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Short communication

SHORT COMMUNICATION

**Coulometric–potentiometric determination of  $pK_A$  of several organic bases in propylene carbonate**

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**Abstract:** The  $pK_A$  values of protonated triethylamine, pyridine and 2,2'-dipyridyl in propylene carbonate (PC) were determined by applying the coulometric–potentiometric method and a hydrogen/palladium generator anode ( $H_2/Pd$ ). The investigated and reference base were titrated to 50 % with protons electro-generated from hydrogen-saturated palladium, in the presence of sodium perchlorate as the supporting electrolyte. The half-neutralization potentials  $E_{1/2(x)}$  and  $E_{1/2(st)}$  of the investigated and standard base, respectively, were measured using a glass–SCE pair. The obtained  $pK_A$  values were compared with those reported in the literature.

**Keywords:** coulometry;  $pK_A$  of base; propylene carbonate; hydrogen/palladium electrode.

INTRODUCTION

There are only a few papers in the literature concerning the determination of the  $pK_A$  of bases in PC.<sup>1–3</sup> The presented procedures for the determination of  $pK_A$  values are based on the potentiometric titrations of bases with a standard solution of perchloric or hydrochloric acid. The  $pK_A$  values for protonated amines reported in the literature differ considerably between one another.<sup>2,3</sup>

PC is an aprotic dipolar solvent which has some advantages ("environmental friendly" solvent) over other protophobic solvents such as acetone or acetonitrile. This solvent has been recommended as a medium for electrochemical investigations<sup>4</sup> and acid base titrations.<sup>5–8</sup> The principal disadvantage of PC, is that it hydrolyzes fairly rapidly in the presence of strong acids. In previous papers<sup>7,8</sup> it was shown that the use of a standard perchloric acid solution for titration of bases

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in PC can be avoided by generating perchloric acid coulometrically at a H<sub>2</sub>/Pd electrode. Furthermore, a H<sub>2</sub>/Pd electrode was applied as a generator electrode for the determination of the autoprotolysis constant of PC<sup>9</sup> and other aprotic solvents,<sup>10</sup> as well of protonization constants of electrolytes in ketones.<sup>11–12</sup> The aim of this work was to confirm whether the coulometric–potentiometric method and a hydrogen/palladium generator electrode can be employed for the determination the pK<sub>A</sub> values of some organic bases in PC.

#### EXPERIMENTAL

##### *Apparatus and electrodes*

The apparatus and electrodes used in this study were described earlier.<sup>10</sup>

##### *Reagents and solutions*

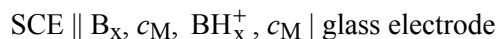
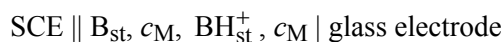
All chemicals were of p.a. purity (Merck and Fluka). Propylene carbonate was distilled under reduced pressure (b.p. about 80 °C) before use. The supporting electrolyte was a 0.10 mol dm<sup>-3</sup> solution of sodium perchlorate in PC. The liquid bases triethylamine and pyridine were dried over fused potassium hydroxide and then distilled under reduced pressure. An appropriate amount of a base was weighed into a volumetric flask, dissolved in PC and then diluted to the mark. The base concentration (0.010 mol dm<sup>-3</sup>) was checked by titration with protons generated at a H<sub>2</sub>/Pd electrode, with potentiometric detection of the equivalence point.

##### *Procedure*

A base solution (2.00 ml) and the sodium perchlorate solution (18.00 ml) were put into the anode compartment of the electrolytic vessel. The sodium perchlorate solution was put into the cathode compartment to the same level. The auxiliary electrode (a platinum wire) was immersed in the catholyte. The generator H<sub>2</sub>/Pd anode and the electrode pair glass-modified SCE were immersed in the anolyte. The current was switched on, and H<sup>+</sup> ions were generated at the H<sub>2</sub>/Pd anode in the amount required to half-neutralize the reference base (investigated base) solution. Titration of the base (0.0010 mol dm<sup>-3</sup>) was performed at a constant current (3.0 mA). After thermostating at 25.0±0.1 °C, the potential was read.

#### RESULTS AND DISCUSSION

The dissociation constants of protonated triethylamine, 2,2'-dipyridyl and pyridine in PC were determined in the following cells:



The standard and investigated base at the same concentration  $c_{\text{M}}$  were titrated coulometrically to half-neutralization with protons generated by the anodic oxidation of hydrogen dissolved in palladium in presence of sodium perchlorate as the supporting electrolyte. The half-neutralization potentials  $E_{1/2(\text{st.})}$  and  $E_{1/2(\text{x})}$  of the standard and investigated base, respectively, were measured by a glass–SCE electrode pair. The pK<sub>A</sub> value of the studied base was calculated according to the following equation:

$$pK_{A(x)} = pK_{A(st)} + (E_{1/2(x)} - E_{1/2(st)})/0.059$$

where  $pK_{A(st)}$  represents the dissociation constant of the standard base 1,3-diphenylguanidine ( $pK_{A(st)} = 16.98$ ).

