was 8 mL. All experiments have been conducted at room temperature and atmospheric pressure. After each measurement, the electrodes have been copiously rinsed by distilled water and then thoroughly dried.

Cyclic voltammetry (CV) measurements of the redox potential of the reaction mixtures have been carried out at room temperature using an EG & G Princeton Applied Research potentiostat/galvanostat model 273A. The experiments were conducted in a 15-mL glass electrochemical cell containing 10 mL (total volume) of reagents. In order to provide proper electrolytic conditions, the voltammograms have been taken in the presence of tetra-n-butyl ammonium perchlorate (0.1 mol L^{-1}). The working electrode was a Bioanalytical Systems glassy-carbon (area, 0.09 cm^2) inlay, the auxiliary electrode a platinum wire, and the reference electrode an $Ag/AgCl/Cl^-$ wire, in an aqueous tetramethylammonium chloride solution that was adjusted to give a potential of 0.00 V vs SCE. The later was contained in a Pyrex tube with a cracked soft-glass tip, which was placed inside a Luggin capillary [10]. Before each CV measurement, argon was bubbled through the reaction solution for at least 30 min to remove dissolved oxygen. After the experiment, the deposits, contaminating the active edge of the working electrode, have been removed by polishing it with a Gamma Micropolish II Alumina (0.05 μm, Buehler) paste, followed by copiously rinsing with distilled water and then thorough drying. A microportion of H_2O_2 (usually 0.3 mmol) has been injected into the mixture of reactants under vigorous stirring; that moment was considered as the starting point for current–voltage depended function measurements.

2.3. *Analysis of the reaction products*

The reaction mixture was sampled at regular intervals. The content of products in the samples was analyzed using a GLC Hewlett–Packard 5890, series II (flame-ionization detector, capillary column 30 m × 0.25 mm, immobile phase HP-Innowax) as well as a LKhM-80 one (flame-ionization detector, packed column 3 m × 3 mm, immobile phase OV-17 on Chromaton N-AW). Prior to the analyses, a 2-butylbenzene solution in ethanol was added as internal standard to the withdrawn sample. The identification of the oxidation products was performed by comparison with the retention times of commercial cyclohexanol and cyclohexanone. Subsequently, both the conversion and the selectivity towards the obtained products were determined by the common calculation procedure. The quantification of the oxygenated products was performed using a multi-points calibration line plotted using references of $C_6H_{11}OH$ and $C_6H_{10}O$. In order to determine the proper content of cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide, each probe was analyzed twice by GC – before and after the addition of triphenylphosphane. In the presence of PPh_3, the $C_6H_{11}OOH$ is rapidly and quantitatively transformed into $C_6H_{11}OH$; then the true content of cyclohexylhydroperoxide can be calculated as the difference between the $C_6H_{10}O$ and $C_6H_{11}OH$ concentration before and after the triphenylphosphane addition [13]. Titration of probes of the reaction mixture by an aqueous 0.10 mol L^{-1} solution of $Na_2S_2O_3$ in presence of KI allows to determine the amount of H_2O_2 which has been consumed.

3. Results and discussion

Oxidation of C_6H_{12} has been carried out using from 1 to 10 equivalents of H_2O_2, a catalytic amount of $VO(acac)_2$ (**1**), and various quantities of oxalic acid (**2**). The main results are collected in Table 1 (for all experiments, the process selectivity calculated on the sum of aimed products was 97–99%). Accordingly to the results shown in Table 1, the addition of **2** led to a noticeable improvement of the process. For example, in MeCN, the presence of **2** increases both the conversion and TON (compare entries 1 and 2), the optimal amount of **2** being between 0.011 and 0.022 mol L^{-1} (Fig. 1). Exceeding this amount drops the alkane conversion.

Studies on the positive influence of pyrazine-2-carboxylic [14,15], sulfuric or oxalic acid [16] as a co-catalyst on the V_2O_5 and $NaVO_3$-catalyzed oxidations of alkanes led us to suspect that oxalic acid acts also with the reduced form of catalyst (V^{4+}), this plausibly leading to the coordination of its monoanion to the metal cation. Diminution of the oxidation efficiency caused by an excess of **2** can be attributed to the acceleration of the heterolytic cleavage of H_2O_2 at very low pH values [17] (pH equal −2 was reached in the case of amounts of **2** higher than 0.010 mol L^{-1}). The alkane conversion increases to 30 % in the presence of **2** when the C_6H_{12} concentration was decreased to 0.18 mol L^{-1} (entry 4). According to these data, the most appropriate medium for C_6H_{12} oxidation is