

## Physico-Chemical Characterization of Some Diquaternary Salts of 4,4'-Bipyridine

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The paper presents a study on the physicochemical properties of some new symmetrical diquaternary salts of 4,4'-bipyridine. The properties refer to the acid-basic and thermal behavior of these compounds. The chemical stability of these salts in solution was found to be pH dependant. Thus, in the basic medium they converted into amphionic compounds of the *N*-ylide type and the equilibrium between salt (acid character) and *N*-ylide (basic character) was observed. The acid-basic equilibrium was made evident by pH-meter titrations. The thermal stability was studied by the thermogravimetric analysis under dynamic temperature conditions. The complexity of degradation as a consequence of chemical structure was revealed and the kinetic and thermodynamic parameters of the degradation were determined.

### Key words

diquaternary salts of 4,4'-bipyridine  
acido-basic behavior  
thermal stability

## INTRODUCTION

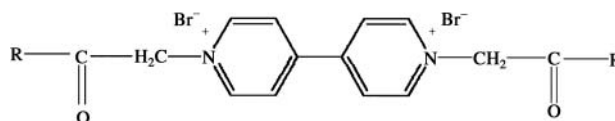
A significant property of 4,4'-bipyridine is the formation of diquaternary salts referred to as »viologens«. This name comes from their property of changing color under the action of some physical factors, such as light. The salts have attracted attention of scientists for being used as electron carriers, model systems in photosynthesis, herbicides,<sup>1–9</sup> cardiovascular agents,<sup>10</sup> hypotensive, and neuromuscular agents.<sup>7–9,10</sup>

In a previous research work we studied the synthesis, structure and reactivity of some new salts of 4,4'-bipyridine ylides.

The objective of this work is to characterize these new compounds using the physical chemistry methods.

Among the methods of synthesis of symmetrical diquaternary salts derived from bipyridine mentioned in li-

terature,<sup>11–14</sup> the alkylation by halogenated derivatives seems to be the most convenient.<sup>15,16</sup> It involves treating the 4,4'-bipyridine with reactive halogenated derivatives in anhydrous solvents. Some  $\alpha$ -halogenated esters of acetic acid and phenacyl halides have been used for this purpose.<sup>17</sup> Elemental analysis data, and IR, <sup>1</sup>H-NMR spectra proved their structure,<sup>18</sup> as shown in Figure 1:



**S<sub>1</sub>** R = CH<sub>3</sub>O

**S<sub>2</sub>** R = CH<sub>3</sub>CH<sub>2</sub>O

**S<sub>3</sub>** R = C<sub>6</sub>H<sub>5</sub>

**S<sub>4</sub>** R = *p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>

**S<sub>5</sub>** R = *p*-CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>

Figure 1. The structure of symmetrical diquaternary salts of 4,4'-bipyridine.

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The following compounds were used in this study: *N,N'*-dicarbomethoxymethyl-4,4'-bipyridiniumdibromide (**S**<sub>1</sub>); *N,N'*-dicarboethoxymethyl-4,4'-bipyridiniumdibromide (**S**<sub>2</sub>); *N,N'*-diphenacyl-4,4'-bipyridiniumdibromide (**S**<sub>3</sub>); *N,N'*-bis(4-nitrophenacyl)-4,4'-bipyridiniumdibromide (**S**<sub>4</sub>); *N,N'*-bis(4-methoxyphenacyl)-4,4'-bipyridiniumdibromide (**S**<sub>5</sub>).

By dehydrohalogenation in basic medium, the cycloimmonium salts give cycloimmonium ylides of »zwitterion« structure, which are active as both nucleophilic agents and dipoles in cycloaddition reactions. Due to its nucleophilic character,<sup>19</sup> the ylide carbanion gives again the initial salt in the presence of a mineral acid. The study of the reaction of cycloimmonium salts with inorganic bases revealed their acid character and the basic character of cycloimmonium ylides, respectively, which allowed some conclusions on the structural stability of these salts and ylides. According to Ratts and co-workers,<sup>20,21</sup> the alkalinity and, hence, the nucleophilicity of an ylide may be estimated by means of the  $pK_a$  values of conjugated acids. The lower the  $pK_a$  value, the lower is the ylide basicity and the higher is its stability.

