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# Herbicidal ionic liquid with dual-function

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## ABSTRACT

Herbicidal ionic liquid with dual functions has been synthesized and characterized (properties, chemical stability and biological activity). 2-Chloroethyltrimethylammonium (4-chloro-2-methylphenoxy)acetate prepared in an alkaline environment undergoes the reaction of dehydrochlorination by the E2 mechanism. This may be described as a specific instance of providing third generation ILs with high potential of application, which preserve both pesticidal properties: the herbicidal activity due to their anions and plant growth inhibition effect due to their cations.

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## 1. Introduction

Herbicidal ionic liquids (HILs)<sup>1–4</sup> represent a group of ionic liquids (ILs) with targeted herbicidal properties combined with specific physical and chemical properties. They are new phytopharmaceuticals representing the third generation of ILs.<sup>5–8</sup> Recently, also in the field of agrochemistry, novel hydrophobic fungicide forms of the active thiabendazole and imazalil have been suggested to be used as ILs.<sup>9</sup>

Much of the interest in ILs has been focused on their possible use as 'green' alternatives to volatile organic compounds. This claim usually rests on the fact that under ambient conditions ILs are generally non-volatile.<sup>10-12</sup> ILs are also known as 'designer solvents'. The physical, chemical and biological properties of these salts can be tuned to their particular function. Depending on the appropriate combination of cation and anion, they can be thermally and electrochemically highly stable, be liquid over a wide range of temperatures, and have a negligible vapour pressure. The different combinations of cation and anion correspond to the dual-functional nature of ILs, as exemplified by the earlier described by us 2chloroethyltrimethylammonium (2,4-dichlorophenoxy)acetate, manifesting a very good herbicidal activity and also used as a plant growth regulator.<sup>4</sup> (2,4-Dichlorophenoxy)acetic acid (2,4-D) is one of the earliest to be designed and a widely used herbicide in agriculture, but high volatility manifested by some of its formulations is a factor that limits the use due to high risk of damage off target broad-leaved plants. 2,4-D as the high volatile ester has been banned in some countries to reduce the risk of crop damage.<sup>13</sup> Various formulations of MCPA also differ in their volatility,<sup>14</sup> thus, the search for its new non-volatile forms carries practical importance.

The study presented here demonstrates reactivity, stability and biological activity of 2-chloroethyltrimethylammonium (4-chloro-2-methylphenoxy)acetate.

## 2. Materials and methods

2-Chloroethyltrimethylammonium chloride (CCC) was purchased from Sigma–Aldrich and had a purity of 98% while 97.5% pure MCPA was obtained from Organika Sarzyna SA. 2-Chloroethyltrimethylammonium (4-chloro-2-methylphenoxy)acetate [CC][MCPA] was synthesized by anion exchange reaction using the earlier described technique.<sup>1</sup>

## 2.1. Dehydrochlorination of CCC or [CC][MCPA]

In a round-bottom flask CCC (7.90 g, 50.0 mmol) or [CC][MCPA] (16.11 g, 50.0 mmol) was dissolved in distilled water (25 mL). Then, a solution of potassium hydroxide (2.81 g, 50.0 mmol) in distilled water, was added and the mixture was stirred for 24 h at 50 °C. Then, water was evaporated using a rotary evaporator and the residue was dissolved in isopropanol. The inorganic by-product—potassium chloride (3.73 g, 50.0 mmol) precipitated as a white solid and was separated carefully from the solution. After removal of isopropanol the product was dried under reduced pressure at 50 °C for 24 h. The reaction yield was 95% for





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trimethylvinylammonium chloride and 96% for trimethylvinylammonium (4-chloro-2-methylphenoxy)acetate.

2.1.1. Trimethylvinylammonium chloride. <sup>1</sup>H NMR (DMSO- $d_6$ , 298 K, 400 MHz)  $\delta$  ppm=3.40 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>), 5.54–5.57 (m, 1H, N<sup>+</sup>CH= CHH), 5.84 (d, *J*=15.3 Hz, 1H, N<sup>+</sup>CH=CHH), 6.83–6.91 (m, 1H, N<sup>+</sup>CH=CH<sub>2</sub>); <sup>13</sup>C NMR (DMSO- $d_6$ , 298 K, 100 MHz)  $\delta$  ppm=53.2, 111.3, 143.1. Elemental analysis calcd (%) for C<sub>5</sub>H<sub>12</sub>ClN (*M*=121.61) C 49.38, H 9.95, N 11.52; found: C 49.55, H 10.13, N 11.26. IR (KBr)  $\nu_{max}$ : 3429, 3085, 3018, 1658, 1634, 1603, 1491, 1473, 1414, 1401, 1071, 952, 895, 713, 543 cm<sup>-1</sup>. Decomposition temperature of 5% sample,  $T_{onset5\%}$ =185 °C and decomposition temperature of 50% sample,  $T_{onset}$ =228 °C (TG analysis).

