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Oxidation of Aromatic Hydrocarbons under Phase Transfer Catalysis Conditions †

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Abstract: The oxidation of alkylaromatic substrates under phase transfer catalysis conditions for obtaining carboxylic and carbonilic derivatives is reported (cetyltrilmethilamonium, $MnO4^{-}$, CH2Cl2/H2O, range of temperaturas, molar rates and relations of reagents, volumes of reaction mixture, reaction times, etc.) are detailed. This procedure inhibits the autocatalytic process of destruction of the $KMnO_4$ under the reaction conditions and the adsorption of target compounds onto manganese (IV) oxide. The described procedure minimizes the production and volume of residual wastes. A hypothetical mechanism of the oxidation is proposed. The obtained compounds were properly characterized using physico-chemical methods, corroborating the proposed structures for generated acids and ketoderivatives.

Keywords: oxidation; phase transfer catalysis; permanganate; ammonium salt; alkylaromatics

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1. Introduction

The oxidation of alkyl aromatic derivatives to acids is one of the fundamental problems of contemporary organic chemistry, due to the wide use of aromatic acids in the pharmaceutical, food, cosmetic and polymer industries [1]. Generally the oxidation process is carried out with atmospheric oxygen in the presence of transition metal salts ($CoBr$-$MnBr_4$; O_2/Co^{2+}-Ni^{2+}/Br^{-}) under extreme conditions of pressure (105–106 Pa) and temperatures (350–400 °C), reaching yields ranging from 55 to 75%. A classic example is the oxidation of mesitylene (2 g mesitylene-15.8 g $KMnO_4$-250 mL H_2O) which proceeds within 24 h at temperatures of 120 °C with yields below 55%.

The aqueous solution of potassium permanganate, KMnO4, is a recognized oxidant for a wide variety of organic substrates [2,2ª] and its history of use dates back to the time of Kekule and Wagner at the end of the 19th century when they described the cis-hydroxylation of maleic and fumaric acids [3,4]. The most general procedures use an excess (more than 100%!!) of poly-oxoanion [MnO4]-which has serious disadvantages: the solubility of KMnO4 in water, the need to work with large volumes and collateral phenomena of over oxidation of the substrates. Under normal aqueous conditions, KMnO4 is thermodynamically unstable and partially decomposes to MnO2 and O2, this process having an autocatalytic character [5].

$$4\,[MnO_4]^{-} + 2H_2O \longrightarrow 4MnO_2 + 3O_2 + 4\,OH^{-}$$

The oxidation products of organic substrates are strongly adsorbed on the manganese dioxide-MnO2 precipitate; repeated washing with a specific solvent and even extraction of the reaction mixture with Sohlext apparatus is necessary, which makes the oxidation process considerably more expensive.

The oxidation of hydrocarbons with $KMnO_4$ is limited, operationally, by these reasons and also by the low rate of the heterogeneous reactions and the relatively low yields observed, related to the catalytic decomposition of the oxidant already described *vide supra*.

Potassium permanganate, however, is today recognized as a versatile industrial *green* oxidant, used in the pharmaceutical production of 2-acetamidobenzoic, cycloxyl, dinicotinic, isocinchomeronic, 2,3-pyrazino dicarboxylic, 2,6-pyridinodicarboxylic, 4-sulfobenzoic and trimethylpyruvic acids [6] as well as other important derivatives.

Currently, for the last 10 years, the attention of researchers is focused on biphasic catalysis method [7–9], which due to its simplicity, effectiveness and versatility, is widely used in fine organic synthesis in oxidation processes of organic substrates [10]. The interphase catalytic oxidation method using $KMnO_4$ is free of the described drawbacks. This procedure has been employed for the oxidation of oximes [11], olefins [12–15], in the synthesis of 1(3)-acylglycerols [16] and substituted guanidines [17], in oxidative deoximation [18] and has demonstrated remarkable possibilities and satisfactory yields [19,20]. As catalysts for permanganate oxidation in non-aqueous solvents, quaternary ammonium salts, phosphonium [21], arsonium, complexes with polyethylene glycols [22] and crown ethers [23] are used. As alternative oxidants, tetraalkylammonium permanganates can be used for mild oxidations [24,25] but these are explosive and detonate under varying conditions [26]. Considering the high cost of crown ethers and the hazardous nature of arsonium salts, the use of quaternary ammonium salts as potential catalysts in two-phase systems: aqueous solution/organic solvent is more economically and productively profitable, besides, the handling is simple and does not offer danger for the synthesis technician, facilitating the recovery of residues (MnO_2, ammonium salts, solvent mixture) and their reuse.