The stability of the salts was also followed by means of thermogravimetric analyses. The results obtained revealed a multi-step degradation developed by a complex mechanism involving aromatic ring openings, substituent detaching and releasing of small-molecule compounds. The kinetic parameters and thermogravimetric characteristics of each stage were estimated.

## EXPERIMENTAL

### Acido-Basic Behavior of 4,4'-Bipyridine Diquaternary Salts

An experimental study on the acid character of the diquaternary salts of 4,4'-bipyridine was performed by determining the  $pK_a$ -values of the salts and the  $pK_b$  values of the conjugated bases of diquaternary salts. The results afforded some correlations between these values, acidity and salt structures. The acid-basic characterization was made using

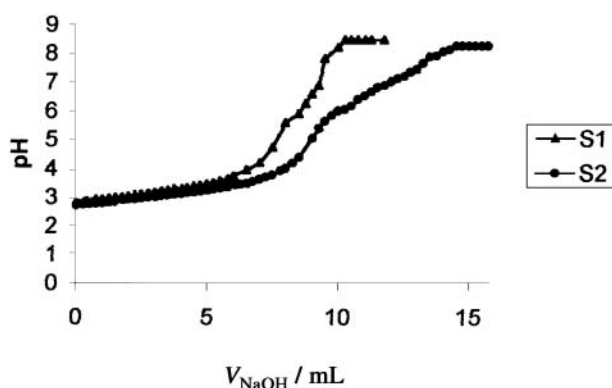


Figure 2. Titration curves of the compounds **S**<sub>1</sub>, **S**<sub>2</sub>.

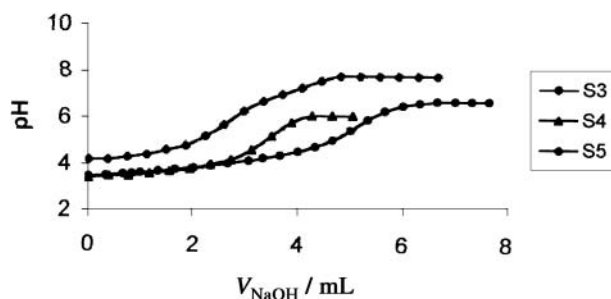


Figure 3. Titration curves of the compounds **S**<sub>3</sub>, **S**<sub>4</sub>, **S**<sub>5</sub>.

a pH-meter-potentiometer with a glass electrode, of the CONSORT C831-Belgium type.

A  $10^{-3}$  M aqueous solution of the conjugated acid (salt) was titrated with a  $5 \times 10^{-3}$  M NaOH solution. The titrations were performed using a pH-meter-conductometer with a glass electrode at 20 °C.

The equivalence pH values were estimated from the titration curves depicted in Figures 2 and 3.

The calculation relationships of  $pK_a$  were considered similarly to those for the titration of a weak acid ( $K_a \leq 10^{-5}$ ) with a strong base.

### Thermal Behavior of 4,4'-Bipyridine Diquaternary Salts

The paper reports the results of a kinetic study of nonisothermal degradation of 4,4'-bipyridine diquaternary salts. The kinetic data on their decomposition at the programmed increasing temperature allow the characterization of the conversion rate, thus providing information on the kinetic stability. Thermal characterization was performed by means of the MOM Budapest derivatograph with simultaneous recording of thermogravimetric TG, derived thermogravimetric DTG, differential thermal DTA, and temperature variation T.

