Oligomers with imidazolidinetrione elements of the structure obtained from parabanic acid and urea

Iwona Zarzyka[*)]

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Abstract: The paper is a review of the literature, including studies carried out with involvement of the author, concerning the high thermal stability of products formed by ring-opening of parabanic acid. A significant advantage of discussed reactions is that environmentally friendly alkylene carbonates have been applied as hydroxyalkylating agents. The cited results of structure and properties investigations of the products of urea and parabanic acid reaction with alkylene carbonates prove that the presence of carbamic groups has an impact on their high thermal stability.

Keywords: parabanic acid, urea, ethylene carbonate, propylene carbonate, hydroxyalkylation, structure, thermal stability.

Oligomery zawierające fragmenty strukturalne imidazolidynotrionu otrzymywane z kwasu parabanowego i mocznika

Streszczenie — Artykuł stanowi przegląd literatury, uwzględniający doniesienia z badań własnych, prowadzonych z udziałem autorki, na temat dużej odporności termicznej produktów powstających wskutek otwarcia pierścienia kwasu parabanowego, czyli produktów niezawierających w swej strukturze pierścieni trioksoimidazolidynowych. Istotną zaletą omawianych reakcji jest to, że jako czynniki hydroksyalkilujące zastosowano przyjazne ekologicznie węglany alkilenowe. Przytaczane wyniki badań struktury i właściwości otrzymanych produktów reakcji mocznika i kwasu parabanowego z węglanami alkilenowymi dowodzą, że obecność ugrupowania karbamidowego ma wpływ na ich wysoką odporność termiczną.

Słowa kluczowe: kwas parabanowy, mocznik, węglan etylenu, węglan propylenu, hydroksyalkilowanie, struktura, odporność termiczna.

Parabanic acid (1,3-imidazolidine-2,4,5-trione) [formula (I) in Scheme A] is a heterocyclic compound with nitrogen atoms. It is soluble in water, warm ethanol, methanol, *N*,*N*-dimethylformamide, or dimethylsulfoxide. It crystallizes reasonably only from water [1]. It is a dibasic acid with ionization constants $6.0 \cdot 10^{-7}$ and $1.6 \cdot 10^{-11}$ [2]. Parabanic acid melts at 242—243 °C with decomposition [2]. High decomposition temperature of parabanic acid makes it an interesting starting material in the synthesis of polymeric materials of improved thermal stability.

Due to high thermal stability, good electrical insulating properties and mechanical strength the polymers were used for the production of insulating tapes, insulating varnishes or thermally stable paints and fibers [3—5]. It should be noticed that apart from trioxoimidazolidine ring, aromatic rings — mainly benzene and naphthalene — are also present [3—11] in the structure of the polymers which contribute to their high thermal stability.

A review of the literature showed that the polymers with a ring of parabanic acid (trioxoimidazolidine ring) were not obtained using the acid or any of its derivatives. Instead, the ring was formed by polyreaction, *e.g.* polymerization of cyanoformamidyl isocyanate [6] or polycondensation of alkylene isocyanates with oxamidesters [7, 8] or alternatively by superstructure of trioxoimidazolidine ring on previously prepared polymers such as polyureas [9, 10] or polycarbodiimides [3, 11].

In my previous research I obtained monomers and polymers containing trioxoimidazolidine ring in their structure using directly parabanic acid for the synthesis. The monomers were obtained in hydroxyalkylation reactions of parabanic acid by oxiranes.

As it is shown in Scheme A, parabanic acid [formula (I)] in hydroxyalkylation reaction with ethylene or propylene oxides forms, depending on starting molar ratio of reagents (1:1 or 1:2), *N*-(2-hydroxyalkyl)parabanates [formula (II)] or *N*,*N*′-bis(2-hydroxyalkyl)parabanates [formula (III)], respectively [12].