The aim of the present communication is to report the results of the oxidation process of a series of hydrocarbons and alkylaromatic derivatives to corresponding acids and ketones, under phase transfer catalysis conditions under the action of the cetyltrimethyl ammonium- ion $[MnO_4]^-$ system.

2. Materials and Methods

Melting temperatures were determined with Electrothermal 9100 capillary furnace equipment. FTIR spectra were analyzed on a Philips Analytical PU 9600 FTIR spectrophotometer (USA) in KBr pellets at 25 °C. The reagents, available from commercial firms Merck, BDH and Fluka, were used without prior purification. Cetyltrimethylammonium chloride was used after recrystallization (twice) from ethanol-toluene-ether mixtures (2:1:0.5 *v*/*v*), being of pharmaceutical grade. All chemical-physical parameters of the products obtained were in concordance with those reported in the literature. The ^{13}C- and ^{1}H NMR spectra of the synthesized derivatives were recorded on a Bruker ACF-250 spectrometer (Dorstmund, Germany) at 238K operating at 62.50 and 250.13 MHz respectively. $(CD3)_2SO$ (DMSO-d6) was used as solvent and TMS as internal standart. The chemical shifts were expressed in δ scale.

The reactions were monitored by thin layer chromatography using 0.25 mm thick silica gel 60G chromatoplates (Merck, Germany) and as developer a 1% solution of vanillin in 50% $HClO_4$ or chambers with iodine vapors. For the detection of carbonyl derivatives, silica gel was used with the addition of polyethylene glycol 4000 (30 g SiO_2 + 12 g Polyethyleneglycol-4000) plus 25 mL of water and 25 mL of ethanol, heating the plates at 100 °C for 1 h. Elution is developed with a solvent mixture: CCl_4-ethanol (120:1 *v*/*v*) and developing with iodine vapors.

The reagents used in the different syntheses are commercially available from Merck (Germany), BDH (UK) and Panreac (Spain). The solvents, of technical quality, were previously distilled and dried over Na_2SO_4 [27]. The ammonium salts:

cetyltrimethylammonium bromide, triethylbenzylammonium chloride and tetrabutylammonium iodide were used without purification.

The quaternary salt used as catalyst, cetyltrimethylammonium permanganate, was synthesized and purified from ethanol/water (96:4 *v*/*v*).

2.1. Cetyltrimethylammonium Permanganate

A solution of 1.58 g (9.9 mmoles) of KMnO4 in 25 mL of water is added, by driping, to a solution of 3.55 g (9.68 mmoles) of cetyltrimethylammonium bromide in 25 mL of distilled water at room temperature (25 °C) and with magnetic stirring (250 rpm). The reaction mixture is cooled to 0 °C and the iridescent purplish precipitate is rapidly filtered off cold to avoid decomposition, dried under vacuum and stored at 5 °C. Yield. 3.37g (8.37 mmoles) 86%. Tm (°C) < 186, (with decomposition!) NMR-^{1}H (δ, ppm): 3.11 s (9H, N-$(CH_3)_3$); 3.09 m (tt, 2H, CH_2-N+(CH_3); 2.07 m (2H, -CH_2-CH_2-N+(CH_3); 1.33 m (26H (–CH_2-)14); 0.96 m (3H, CH). NMR ^{13}C (δ, ppm): 14.27 (R-CH_3); 22.1-31.02 (14 C, H_3C-(-CH_2-R-CH_2-)$_{14}$-CH_2-N-(CH3)3); 54,1 N-(CH3)3; 66.4 R-CH2-N+$(CH_3)_3$.