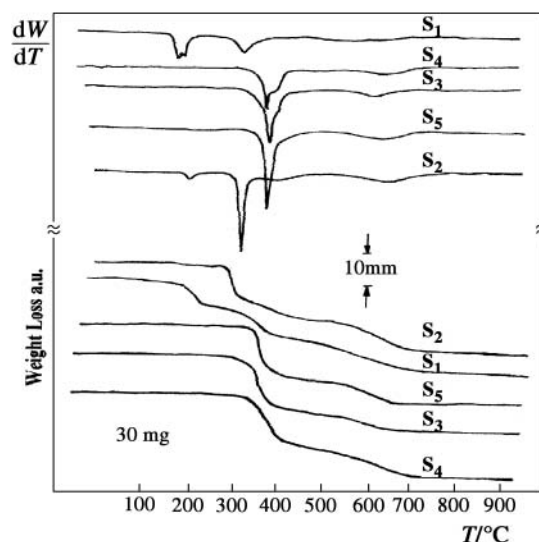


Figure 4. DTG and TG curves.

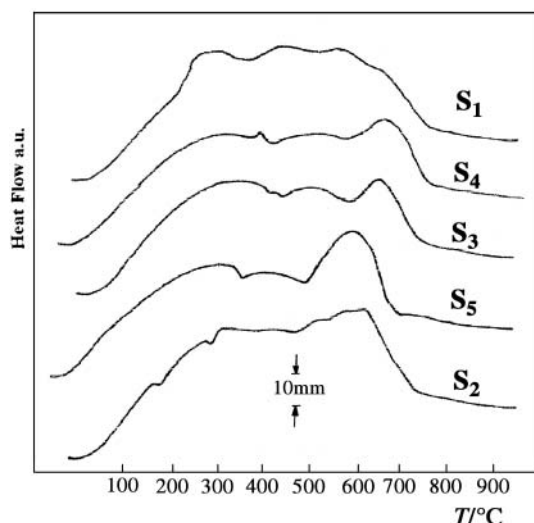


Figure 5. DTA curves.

Thermogravimetric data were processed automatically by applying the integral methods Coats-Redfern<sup>22</sup> and Reich-Levi<sup>23</sup> as well as the Freeman-Carroll differential method.<sup>24</sup>

The thermograms obtained by thermal degradation of the compounds under study are represented in Figures 4 and 5.

## RESULTS AND DISCUSSION

The  $pK_a$  values of the conjugated acids corresponding to the *N*-bisylides (4,4'-bipyridine quaternary salts) and the alkalinity constants of the *N*-bisylides are listed in Table I.

The data in Table I allowed the following conclusions:

- The basicity constant of compound **S<sub>2</sub>** is higher than that of compound **S<sub>1</sub>** due to the supplementary +*I* inductive effect of the –CH<sub>3</sub> group in the esteric residue.

- As revealed by the variation of the basicity constants of the salts,  $K_b$  shows the lowest value when the phenacyl *p*-substituent (NO<sub>2</sub> group) has an electron-withdrawing effect (**S<sub>4</sub>**) while with an electron-releasing group the alkalinity is the highest.

The alkalinity variation may be explained by the influence of different substituents on the ylide carbanion, which differently promote delocalization of the negative

charge. Thus, the  $pK_a$  of **S<sub>3</sub>** lower than that of **S<sub>1</sub>** can be explained by the amplification of the negative charge by the phenyl radical. The **S<sub>4</sub>** salt in the series **S<sub>3</sub>–S<sub>5</sub>** has the lowest  $pK_a$  due to the strong –*I* and –*E* effects promoting a supplementary delocalization of the anionic charge.

As revealed by the experimental findings, the 4,4'-bipyridine diquaternary salts can act as acid-basic indicators in neutralization reactions due to their stability and the property of changing color according to the pH: yellow in acid medium to violet (**S<sub>2</sub>, S<sub>3</sub>, S<sub>4</sub>, S<sub>5</sub>**) or pink (**S<sub>1</sub>**) in basic medium.

The following acidity series of the compounds was determined:



Figure 4 presents a complex thermal degradation, probably due to the succession of several exothermal degradation steps, as shown in Figure 5. The degradation proceeds in three stages in the case of salts **S<sub>1</sub>** and **S<sub>2</sub>** and in two stages with **S<sub>3</sub>, S<sub>4</sub>, S<sub>5</sub>**, the weight losses being different and dependent on the nature of substituents at the quaternary nitrogen, as can be seen in Tables II and III.