The products were used to obtain esters and urethanes possessing trioxoimidazolidine ring [13], and next to obtain polyacrylates, polymethacrylates and polyuretha-

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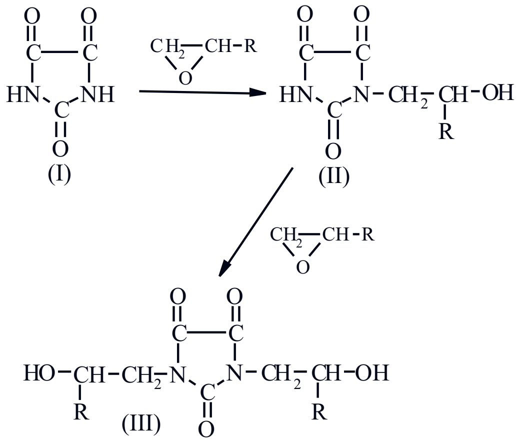
[*)] Rzeszow University of Technology, Department of Organic Chemistry, Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland.
E-mail: izarzyka@prz.edu.pl

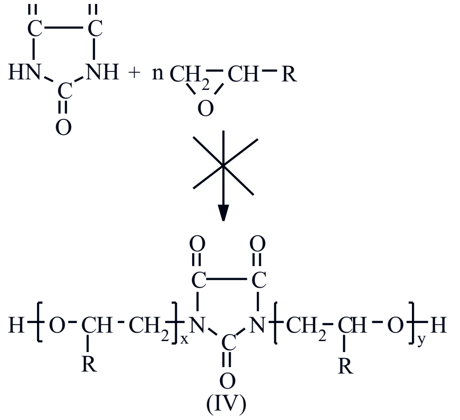


Scheme A

where: R = -H, $-CH_3$.

nes [14] as well as polyester resins with high thermal stability [15].

A comparison of thermal stability of polyacrylates and polymethacrylates possessing trioxoimidazolidine ring with those of classical aliphatic polyacrylates and polymethacrylates [16, 17], points to substantial effect of the presence of trioxoimidazolidine rings on increasing the thermal stability. It has also been noticed that in the presence of other rings in the polymer structure, *e.g.* benzene, as it is in the case of polyurethanes obtained using Izocyn T-80 and butane-1,4-diol, the replacement of butane-1,4-diol by *N*,*N*′-bis(2-hydroxyalkyl)parabanates brought about only a slight increase in the polymer thermal stability [14]. The same holds true when maleic anhydride, phthalic anhydride, diethylene glycol or *N*,*N*′-bis(2-hydroxypropyl)parabanate is used instead of propylene glycol [15]. Therefore an introduction of trioxoimidazolidine rings into the structure of polymer containing at the same time aromatic rings, only slightly increases its thermal stability.

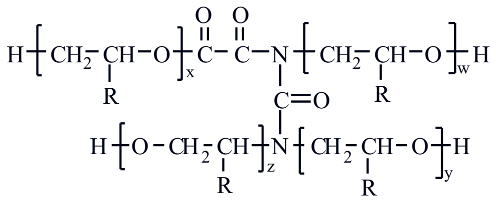


Scheme B

where: x + y > 2, R = -H, $-CH_3$.

The main problem during *N*,*N*′-bis(2-hydroxyalkyl)parabanates synthesis is easy trioxoimidazolidine ring opening with a slight change of conditions of parabanic acid reaction with oxiranes. Under the excess of oxiranes, in the presence of triethylamine (catalyst) or at elevated temperature (> 40 °C), as it is shown in Scheme B, parabanic acid does not form bifunctional polyetherols [formula (IV)].

It does not behave as other azacyclic compounds containing imide groups in the ring. Instead it opens a ring and formation of oligomeric products [formula (V)] takes place. In the case of the reaction with ethylene oxide the products [formula (V), R = H-, z = 0] are precipitated from the solution [18].



(V)

where: x + y + z + w = n = 2—10, R = -H, $-CH_3$.

In turn, in the reaction with propylene oxide, secondary amide groups present in the polymer product react with excess oxirane, resulting in the formation of liquid oligomer [formula (V), R = CH_3-, z ≥ 1] containing mainly tertiary amide groups [18, 19].

Mentioned above, easy opening of parabanic acid ring may be the easy explanation for the absence of the literature examples of the polymer synthesis methods using trioxoimidazolidine ring monomers.