2.2. Toluene Oxidation

In a 500 mL flask, 10.6 mL (0.1 moles) of toluene; 15.8 g (0.1 moles) of $KMnO_4$; 250 mL of water; 0.13 g of cetyltrimethylammonium bromide (0.3 moles) are placed and the reaction mixture is stirred at 650 rpm at 85 °C for 2 h. Benzene (60 mL) is added to separate and extract the catalyst. The aqueous phase is filtered to remove the MnO_2. This is washed with several volumes (4 × 100 mL) of ice water. Concentrated HCl (6N) is added to pH 1–1.5. The obtained benzoic acid precipitate is filtered and dried under vacuum.

All carboxy- and carbonyl-derivatives obtained are recrystallized from 1:3 v/v methanol-water mixture and their melting temperature (melting points) is determined by comparison with literature reports as well as by ^{1}H NMR.

2.3. Oxidation of p-Xylene

A mixture of 11.5 g (0.108 moles) of p-xylene; 63 g (0.39 moles) of $KMnO_4$; 0.5 g (1.37 mmoles) of cetyltrimethylammonium bromide and 100 mL of water is stirred vigorously (750 rpm) at 75 °C for 1 h and 40 min. The reacting mixture is extracted with benzene for separation of the catalyst. The aqueous phase is filtered. The MnO_2 is washed with small volumes of ice water (4 × 50 mL). The filtrates are evaporated to half volume and acidified with concentrated HCl (6N) to pH 2. The white precipitate of terephthalic acid is filtered and dried under vacuum.

2.4. Oxidation of Diphenylmethane and Fluorene

4.03 g of cetyltrimethylammonium permanganate (10 mmoles) is gently added to 75 mL of distilled water under conditions of intense stirring (550 rpm). Diphenylmethane (0.84 g, 5 mmoles), dissolved in dichloromethane is gently added into the reaction mixture which is allowed to stir for 90 min at a temperature of 50 °C. The development of the oxidation process is monitored by thin layer chromatography (the mixture remains homogeneous during the reaction). 20 mL of CH_2Cl_2 are added and the colloidal derivative MnO_2-quaternary ammonium salt is filtered under vacuum over a small bed of SiO_2 (5 g) plus $CaCl_2$ (1 g), the organic phase is separated, dried and evaporated to obtain the carbonyl product, benzophenone with a yield of 88%. For fluorene (0.83 g, 5 mmoles) the same procedure is used with the variation in the amount of catalyst (cetyltrimethylammonium permanganate 5 mmoles, 2.0 g) obtaining 9-fluorenone with a yield of 81%.

The oxidation procedure is similar for the other substrates (Table 1). The physicochemical characteristics of the aromatic carboxylic acids obtained agree satisfactorily with the data reported in the literature. (Table 2).

Table 1. Molar ratios and reaction parameters.

Alkylaromatic Substrate	Molar Ratio $ArH:KMnO_4:H_2O:R_4N^+Br^-$	Catalyst (g)	T, °C Reaction Mixture	Reaction Time (min.)
p-xylene	$1:4:70:6.8 \times 10^{-3}$	0.25	75	100
m-xylene	$1:4:70:6.8 \times 10^{-3}$	0.25	75	100
ethylbenzene	$1:1.5:140:3.5 \times 10^{-3}$	0.13	85	150
diethylbestrol	$1:1.5:140:7.0 \times 10^{-2}$	0.3	70	30
styrene	$1:1.5:140:7.0 \times 10^{-2}$	0.3	70	30
stilbene	$1:1.5:140:7.0 \times 10^{-2}$	0.25	60	20
diphenylmethane	$1:9:135:7.0 \times 10^{-2}$	0.50	50	90
fluorene	$1:5:135:9.5 \times 10^{-2}$	0.50	50	90

Table 2. Characterization of synthetized compounds.