The greatest weight losses were observed in the first stage temperature range with compounds **S<sub>1</sub>, S<sub>2</sub>** and with **S<sub>3</sub>, S<sub>4</sub>, S<sub>5</sub>**, the melting points of the salts being situated within these temperature intervals.

As shown in Figure 4, the thermostability decreases from compound **S<sub>1</sub>** to **S<sub>4</sub>** according to the following scheme: **S<sub>1</sub> < S<sub>2</sub> < S<sub>3</sub> ≈ S<sub>5</sub> < S<sub>4</sub>**. It reveals that compound **S<sub>4</sub>** shows the highest thermal stability.

The estimation of the kinetic parameters from thermogravimetric data is based on the calculation methods (differential or integral methods). The thus obtained kinetic parameters in Tables IV and V were: apparent

TABLE II. Thermogravimetric data for degradation of **S<sub>1</sub>** and **S<sub>2</sub>**

Compounds	First stage	Second stage	Third stage
<b>S<sub>1</sub></b>	$\Delta T_1 = 140\text{--}245\text{ }^\circ\text{C}$ $W_I = 31.39\%$	$\Delta T_2 = 245\text{--}455\text{ }^\circ\text{C}$ $W_{II} = 38.37\%$	$\Delta T_3 = 455\text{--}675\text{ }^\circ\text{C}$ $W_{III} = 30.24\%$
<b>S<sub>2</sub></b>	$\Delta T_1 = 205\text{--}280\text{ }^\circ\text{C}$ $W_I = 40.74\%$	$\Delta T_2 = 280\text{--}450\text{ }^\circ\text{C}$ $W_{II} = 24.70\%$	$\Delta T_3 = 450\text{--}690\text{ }^\circ\text{C}$ $W_{III} = 34.56\%$

TABLE III. Thermogravimetric data for degradation of **S<sub>3</sub>, S<sub>4</sub>, S<sub>5</sub>**

Compounds	First stage	Second stage
<b>S<sub>3</sub></b>	$\Delta T_1 = 280\text{--}475\text{ }^\circ\text{C}$ $W_I = 76.82\%$	$\Delta T_2 = 475\text{--}745\text{ }^\circ\text{C}$ $W_{II} = 23.18\%$
<b>S<sub>4</sub></b>	$\Delta T_1 = 300\text{--}430\text{ }^\circ\text{C}$ $W_I = 63.15\%$	$\Delta T_2 = 430\text{--}675\text{ }^\circ\text{C}$ $W_{II} = 36.85\%$
<b>S<sub>5</sub></b>	$\Delta T_1 = 280\text{--}480\text{ }^\circ\text{C}$ $W_I = 70.88\%$	$\Delta T_2 = 480\text{--}660\text{ }^\circ\text{C}$ $W_{II} = 29.12\%$

TABLE I. The  $pK_a$ ,  $pK_b$ ,  $K_a$ ,  $K_b$ , values of conjugated acids

Compounds	R-	$pK_a$	$K_a$	$pK_b$	$K_b$
<b>S<sub>1</sub></b>	CH <sub>3</sub> O–	8.40	$3.981 \cdot 10^{-9}$	5.6	$2.511 \cdot 10^{-6}$
<b>S<sub>2</sub></b>	C <sub>2</sub> H <sub>5</sub> O–	9.10	$7.943 \cdot 10^{-10}$	4.9	$1.258 \cdot 10^{-5}$
<b>S<sub>3</sub></b>	C <sub>6</sub> H <sub>5</sub> –	7.84	$1.445 \cdot 10^{-8}$	6.16	$6.981 \cdot 10^{-7}$
<b>S<sub>4</sub></b>	<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> –	7.40	$3.981 \cdot 10^{-8}$	6.60	$2.511 \cdot 10^{-7}$
<b>S<sub>5</sub></b>	<i>p</i> -CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> –	9.34	$4.570 \cdot 10^{-10}$	4.66	$2.187 \cdot 10^{-5}$

TABLE IV. Kinetic data for thermal degradation of **S<sub>1</sub>**, **S<sub>2</sub>**