A content of trioxoimidazolidine rings in the structure of product of the parabanic acid reaction with an excess of propylene oxide is from several to several dozen percent (up to 80 mol. %) but still the products show high thermal stability — the temperature of maximum decomposition is about 280 °C [20]. Their thermal stability is comparable with that of polyurethanes obtained with the participation of *N*,*N*′-bis(hydroxyalkyl)parabanates, in which trioxoimidazolidine rings have been preserved [14].

It was thought that the increased thermal stability of these products depends not on the presence of trioxoimidazolidine ring only, but also on the structure which is formed as a result of trioxoimidazolidine ring opening *i.e.* oxamidoester and carbamide groups linked by imide bond. Then oligomers containing separate oxamidoester and carbamide fragments in the structure should also exhibit high thermal stability.

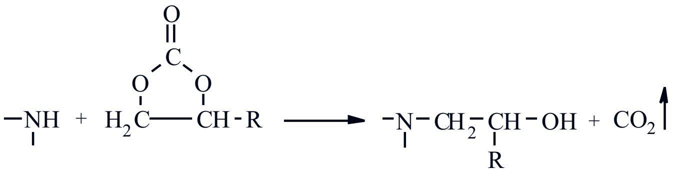
In this work the high thermal stability of the products formed as a result of parabanic acid ring opening *i.e.* the products, which do not contain trioxoimidazolidine rings in their structure have been discussed. Environmentally friendly alkylene carbonates have been used as the hydroxyalkylating agents.

Moreover, the influence of the presence of a carbamide groups on the high thermal stability of the products of the reaction of urea and parabanic acid with alkylene carbonates has been demonstrated.

Complex studies concerning the reactions of parabanic acid and urea with ethylene carbonate and propylene carbonate have been presented. The structure, composition and properties of the products were examined by instrumental methods *i.e.*: structure by ^{1}H NMR and ^{13}C NMR, IR, UV, MS, composition by AE, GC, GC-MS, MALDI-ToF and properties by GPC and TGA.

REACTIONS OF PARABANIC ACID WITH ALKYLENE CARBONATES

Alkylene carbonates, as it is shown in Scheme C, react with azacyclic compounds giving products of analogical structure to those obtained in the reaction with oxiranes [21, 22].



Scheme C

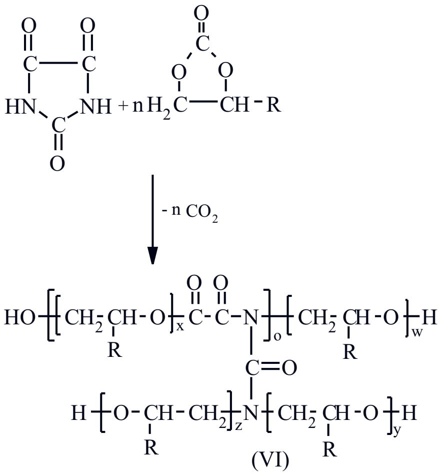
where: R = -H, $-CH_3$.

An additional advantage of alkylene carbonates in comparison with oxiranes is their incombustibility [23], non-toxicity and large polarity, so that they can be solvents for other reactants at the same time.

Therefore reactions of parabanic acid with alkylene carbonates take place in the absence of solvent because parabanic acid is well soluble in ethylene carbonate (EC) and propylene carbonate (PC). The reactions were conducted in the temperature range 120—180 °C, with potassium carbonate and diazabicyclo[2.2.2]octane (DABCO) as the catalysts, respectively [20, 24, 25].

