

# Oxidation of alkyltrimethylammonium salts with herbicidal anion

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## Introduction

One of the main problems of the agriculture is the presence of unwanted plants in the crops, which reduces harvest yield. The weeds compete with crops for light, water and mineral salts, thus increasing the costs of agricultural production, while decreasing the harvest. In order to maximize the production capacity per unit of farming area, plant protection products are applied, 90% of which are chemical formulations. Among many substances of herbicidal activity available on the market, special attention shall be paid to phenoxyherbicides, which include: 4-chloro-2-methylphenoxyacetic (MCPA), 2,4-dichlorophenoxyacetic (2,4-D), 2-(4-chloro-2-methylphenoxy)propionic (MCPP) and 4-(4-chloro-2-methylphenoxy)butyric (MCPB) acid [1]. Undeniable advantages of application of these herbicides is their high biological activity and selectivity, which helps to destroy the selected weed species with no negative impact on crops. Despite many attractive benefits, herbicides bring certain disadvantages, which mainly include their toxicity, high soil persistence and weeds gaining resistance to herbicides [2, 3]. In order to reduce the negative environmental impact of herbicides, it is possible to modify the existing and commonly used herbicides. Such an approach resulted in reports on herbicidal ionic liquids in the literature in 2011 [4]. The salts with the following anions were described: MCPA [4÷7], 2,4-D [8÷9], MCPP [10], MCPB [11] and 4-CPA [12]. The presence of cations with surface activity improves their wettability, which helps to reduce costs by using lower doses of herbicidal ionic liquids in relation to their commercial counterparts [4, 5].

Multifunctional herbicidal ionic liquids were also identified such as e.g. growth regulators and herbicides [13÷15]. However, the problem – liquidwaste from washing sprayers, emptied packages and disposal of the expired plant protection product – remains. Due to rather high concentrations of active substances, biological methods are unsuccessful. The only solution is to apply physical, electrochemical or chemical methods [16÷18]. They are often used as a pre-treatment before the biodegradation. A chemical method that allows a quick degradation of active substances is oxidation with strong oxidizing agents, e.g. potassium manganate(VII) [19] or ozone [20]. The application of the ozonation process provides good efficacy of pesticide degradation, even in diluted aqueous solutions. Moreover, this method is free of hazardous products of the oxidizer decomposition [21÷24].

This study checks the susceptibility of alkyltrimethylammonium salts with herbicidal anions: MCPA, MCPP, 2,4-D to strong oxidizing agents such as potassium manganate(VII) and ozone in aqueous solutions.

## Experimental part

The ozonation was conducted in a semi-continuous glass reactor of 500 cm<sup>3</sup> volume by passing ozonised gas of a mass flow rate of

3.07 g/hour through 250 cm<sup>3</sup> of an aqueous solution with the 0.001 M concentration of the test compound. The compound concentration was chosen in such a manner to ensure its solubility in water, while the mass flow rate was selected to provide a continuous excess of ozone in the solution. Ozone was produced from oxygen in ozone generator BMT 802N (BMT Messtechnik GMBH). The mass flow rate of ozone was determined by means of iodometry. During the ozonation, samples for analysis were collected every 5 minutes (1 cm<sup>3</sup>, subsequently diluted tenfold and analysed by means of spectrophotometry). The phenoxyacetate content was determined using Spectrophotometer UV1601 (Rayleigh) at 229 nm wavelength for compounds with 2,4-D and MCPP anions and at 226 nm wavelength for MCPA. The content of cationic active substance for ionic liquids was determined by means of a two-phase titration (ISO 2871–2:1990). The solutions of phenoxyacetates were alkalisied to pH 7 and 12 by adding NaOH.

The permanganate index (oxygen consumption) was determined according to PN-EN ISO 8467:2001.

## Result discussion

Ozone is a very strong oxidizer (standard redox potential of O<sub>3</sub> is 2.07 V, while KMnO<sub>4</sub> is only 1.51 V). It is a more effective than normally used oxidizers and it decomposes into environmentally neutral products without causing secondary pollution. Ozonation in the aqueous solution causes ozone decompose into even stronger and less selective oxidizers – hydroxyl radicals. Most of the commercially available quaternary ammonium salts are resistant to ozone in the aqueous solutions [25]. This is especially true for tetralkylammonium salts. On the other hand, the decomposition of phenoxy acid herbicides is effective and well described in the literature [21÷24].

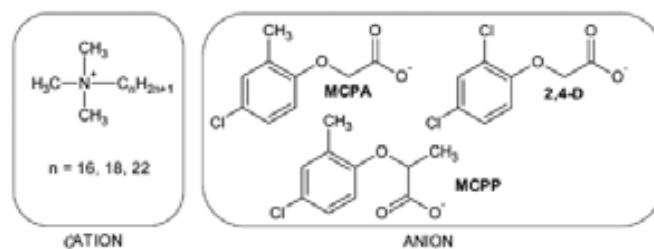


Fig. 1. Herbicidal ionic liquids used in tests

These studies involved the ozonation of aqueous solutions of sodium salts of MCPA, MCPP and 2,4-D, as well as herbicidal ionic liquids (Fig. 1).