## 2.2. Preparation of trimethylvinylammonium (4-chloro-2methylphenoxy)acetate [TMVA][MCPA]

In a round-bottom flask MCPA as acid (10.03 g, 50.0 mmol) was added. Then, a solution of potassium hydroxide (2.81 g, 50.0 mmol) in distilled water (30 mL) was added dropwise and the mixture was stirred at room temperature until the solution became homogeneous. Subsequently, a trimethylvinylammonium chloride (6.08 g, 50.0 mmol) was added and the mixture was stirred vigorously. After 24 h the water was evaporated using a rotary evaporator and the residue was dissolved in acetonitrile. The inorganic by-product—potassium chloride (3.73 g, 50.0 mmol) precipitated as a white solid and was separated carefully from solution. After removal of solvent the product was dried under reduced pressure at 50 °C for 24 h. The reaction yield was 97%. After recrystallization from acetone the product had a melting point of 120–122 °C.

2.2.1. Trimethylvinylammonium (4-chloro-2-methylphenoxy) acetate. <sup>1</sup>H NMR (DMSO- $d_6$ , 298 K, 400 MHz)  $\delta$  ppm=2.17 (s, 3H, CH<sub>3</sub>C=CCO), 3.30 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>), 4.69 (s, 2H, OCH<sub>2</sub>COO<sup>-</sup>), 5.50-5.53 (m, 1H, N<sup>+</sup>CH=CHH), 5.78 (d, J=15.1 Hz, 1H, N<sup>+</sup>CH= CHH), 6.67–6.75 (m, 1H, N<sup>+</sup>CH=CH<sub>2</sub>), 6.82 (d, J=8.7 Hz, 1H, CICCH= CHC), 7.16 (dd, <sup>1,2</sup>J=8.7 Hz, <sup>1,3</sup>J=2.5 Hz, 1H, ClCCH=CHC), 7.21 (d, J=2.7 Hz, 1H, CCH<sub>3</sub>CCH=CCl); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 298K, 100 MHz) δ ppm=15.8, 53.4, 65.1, 111.4, 112.9, 124.1, 126.3, 128.4, 130.0, 143.1, 154.9, 170.0. Elemental analysis calcd (%) for C14H20CINO3 (M=285.77) C 58.84, H 7.05, N 4.90; found: C 58.69, H 7.22, N 4.72. IR (KBr) *v*<sub>max</sub>: 3418, 3108, 3018, 2988, 2907, 1657, 1635, 1603, 1492, 1478, 1447, 1432, 1426, 1412, 1404, 1343, 1291, 1275, 1239, 1192, 1140, 1063, 954, 943, 893, 877, 801, 759, 710, 696, 620, 577, 554 cm<sup>-1</sup>. Decomposition temperature of 5% sample, Tonset5%=144 °C and decomposition temperature of 50% sample, Tonset=227 °C (TG analysis).

#### 2.3. Analysis of dehydrochlorination kinetics

The temperature was maintained with an accuracy of 0.1 °C. The concentration of substrates in water or methanol was determined using semi-automated reactor system for the laboratory synthesis (EasyMax<sup>™</sup>, Mettler, Toledo). The temperature of the reactor contents was controlled with an accuracy of 0.01 °C, using a Pt100 sensor. Connecting SevenMulti Mettler Toledo instrument, equipped with a suitable electrode, allowed for precise measurement of decrease in pH of the mixture as a result of the proceeding reaction.

The reaction order of *n* was calculated by the Ostwald-Zawicki method, using the equation:

$$n = 1 + \frac{\log\left(\frac{\tau_{1/2,l}}{\tau_{1/2,ll}}\right)}{\log\left(\frac{Cm_{0,l}}{Cm_{0,ll}}\right)}$$

where  $\tau_{1/2}$  is the reaction half-life time, and  $Cm_0$  is the initial concentration of reactants. Measurements of  $\tau_{1/2}$  were

performed both in water or methanol. Activation energy ( $E_a$ ) and entropy ( $\Delta S^{\neq}$ ) were calculated from the equation of Arrhenius and Eyring.