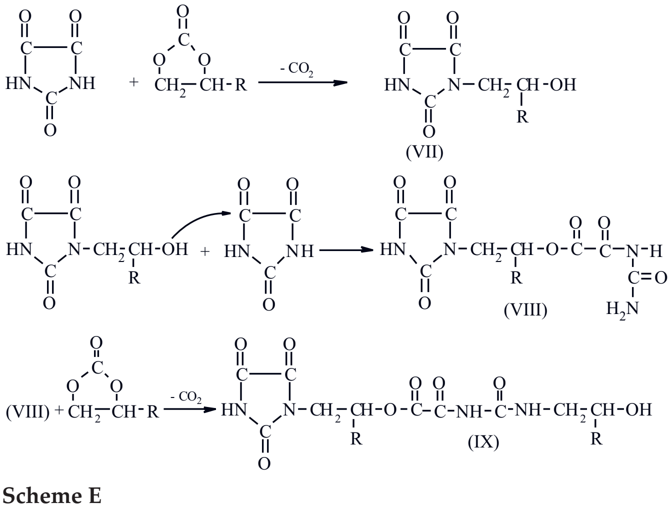
The reactions of parabanic acid with alkylene carbonates, shown in Scheme D, give similar products as these with oxiranes [18], *i.e.* an opening of trioxoimidazolidine ring and the formation of oligomers possessing the structure of [formula (VI)] is observed.

The structure of the products obtained has been examined by spectroscopic methods (spectroscopy ^{1}H NMR, IR and MALDI-ToF), what has been described in [20, 24, 25]. The analysis of ^{1}H NMR spectrum for the products obtained at starting molar ratio of parabanic acid to EC or PC equal to 1:1, showed the presence of signals at 6.5, 7.9 and 8.4 ppm, which are characteristic for the protons of primary and secondary amide groups and imide groups, respectively [24, 25]. The presence of primary and secondary amide groups can be explained by an opening of the acid ring and formation of compound given by formula (VIII) and consequently (IX) in Scheme E. Moreover, in ^{1}H NMR spectrum of the products of parabanic acid reaction with EC or PC the signals at 4.2 ppm and 4.6 ppm are presented, respectively. The first one comes from protons of methylene [formula (VIII) and (IX), R= -H] and the second from methine [formula (VIII) and (IX), R= $-CH_3$] groups, adjacent to ester group.



Scheme D

where: o = 1—4, R = -H, $-CH_3$.



Scheme E

where: R = -H, $-CH_3$.

The presence of structural fragments discussed above in the products obtained was also confirmed by IR spectra [24, 25], in which there were observed:

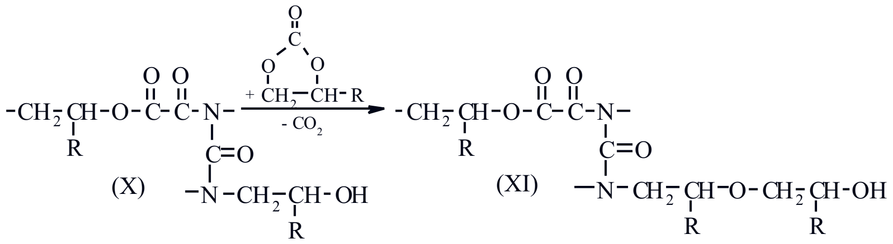
— I and II amide bands of secondary amide at 1670 and 1516 cm^{-1} (I and II amide bands of primary amide imposed on the I amide band of secondary amide),

— III amide band of the primary and secondary amide at 1410 and 1320 cm^{-1},

— valence vibration band of imides and esters C=O bond at 1720 cm^{-1},

— symmetric and asymmetric valence vibration bands of C-O bond in ester group at 1240 and 1180 cm^{-1}.

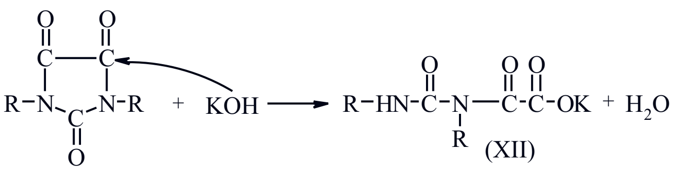
The primary amide groups disappear at molar excess of EC or PC relative to parabanic acid equal to 2, imide groups at 3-molar excess of PC and 4-molar excess of EC and secondary amide groups at 4-molar excess of PC [25] and 8-molar excess of EC [24]. The disappearance of secondary amide groups in the product structure when a greater excess of EC or PC is applied, results from the fact that reactivity of primary hydroxyl groups in reaction with EC is greater than that of secondary amide groups. Already at 2-molar EC or PC excess in relation to parabanic acid a band at about 1110 cm^{-1}, from C-O-C valence vibrations in ethers occurs in the IR spectrum of the products. The intensity of the band increases with an increase of alkylene carbonate excess in the reaction. It proves that consecutive reactions of the products' hydroxyl groups with unreacted alkylene carbonate shown in Scheme F run easier.