Alkylaromatic substrate	Reaction Product (TLC + Tm, °C)	Yield (%)	Analytical signals NMR (1H-13C), δ, ppm
p-Xylene	Terephtalic acid	82	7.99 s. broad (5H, arom.); 9.87 (OH) 168.0 (C=O)
	Isophtalic acid (344.1)		
	Phenylacetic acid (74-76)		8.59 s broad (OH); 8.55 s broad (1H) H^{2}; 7.86 dd (2H, arom.) H^{4,6} ; 7.27 m (1H, arom.) H^{5}; 166.4 (C=O)
m-Xylene		76	
Ethylbenzene		70	3.52 m (2H) C-$\mathbf{H}_2$-COOH; 7.18 t (1H arom.) H^{4}; 7.38 d (2H, arom.) H^{2,6}; 7.30 d (2H, arom.) H ^{3,5}.
Diethylbestrol	3-Phenyl-propyl-3-ona (207)	91	1.19 m (3H) CH_3; 2.87 q (2H) -CH_2-; 7.86 m (2H, arom.); 7.29 t (2H, arom.) H^{3,5}; 7,38 t (1H, arom.) ; 197.2 (C=O)
Styrene		95	
Stilbene	Benzoic acid + unidentified compounds	82	9.20 s broad (OH); 7.81 m (2H, arom.) H ^{2,6}; 7.41 m (2H, arom.) H ^{3,5}; 7.46 m (1H, arom.) H ^{4}; 169.9 (C=O)
Diphenylmethane		88	
Fluorene	Benzoic acid + unidentified compounds	85	9.22 s broad (OH); 7.89 m (2H, arom.) H ^{2,6}; 7.45 m (2H, arom.) H ^{3,5}; 7.56 m (1H, arom.) H ^{4}; 169.4 (C=O)
	Benzophenone (48.3)		7.57 m (4H, arom.) H ^{2,2*,6,6*}; 7.41 m(tt) (4H, arom.) H^{3,3*,5,5*}; 7.49 m (2H, arom.) H ^{4,4*}; 196.7 (C=O)

9-fluorenone (82.3)	7.31 m (2H arom) $H^{2,7}$; 7.38 m (qq) (2H arom) $H^{1,8}$; 7.53 m (4H) $H^{3,4,5,6}$; 192.80 (C=O)

3. Results and Discussion

Early attempts to oxidize alkylaromatic compounds with permanganate anion in two-phase $KMnO_4/R_4NX$/benzene/H_2O systems at temperatures above 60 °C were not significant and the use of crown ethers required 72 h to achieve yields of 75–80%.

The oxidation reactions were carried out in the hydrocarbon-water-KMnO4-catalyst system, or directly using cetytrimethylammonium permanganate; for the solid alkylaromatic derivatives, dichloromethane (CH_2Cl_2) was used as reaction solvent. The use of benzene is not recommended, not only because of its toxicity, but also due to the ostensible decrease of the reaction rate (4.2–5 h) and the yield of the products (terephthalic acid 63%, benzoic acid 72%), attributable to the poor solubility of the ionic pair $[R_4N]^+[\ MnO_4]^-$ in an apolar and lipophilic medium.

Several catalysts were investigated: cetyltrimethylammonium bromide, triethylbenzylammonium chloride, cetyltrimethylammonium permanganate, 18C6, tetrabutylammonium iodide. The most effective in the oxidation process, given their extractive properties and solubility in the organic phase, were cetyltrimethylammonium bromide and cetyltrimethylammonium permanganate, the latter being considered the most effective and versatile.

The reaction time in the presence of cetyltrimethylammonium salts is 1.5–2 times shorter, the increasing in yields being in the order of 15–20%. This is explained by an increasing of the solubility of the cetyltrimethylammonium permanganate, generated in situ or added to the reaction mixture, in the organic phase and therefore in an increasing of the transfer capacity towards the organic solvent-water interface zone, where the oxidation process of the alkylaromatic derivatives initially takes place, but also by a decrease of the autocatalytic decomposition processes of the ammonium permanganate salt. The experimentally observed correlation between the yield of the oxidation products and the rate of the reaction is described in [29], depending on the nature (lipophilicity) of the catalyst.

As the amount of catalyst increases (more than 6–7% relative to the oxidant) the reaction time decreases slightly due to the limited solubility of cetyltrimethylammonium permanganate in the organic phase, and the yields of the products decrease due to the adsorption of the salts of the carboxylic acids on the surface of MnO_2, and to the inevitable decomposition of the catalyst in the aqueous phase. In some cases the increase in yield is favored by the use of a slight excess of oxidant (10–12%). An excess (20%) causes a significant decrease in yields.