The  $pK_A$  values of the investigated bases determined coulometrically using a  $H_2/Pd$  anode and a  $0.10 \text{ mol dm}^{-3}$  sodium perchlorate as the supporting electrolyte, as well as the literature data obtained by other experimental techniques, are summarized in Table I.

TABLE I. Dissociation constants of protonated organic bases obtained by coulometry at  $25.0 \pm 0.1 \text{ }^\circ\text{C}$  (supporting electrolyte,  $0.10 \text{ mol dm}^{-3}$  sodium perchlorate in propylene carbonate; generation current  $3.0 \text{ mA}$ )

Base	$pK_A \pm SD^a$	$pK_A$ , literature data <sup>2</sup>
Triethylamine	$17.28 \pm 0.09$	17.94
2,2'-Dipyridyl	$13.20 \pm 0.07$	–
Pyridine	$11.32 \pm 0.10$	11.92

<sup>a</sup>Standard deviation; number of determinations: 5

No data have been published in the literature for 2,2'-dipyridyl. The experimental  $pK_A$  value for 2,2'-dipyridyl obtained in this study by coulometry is  $13.20 \pm 0.07$ . The  $pK_A$  values for pyridine and triethylamine determined by the herein proposed procedure are lower by approximately  $0.60 \text{ pK}$  units than those obtained by the classic potentiometric method.<sup>1</sup> This can be explained by the different conditions of the investigation in the present work in comparison with those applied by other authors.

In the herein proposed procedure, the use of a  $H_2/Pd$  anode as the source of hydrogen ions in the coulometric determination of the dissociation constants of bases in PC makes this simpler than the classical method. The oxidation of hydrogen generates "dry" hydrogen ions, hence, as the introduction of a titrant into the solution is avoided, the titrated volume and the ionic strength remain unchanged. Particularly, since the ionic strength of the solution in PC cannot be calculated, the coulometrically determined acid dissociation constants of protonated bases are only valid for the applied supporting electrolyte, sodium perchlorate at a concentration of  $0.10 \text{ mol dm}^{-3}$  and thus represent conditional dissociation constants.

Based on the values of the dissociation and homoconjugation constants of acids in PC and acetonitrile, it was shown that an enhanced polarity of the aprotic solvent is favorable for the dissociation of the cationic acids and that PC is a somewhat stronger base than acetonitrile.<sup>1</sup> In accordance with this consideration, the  $pK_A$  values of bases in PC determined either by coulometry or the classic method are smaller than those obtained in acetonitrile.<sup>2</sup>

PC has a small autoprotolysis constant, a relatively high permittivity and dipole moment, as well as a pronounced differentiating effect, relative to many electrolytes. On account of these properties, PC is suitable for the determination of mixtures of bases. A differential titration of bases in this solvent is only pos-

sible if the difference between the  $pK$  values of the bases in the employed solvent is sufficiently high. From this point of view, the conditional dissociation constants of protonated bases in PC are important physico-chemical parameters, which can be used for predicting the conditions for the differential coulometric-potentiometric titration of bases in mixtures in this solvent.

#### CONCLUSIONS

The conditional dissociation constants of triethylamine, pyridine and 2,2'-dipyridyl in propylene carbonate were determined by applying the coulometric-potentiometric method and a hydrogen/palladium generator anode. Employing this procedure, the preparation of a standard solution of perchloric acid, which is unstable in this solvent, is avoided and the effect of dilution of the solution in the course of the titration is eliminated. This method is simpler than the classical potentiometric method.

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#### ИЗВОД

#### КУЛОНОМЕТРИЈСКО-ПОТЕНЦИОМЕТРИЈСКО ОДРЕЂИВАЊЕ $pK_A$ НЕКИХ ОРГАНСКИХ БАЗА У ПРОПИЛЕНКАРБОНАТУ

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Применом кулонометријско-потенциометријске методе и водоник-паладијумове генераторске електроде одређене су  $pK_A$  вредности протонисаног триетиламина, пиридина и 2,2'-дипиридила у пропиленкарбонату. Испитивана и референтна база титрисане су кулонометријски до 50 % протонима добијеним анодном оксидацијом водоника раствореног у паладијуму у присуству натријум-перхлората као основног електролита. Полу-неутрализациони потенцијали ( $E_{1/2(x)}$  and  $E_{1/2(st.)}$ ) испитиване и стандардне базе мерени су применом електродног пара стаклена електрода-ЗКЕ. На основу вредности полу-неутрализационих потенцијала и  $pK_{A(st)}$  вредности стандардне базе израчунате су константе дисоцијације испитиваних база. Добијене  $pK_A$  вредности упоређене су са литературним подацима.

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