Scheme F

where: R = -H, -CH_3.

A content of trioxoimidazolidine rings preserved in the structure of parabanic acid and alkylene carbonate reaction products has been estimated on the basis of acid number (*AN*) determination. *AN* of the products were determined by titration with potassium hydroxide, based on, shown in Scheme G, reaction of hydroxide hydroxyl group with carbonyl group of trioxoimidazolidine ring, followed by opening of the ring and formation of *N*-hydroxyalkyl derivative of oxaluric acid [formula (XII)] [26].



Scheme G

where: alkyl or hydroxyl group.

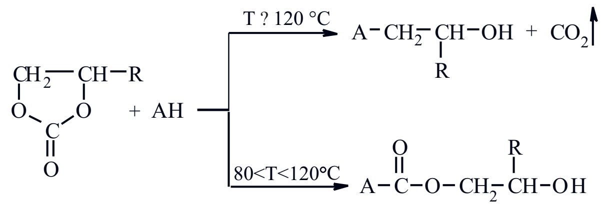
A comparison of experimental *AN* values for oligomeric products with those calculated theoretically (assuming that all acid rings have been preserved in oligomer structure) allows to determine the ring content of the products. The content of trioxoimidazolidine rings in oligomeric structure is generally small and depends on the kind of alkylene carbonate, its excess in the reaction, the reaction temperature and the amount of the catalyst. The most rings (36 mol. %) have been preserved for the products obtained with 2-molar excess of PC at 110—140 °C [25].

In other conditions the content of the rings is about 2 mol. % and increases with the increase of EC excess reaching the value of about 21 mol. % at 12-molar EC excess [24]. In the case of products obtained in the reaction with PC, the content of the rings is even smaller, increases slightly with PC excess and its maximal value is 8 mol. % in the product obtained at 10-molar excess of PC [25]. The product obtained at 12-molar PC excess did not contain trioxoimidazolidine rings in its structure (*AN* = 0).

Parabanic acid ring reacts with metal hydroxides and therefore the course of its reaction with alkylene carbonates cannot be controlled analogously as in the case of other azacyclic compounds such as melamine or isocyanuric acid [27, 28], *i.e.* by determining the content of unreacted carbonate. The analytical method is based on the reaction of alkylene carbonate with barium hydroxide, which can also react with trioxoimidazolidine rings present in the structure under these conditions, causing them to break down [18].

Therefore the other method for the reaction course control has been developed using IR spectroscopy. It has been observed that valence vibration bands of EC carbonyl groups (1800 and 1767 cm^{-1}) are situated at different range as compared with carbonyl group band position for parabanic acid (1832, 1785 and 1745 cm^{-1}) and for the product of the acid reaction with EC (1730 cm^{-1}). The bands originating from acid at 1832 and 1785 cm^{-1} disappear during the reaction and the third band shifts from 1745 cm^{-1} to 1730 cm^{-1}. By observing the decrease, and consequently disappearance of the band at 1800 cm^{-1} originating from EC in the spectrum of the reaction mixture it was possible to determine the end of the reaction [24]. The course of parabanic acid reaction with PC has been controlled in a similar way [25].

A qualitative analysis of the products of parabanic acid reaction with alkylene carbonates using MALDI-ToF spectroscopy indicated the presence of oligomers containing a few structural units of parabanic acid in their structure (trioxoimidazolidine rings or structures resulting from the opening of the ring). During the reaction with 8-molar or greater excess of EC or PC oligomers containing up to four units of this type are formed [20]. As it follows from the determined molar masses of the products (by GPC), they can contain two structural units of parabanic acid. Therefore the content of oligomers containing several structural units of the acid is small. However mainly the products containing only one parabanic acid unit are formed and these vary in the number of oxyalkylene units. In reactions of parabanic acid with 12-molar excess of EC — oligomers containing up to 11 oxyethylene units per 1 acid mole [20], and in reactions of the acid with 8-molar excess of PC — oligomers containing up to 9 oxypropylene units per 1 acid mole [20] have been obtained.