## 2.4. Greenhouse experiments

The seeds of common lambsquarters (*Chenopodium album*) were sown into soil-filled plastic pots to the depth of 0.5 cm. After emergence, the plants were thinned to five plants in each pot. The treatments were applied at fourth leaf stage using a spray chamber with Tee Jet 1102 flat-fan nozzles delivering 200 L of spray solution per 1 ha at 0.2 MPa pressure. The sprayer was moving above the plants at a constant speed of 3.1 m s<sup>-1</sup>. The distance from nozzles to the tips of the plant was 40 cm. The plants were treated once with a water solution of tested herbicides and they were placed in a greenhouse at the temperature of 20 °C, humidity of 60% and photoperiod (day/night hours) of 16/8. The tank mixture of commercial products, containing MCPA as sodium-potassium salt (Chwastox Extra 300 SL-300 g MCPA per 1 L) and plant growth regulator, Antywylegacz 725 SL (725 g of chlormequat chloride—CCC per 1 L) were used as the comparable treatments. The study was carried out in four replications in a completely randomized setup. After 2 weeks, the plants were cut to soil level and weighed (at 0.1 g accuracy). The reduction of plant fresh weight was measured, as compared to control (not sprayed plants).

#### 2.5. Field experiments

The field trials were carried out in winter wheat in 2010 and 2011 at the Experimental Station in Winna Gora, western Poland (the E:  $17^{\circ} 26'$ , N:  $52^{\circ} 12'$ ). Winter wheat was cultivated according to the local agricultural practice. The plot size was  $16.5 \text{ m}^2$ . The experimental design involved a randomized block with four replications. Water solutions of the tested herbicides were applied at the growth stage of first detectable node (BBCH 31) using a small plot spraying equipment with XR 11003 flat-fan nozzles with a water volume of 200 L ha<sup>-1</sup> and an operating pressure of 0.3 MPa. The standard treatments were the same as mentioned above in greenhouse experiments. The doses used in the field trial are presented in Tables 2 and 3. Weed control was evaluated visually 4 weeks after herbicide application using a scale of 0 (no control) to 100% (a complete weed destruction).

### 2.6. Statistical analyses

The data from field trials were analysed by ANOVA. Tukey's test was used for the comparison of averages and the lowest significant difference (LSD) was determined at the level of 5%. All calculations were performed using Agriculture Research Manager (ARM) software.

## 3. Results and discussion

Thermal analysis (DSC and TG) demonstrated that 2chloroethyltrimethylammonium (4-chloro-2-methylphenoxy)acetate [CC][MCPA] was thermally stable. Decomposition temperature of 5% sample,  $T_{\text{onset5\%}}$  was 198 °C and decomposition temperature of 50% sample,  $T_{\text{onset5\%}}$  amounted to 238 °C, the glass transition temperature was -5 °C. The compound involved a white salt, forming a hydrate manifesting melting temperature of 94–96 °C.<sup>1</sup> Thus, [CC] [MCPA] represented an IL. In DSC analysis neither melting temperature nor crystallization could be noted. However, the compound was chemically unstable: in presence of strong bases, such as KOH, NaOH or CH<sub>3</sub>ONa [CC][MCPA] underwent dehydrochlorination. The product of bimolecular dehydrochlorination of [CC][MCPA] involved

Table 1		
Summary of calculated	kinetic	parameters

Substrate	Solvent	Temp [K]	$k  [\mathrm{dm^3 \ mol^{-1} \ min^{-1}}]$	$\tau_{1/2}$ [min]	$E_{\rm a}$ [kJ mol <sup>-1</sup> ]	$\Delta H^{\neq}[k] \text{ mol}^{-1}]$	$\Delta S^{\neq}$ [J mol <sup>-1</sup> K <sup>-1</sup> ]	$\Delta G^{\neq} [kJ mol^{-1}]$
CCC	Water	293.2	0.011	952.4	85.6	83.2	-33.0	92.8
		303.2	0.034	295.0		83.1	-33.1	93.1
		313.2	0.105	95.5		83.0	-33.1	93.4
		323.2	0.261	38.3		82.9	-34.2	94.0
		333.2	0.734	13.6		82.8	-33.8	94.1
[CC][MCPA]		293.2	0.010	1041.7	81.7	79.3	-47.0	93.1
		303.2	0.027	377.4		79.2	-48.0	93.8
		313.2	0.080	125.5		79.1	-47.7	94.1
		323.2	0.206	48.6		79.0	-48.2	94.6
		333.2	0.528	18.9		79.0	-48.2	95.0
CCC	Methanol	298.2	0.215	46.5	124.6	122.1	117.9	87.6
		303.2	0.476	21.0		122.1	117.4	86.5
		308.2	1.156	8.6		122.0	117.8	85.1
		313.2	2.308	4.3		121.9	116.8	84.1
		318.2	5.061	2.0		121.8	116.6	83.0
[CC][MCPA]		298.2	0.227	44.0	100.2	97.8	36.8	87.0
		303.2	0.413	24.2		97.7	35.9	86.8
		308.2	0.819	12.2		97.6	36.0	86.4
		313.2	1.570	6.4		97.6	35.9	85.9
		318.2	2.794	3.6		97.5	35.4	85.7