The results obtained clearly show that the ozonation effects depend on the type of a herbicidal anion (Figs. 2÷4). The best degradation was observed for compounds containing a MCPP 2-(4-chloro-2-methylphenoxy)propionate anion. Slightly slower degradation was reported for a MCPA (4-chloro-2-methylphenoxyacetate) anion and much slower for a 2,4-D (2,4-dichlorophenoxyacetate) anion. The small difference in results for the MCPP and MCPA is due to the small structural differences between anions. On the other hand, the presence of a second chlorine atom in the phenoxy acid 2,4-D

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molecule withdraws the electrons so strongly from the aromatic ring that its reaction with electrophilic ozone is a much slower. The compound is almost completely degraded, but in a much longer time, which increases the costs. An alternative may be to pre-treat the solutions containing herbicidal ionic liquids with ozone and their subsequent biodegradation.

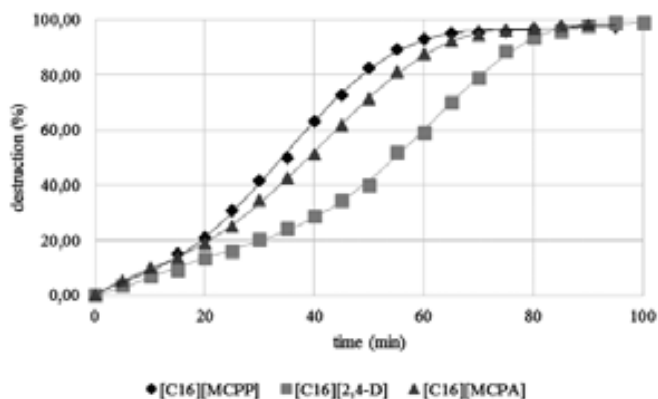


Fig. 2. Destruction of herbicidal ionic liquids with hexadecyltrimethylammonium cation

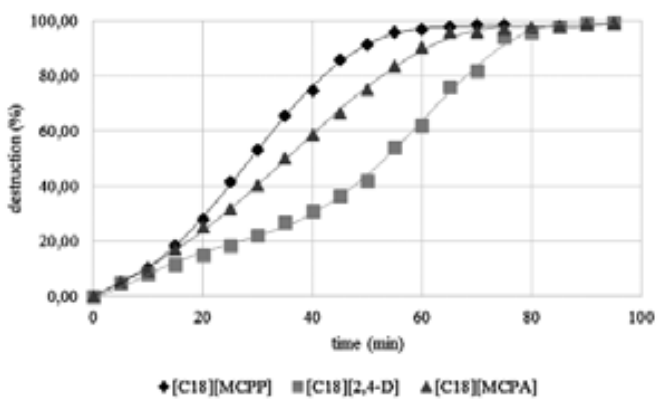


Fig. 3. Destruction of herbicidal ionic liquids with octadecyltrimethylammonium cation

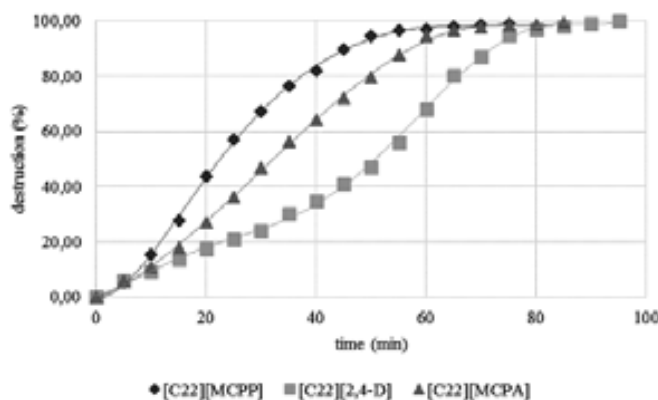


Fig. 4. Destruction of herbicidal ionic liquids with docosyltrimethylammonium cation

The effect of a cation on the decomposition rate of herbicidal ionic liquid is also noticeable. They react with ozone faster than sodium salts of phenoxyacids (Figs. 5 ÷ 7). This is probably related to a better solubility of ozone in ionic liquid solution (ionic liquids are good gas solvents [26]). On the other hand, the number of carbon atoms in an alkyl substituent of an alkyltrimethylammonium cation has virtually no effect on ozonation result, just as in the previous studies [20]. This can be explained by inertness of saturated alkyl substituents to ozone, which was confirmed by Corless [25].