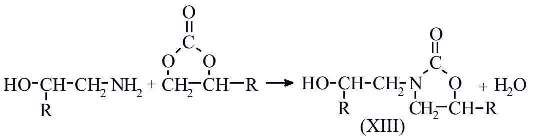
Scheme H

where: R = -H, -CH_3, AH — a compound containing mobile hydrogen atom.

The reactions with the participation of alkylene carbonates, as it is shown in Scheme H, can proceed bidirectionally, *i.e.* with evolution of carbon dioxide or with the preservation of carbonate group in the product structure.

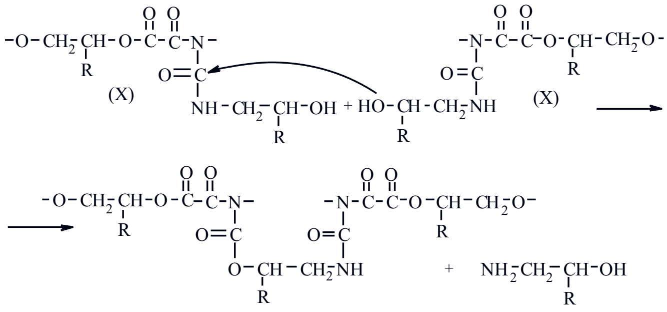
At 120 °C and above the reactions with alkylene carbonates should proceed with total evolution of carbon dioxide [21, 22]. The reactions with PC were conducted at 180 °C and despite this a part of carbonate groups have been preserved in the product structures by MALDI-ToF spectroscopy [20]. The cited above spectroscopic method is not suitable to confirm the presence of carbonate groups in the reaction products with the participation of EC, because molar mass of oxyethylene and carbonate groups is the same — 44 g/mol. But an incorporation of carbonate groups is indicated from the ^{1}H NMR analysis of the products of parabanic acid reaction with EC. A signal at 4.2 ppm is a multiplet resulting from the imposition of two triplets originating from the protons of methylene groups situated at carbonate and oxamidoester groups.

The hydroxyalkylation reaction of parabanic acid by EC or PC is accompanied by side reaction of alkylene carbonates with water resulting in obtaining of ethylene and propylene glycols, respectively and consequently with side reactions of the glycols with alkylene carbonates (GC) [24, 25]. In the presented in Scheme I reaction of aminoalcohol with alkylene carbonate leading to oxazolidinone (XIII) formation water is formed.



Scheme I

where: R = -H [*N*-(2-hydroxyethyl)oxazolidinone (OXON)], R = -CH_3 [*N*-(2-hydroxypropyl)-5-methyloxazolidinone (IPOX)].



Scheme J

where: R = -H, -CH_3.

In turn, aminoalcohols are formed by condensation of hydroxyalkyl derivatives of (X) as it is shown in Scheme J.

By determining the content of oxazolidinones in the products of parabanic acid hydroxyalkylation by alkylene carbonates, a contribution of these derivatives in condensation process has been estimated. In the case of parabanic acid hydroxyethyl derivatives the content of OXON depends on the EC excess, increases slightly with its increase and is within the range of 2.5—3.8 wt. %. In turn the content of IPOX in the products of parabanic acid hydroxyalkylation by PC reaction is about 0.1—0.5 wt. % and does not depend on the carbonate excess.

At lower starting molar ratio of parabanic acid to EC (1:≤4 mole), the resulting products are accompanied by a small amount of ethylene glycol (to 4 wt. %). At 8-molar or greater excess of EC subsequent by-products are present, *i.e.* di-, tri- and tetraethylene glycols in total amount not exceeding 18 wt. %. An increase in the reaction temperature slightly decreases the amount of by-products [24]. A content of propylene glycol and poly(propylene glycols) in the products of parabanic acid reaction with

PC, obtained at molar ratio of reagents 1:2 does not exceed 7 wt. %. An increase of PC excess is accompanied by gradual increase of by-products amount to 20 wt. %, but an increase in the process temperature while preserving the starting amount of PC, causes that the content of glycols decreases usually two times [25].