Table 2

Efficacy of MCPA applied in winter wheat (average from 2010 to 2011)

Treatments	Dose (g h	Dose (g ha <sup>-1</sup> )		BRSNW	MATIN	
	CCC	MCPA	Weed cor	Weed control (%)		
[CC][MCPA]	245	400	83	85	49	
[CC][MCPA]	367	600	88	86	67	
CCC+MCPA	245	400	95	87	60	
CCC+MCPA	367	600	97	90	69	
CCC+MCPA	1232 <sup>a</sup>	900 <sup>a</sup>	92	98	79	

CENCY=Centaurea cyanus (cornflower), BRSNW=Brassica napus (winter rape volunteers).

MATIN=Matricaria inodora (scentless chamomile).

<sup>a</sup> Doses recommended in Poland.

## Table 3

The influence of different forms of CCC and MCPA on stems length and yield of winter wheat

Treatments	Dose (g ha <sup>-1</sup> )		Stems length (cm)		Yield (t $ha^{-1}$ )	
	ссс	MCPA	2010	2011	2010	2011
[CC][MCPA]	245	400	98.4	75.2	8.95	6.67
[CC][MCPA]	367	600	94.2	72.2	8.85	6.84
CCC+MCPA	245	400	98.4	67.7	8.75	7.41
CCC+MCPA	367	600	95.1	63.9	8.78	7.09
CCC+MCPA	1232 <sup>a</sup>	900 <sup>a</sup>	87.7	59.2	8.69	7.16
Untreated	0	0	100.4	79.3	7.85	6.89
LSD(5%)			4.23	4.59	0.39	0.19

<sup>a</sup> Doses recommended in Poland.

trimethylvinylammonium (4-chloro-2-methylphenoxy)acetate [TM VA][MCPA], as presented in Scheme 1.

[TMVA][MCPA] was also obtained with a 97% yield in the anion exchange reaction of potassium (4-chloro-2-methylphenoxy)acetate with trimethylvinylammonium chloride (Scheme 2).

[CC][MCPA] and [TMVA][MCPA] were soluble in water, methanol, DMSO; they were insoluble in acetone, hexane, toluene, ethyl acetate, diethyl ether, and slightly soluble in isopropanol, acetonitrile. [CC][MCPA] was not soluble and [TMVA][MCPA] was poorly soluble in chloroform.

Fig. 1 shows the concentration changes in time for the reaction of [CC][MCPA] and potassium hydroxide in water and methanol at 30 °C (303.2 K), with 0.100 mol  $L^{-1}$  initial concentration of reactants. In addition, for comparison dehydrochlorination of CCC was presented in Fig. 1.

In the performed experiments the calculated order of reaction (n) was 2, which supports the assumed mechanism of the reaction, i.e., E2 elimination.

The linear relationship in the Arrhenius plot demonstrated that the assumption of the kinetic equation and reaction order was correct. Kinetic parameters calculated for both reactions, including rate of elimination reaction (k), reaction half-life time ( $\tau_{1/2}$ ), activation energy ( $E_a$ ), enthalpy of activation ( $\Delta H^{\neq}$ ), entropy of activation ( $\Delta S^{\neq}$ ), Gibbs free energy of activation ( $\Delta G^{\neq}$ ) are summed up in Table 1.



Scheme 1. Elimination reaction of [CC][MCPA].



Scheme 2. Synthesis of [TMVA][MCPA].



Fig. 1. Concentration versus time for the decomposition of CCC and [CC][MCPA] in water and methanol at 30.0  $^\circ$ C (303.2K).