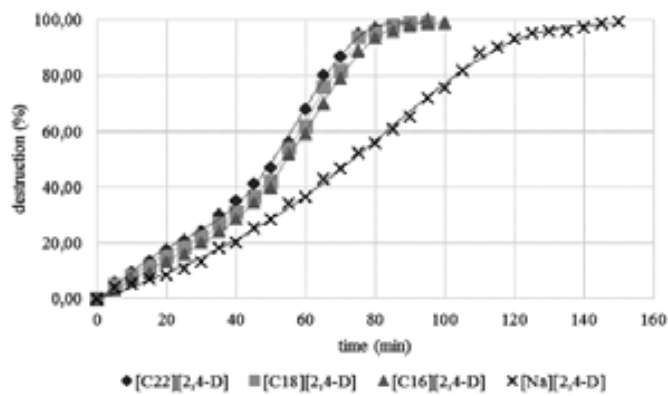


Fig. 5. Destruction of the salt with the anion of 2,4-D

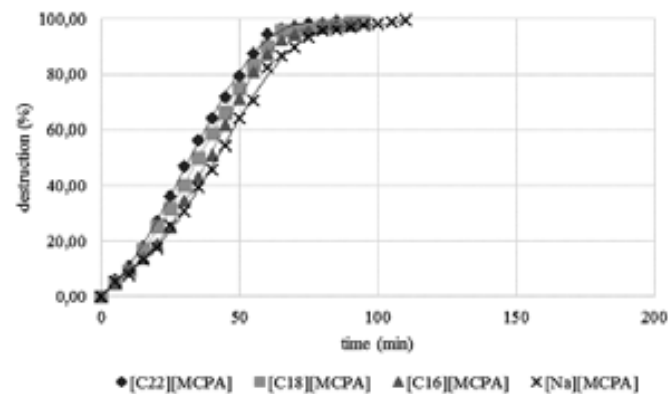


Fig. 6. Destruction of the salt with the anion of MCPA

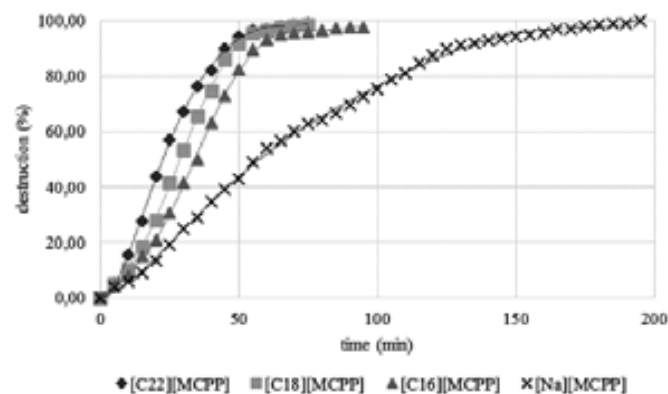


Fig. 7. Destruction of the salt with the anion of MCP

The permanganate index was determined for all the compounds as a measure of compound susceptibility to oxidation. It is known that the index cannot be treated as a measure of theoretical chemical oxygen demand, nor the total content of organic substance. Many organic compounds in this analysis is oxidised only partially, as it is oxidation for a specific time.

Table I

		Permanganate index, $I_{Mn}$ [mg O <sub>2</sub> /dm <sup>3</sup> ]		
	Anion	2,4-D	MCPA	MCP
Cation				
	C <sub>16</sub> H <sub>33</sub> (CH <sub>3</sub> ) <sub>3</sub> N <sup>+</sup>	1.16	8.96	11.08
	C <sub>18</sub> H <sub>37</sub> (CH <sub>3</sub> ) <sub>3</sub> N <sup>+</sup>	2.05	9.66	11.77
	C <sub>22</sub> H <sub>45</sub> (CH <sub>3</sub> ) <sub>3</sub> N <sup>+</sup>	3.45	10.43	12.48
	Na <sup>+</sup>	0.90	7.04	7.49

The salts with the 2,4-D anion have the lowest permanganate index, which indicates that the oxidation rate is low. On the other hand, the indices for compounds with MCPP are highest, as these compounds oxidise at the greatest rate. This is confirmed by results of the ozonation. However, potassium manganate(VII), in contrast to ozone, also oxidises a cation, as the permanganate index increases with the number of carbon atoms in an alkyl substituent, just as shown by the previous research [27].

### Summary and conclusions

Sodium salts of the MCPA, 2,4-D and MCPP, and herbicidal ionic liquids are oxidised in the presence of ozone and potassium manganate(VII). The ozonation results are affected both by an anion (the MCPP is destroyed most easily, while 2,4-D the hardest) and a cation (the salts with an organic cation are more easily oxidised than sodium ones). Ozone does not react with alkyl substituents (a substituent length does not affect the ozonation result), whereas potassium manganate (VII) oxidises them (the permanganate index increases with the number of carbon atoms in a cation). Oxidation is an effective method of degradation of herbicidal ionic liquids.

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