Compounds		First stage	Second stage	Third stage
<b>S<sub>1</sub></b>	<i>n</i>	2	2	1
	<i>E<sub>a</sub></i> <sup>(a)</sup>	119.98	113.15	112.27
	ln <i>A</i>	28.48	19.96	15.24
<b>S<sub>2</sub></b>	<i>n</i>	2	2	1
	<i>E<sub>a</sub></i> <sup>(a)</sup>	165.03	109.04	102.23
	ln <i>A</i>	40.52	18.44	14.59

<sup>(a)</sup>*E<sub>a</sub>* in KJ mol<sup>-1</sup>.TABLE V. Kinetic data for thermal degradation of **S<sub>3</sub>**, **S<sub>4</sub>**, **S<sub>5</sub>**

Compounds		First stage	Second stage
<b>S<sub>3</sub></b>	<i>n</i>	3	1
	<i>E<sub>a</sub></i> <sup>(a)</sup>	119.98	140.77
	ln <i>A</i>	28.48	19.521
<b>S<sub>4</sub></b>	<i>n</i>	2	1
	<i>E<sub>a</sub></i> <sup>(a)</sup>	229.30	116.81
	ln <i>A</i>	42.36	15.45
<b>S<sub>5</sub></b>	<i>n</i>	3	1
	<i>E<sub>a</sub></i> <sup>(a)</sup>	239.83	149.49
	ln <i>A</i>	46.33	20.22

<sup>(a)</sup>*E<sub>a</sub>* in KJ mol<sup>-1</sup>.

energy of activation (*E<sub>a</sub>*), reaction order (*n*) and the pre-exponential factor (ln *A*).

The reaction orders and energies of activation are about the same for the stages (**S<sub>1</sub>**–**S<sub>2</sub>**, **S<sub>3</sub>**–**S<sub>5</sub>**) involved, which indicates a similar degradation mechanism.

The degradation of the compound **S<sub>4</sub>**, proceeds differently in the first stage, as revealed by the different reaction order *n* = 2.

The last degradation stage, common to all compounds (**S<sub>1</sub>**–**S<sub>5</sub>**) is strongly exothermal and corresponds to the temperature higher than 430 °C, the process being probably similar to the thermooxidation of the residual product.

## CONCLUSIONS

The following conclusions can be drawn from the study on the compounds belonging to the class of 4,4'-bipyridine symmetrical diquaternary salts obtained by the quaternization of nitrogen atom with reactive halogenated derivatives:

– The acidity series was determined by means of the acid-basic behavior:



– A non-isothermal kinetic study on the thermal degradation of the mentioned compounds was performed and the following thermostability series was determined:



It was also found that the symmetrical diquaternary salts show a good biological activity on the bacteria (saprophyte, pathogen and facultative pathogen bacteria) *in vitro* at very low concentrations. The tests were done by the researchers of the Department of Organic Chemistry, Faculty of Chemistry, and the Center of Biological Researches of the University »Al. I. Cuza« Iassy. The results obtained indicate a strong antimicrobial action.<sup>25</sup>

In addition, the compounds were found to exert a significant phytotoxic action on the plants, as revealed by the tests on wheat seeds and plants.<sup>26</sup>

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## SAŽETAK

### Fizičko-kemijska svojstva nekih dikvaternih soli 4,4'-bipiridina

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U radu su opisana fizičko-kemijska svojstva nekih simetričnih dikvaternih soli 4,4'-bipiridina koja se odnose na ponašanja tih spojeva u kiselo-bazičnom mediju te na njihova termička svojstva. Opaženo je da kemijska stabilnost ispitivanih soli ovisi o pH otopine. U bazičnom mediju dikvaterne soli prelaze u *N*-ilide, a ravnoteža između tih spojeva koji imaju kiseli (soli) odnosno bazični (ilidi) karakter, dokazana je pH-metrijskim titracijama. Termička stabilnost soli ispitivana je termogravimetrijskom analizom kod dinamičkih uvjeta. Opisana je ovisnost razgradnje soli u odnosu na njihovu kemijsku strukturu te su određeni kinetički i termodinamički parametri razgradnje ispitivanih spojeva.