By varying the volumes of the phases and the amounts of reactants, the optimum ratios ArH:$KMnO_4$:H_2O:catalyst were found (Table 1). Values higher than the optimum generate poor results because the autocatalytic decomposition processes of the permanganate salts are favored. Lower values lead to a decrease in the reaction rate due to the low effective concentration of $KMnO_4$ in the aqueous phase-organic phase interface, where the oxidation of water-soluble intermediates takes place. The general characterization of obtained derivatives are shown in (Table 2).

The potential mechanism of oxidation of aromatic hydrocarbons in phase transfer catalysis conditions is represented in Figure 1.

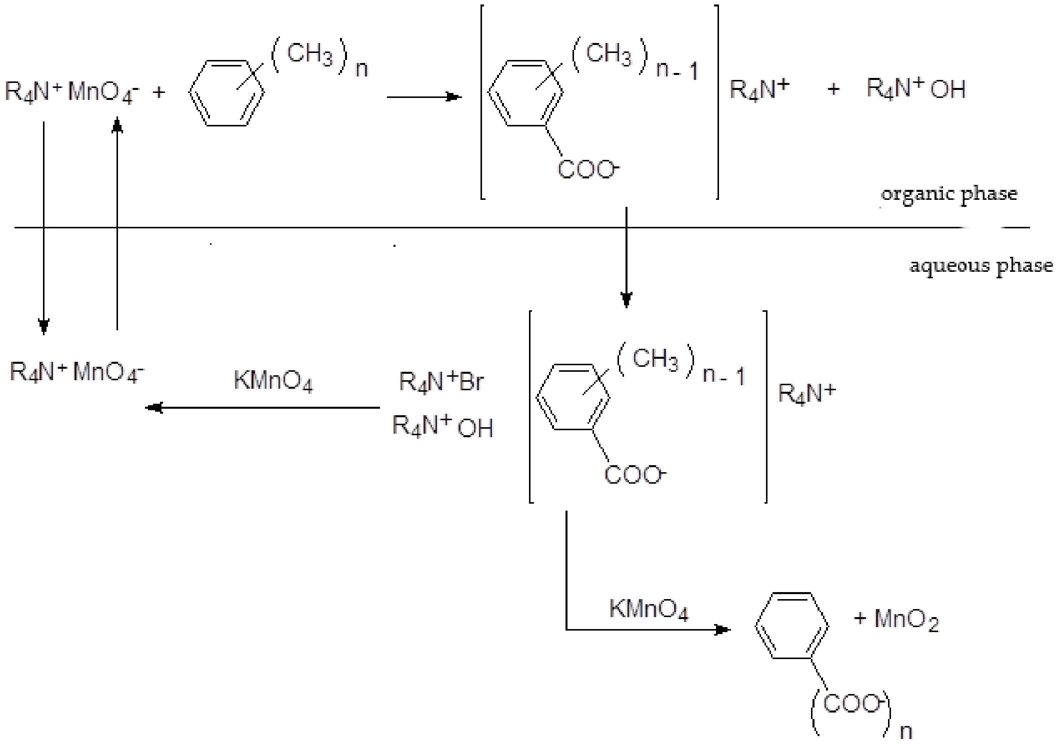

Figure 1. Mechanism of oxidation of aromatic hydrocarbons in phase transfer catalysis conditions using cetyltrimethylammonium permanganate.

4. Conclusions

The proposed oxidation method for alkylaromatic substrates, using quaternary ammonium salts as catalysts and specifically the cetyltrimethyammonium permanganate salt, is characterized by its efficiency and has some operational advantages compared to the classical non-catalytic oxidation in the presence of $KMnO_4$: -Obvious reduction of the reaction time by 15–20 times, increasing the effectiveness of the process. Reduction in the volume of the reaction mixture by 5 times (for 0.1–1.0 mmolar processes), with minimal losses due to adsorption phenomena on MnO_2; -Increases in yields up to 80–90% and a high degree of purity of the products obtained, minimizing the degradation of the aromatic core; -Use of commercially available, non-toxic solvents and the use of simple manipulative techniques. The methodologically simple process constitutes a useful method at laboratory scale due to its simplicity, ease of manipulation, operational safety and the excellent yields (80–93%) that are achieved, without the need to use expensive catalysts or conditions. This way of obtaining aromatic acids and carbonyl derivatives can also be used in Organic Synthesis laboratory practices in undergraduate and graduate university teaching programs in order to develop an ecologically responsible vision.

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