A type of solvent had a decisive influence on the rate of elimination reaction: for CCC k was more than 14 times higher, while for [CC][MCPA] it was about 16 times higher in methanol than in water. The effect of temperature on the reaction rate could be observed by comparing the measured half-life times of the reactants. An increase in the temperature of 40 K caused a decrease in  $\tau_{1/2}$  approximately from 1000 min to less than 20 min for CCC and [CC] [MCPA], when the elimination reaction was conducted in water. However, in methanol, an increase of 20 K led to an intense decrease in  $\tau_{1/2}$  to a few minutes only in both cases. The calculated values of activation energy  $(E_a)$  were average, if compared with the typical values of  $E_a$  and  $\Delta H^{\neq}$  found in the literature of the subject: they used to range between 20 and 150 kJ mol<sup>-1</sup>. The highest value of activation energy  $(E_a)$  was manifested by the elimination reaction of CCC in methanol, which corresponded to the high slope of Arrhenius plot (Fig. 2).



Fig. 2. Arrhenius plot of CCC and [CC][MCPA] E2 elimination reaction in water and methanol.

Decomposition of [CC][MCPA] required an activation energy lower by about 4 kJ mol<sup>-1</sup> in water and 24 kJ mol<sup>-1</sup> in methanol. The negative values for  $\Delta S^{\neq}$  in water indicated that the reaction conditions were unfavourable. The positive value of  $\Delta S^{\neq}$  in methanol indicated a high disorder of the transition state. Also the type of anion affected the  $\Delta S^{\neq}$  value. MCPA, as the large size anion, hindered a favourable arrangement of the whole molecule in the elimination reaction, resulting in decrease of the entropy of activation by about 15 J mol<sup>-1</sup> K<sup>-1</sup> in the water and up to about 80 J mol<sup>-1</sup> K<sup>-1</sup> in methanol. The calculated values of  $\Delta G^{\neq}$  demonstrated that the E2 elimination reaction was faster when the reaction environment involved methanol. The reactions carried out in methanol had values of Gibbs free energy of activation lower by about 7 kJ mol<sup>-1</sup> K<sup>-1</sup>. The results showed a higher chemical stability of [CC][MCPA] than that of CCC, especially in moderate temperatures in which it would be used.

## 4. Biological tests

The preliminary studies conducted in greenhouse showed that [CC][MCPA] had a similar herbicidal activity compared with commercial products containing MCPA as sodium—potassium salt, when doses of 400 g ha<sup>-1</sup> or higher were used. The results of this experiment are presented in Fig. 3. The weak herbicidal efficacy of [CC][MCPA] used at rates below 400 g ha<sup>-1</sup> as compared to the mixture of CCC+MCPA suggests that less of herbicide component was uptake and transported to the sites of action in plants. MCPA being auksin-like compound causes abnormal growth but it can increase the mass of plants, when low rates are used.



Fig. 3. Fresh weight reduction of common lambsquarters (*Chenopodium album*) by different forms of MCPA.

The herbicidal activity of [CC][MCPA] was also confirmed in the field experiments carried out in winter wheat in 2010 and 2011. The results shown in Table 2 indicated that the control of rape seed volunteers and scentless chamomile treated by [CC][MCPA] manifested a similar activity compared to the treatment with tank mixture of CCC and MCPA.

Efficacy of [CC][MCPA] against cornflower was slightly lower than the mixture of commercial products (CCC+MCPA).

The results of our experiments showed that [CC][MCPA] can be used in cereals for weed control as well as a plant growth inhibitor. The shorter stems were more resistant to lodging, then, this IL can be useful not only in weed management, but also can prevent the yield losses due to crop lodging. In our experiments the growth inhibition of winter wheat by [CC][MCPA] varied from 2 to 6%, compared to the untreated control (Table 3).

Tank mixture of commercial products (CCC+MCPA) gave similar effect in 2010 but was more effective in 2011 when they were affected by dramatically low amount of rainfall in the spring.

[CC][MCPA] was selective to the winter wheat and had a positive influence on yield of winter wheat in 2010 but in 2011 we did not find out this effect, probably due to the drought in spring when the treatments were applied.

[CC][MCPA] may be described as a specific instance of third generation ILs with high potential of application, which preserves both pesticidal properties: herbicidal activity exerted by the anion and plant growth inhibition effect resulting from the cation.

## 5. Conclusion

2-Chloroethyltrimethylammonium (4-chloro-2-methylphenoxy) acetate [CC][MCPA] may be described as specific example of third generation ILs with a high potential of application. It was selective to winter wheat plants and had a positive influence on yield of grains.

The compound provides a new example of herbicidal ionic liquids with dual-function, herbicidal activity originating from the anion and plant growth inhibition effect reflecting action of the cation. The compound is non-volatile and shows thermal stability. However, it is unstable in alkaline environment, affected by dehydrochlorination. This is an example of a reaction following the E2 mechanism.

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