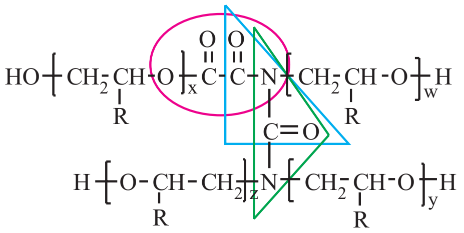
The products of parabanic acid reaction with EC or PC are characterized by high thermal stability, despite small content of trioxoimidazolidine rings in their structure. A temperature of maximum decomposition of the products is within the range of 240—260 °C [24] and 270—300 °C [25], respectively.

The results of investigations show that the presence of trioxoimidazolidine rings does not influence thermal stability of parabanic acid hydroxyalkylation products. The product obtained at molar ratio of parabanic acid and EC equal to 1:2, containing about 35 mol. % of the acid rings preserved is characterized by almost identical thermal stability as the product containing about 3 mol. % of the rings (the maximum decomposition temperature is 250 and 240 °C, respectively). Oligomers obtained in reactions of parabanic acid with an excess of EC contain up to 20 mol. % trioxoimidazolidine rings but show a slightly higher maximum decomposition temperature, *i.e.* 260 °C [20].

Hydroxyalkyl derivatives of parabanic acid, resulting from reaction of the acid with PC, in which the content of acid rings is lower or the rings are not present in the structure exhibit even higher maximum decomposition temperature equal to *ca.* 300 °C [20, 25].

It should be emphasized that molar mass of oligomers obtained in reaction of parabanic acid with alkylene carbonates does not exceed 800 g/mole (by GPC), which means that crosslinking process does not take place during the reaction. High thermal stability is therefore not related to crosslinked structure of the products, which would be possible due to their four-functionality.

In this way it has been shown that high thermal stability of the products of parabanic acid hydroxyalkylation by alkylene carbonates (esteramidoimidoetherols) does not result from the presence of trioxoimidazolidine ring but stems from the presence of structure being a consequence of the ring opening, consisting of carbamide and oxamidoester groups linked by imide bond, which are indicated in Scheme K.



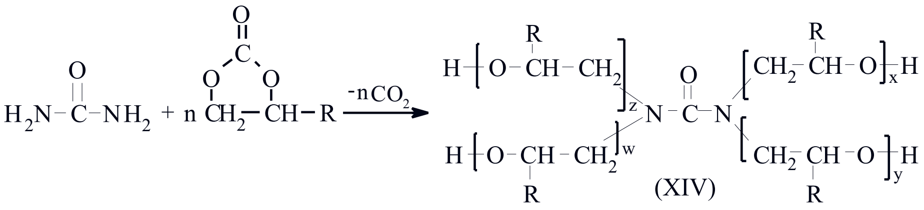
Scheme K

where: R = -H, $-CH_3$.

The accuracy of the above statement was proved by examining thermal stability of hydroxyalkyl derivatives of urea and oxamic acid, *i.e.* of the products containing in their structure carbamide and oxamidoester groups.

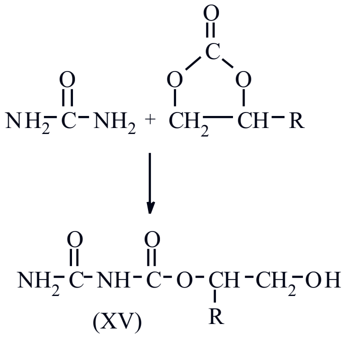
REACTIONS OF UREA WITH ALKYLENE CARBONATES

Reactions of urea with alkylene carbonates were conducted in the presence of potassium carbonate as a catalyst at 140—160 °C, expecting to obtain the products of the structure given by formula (XIV) in Scheme L [29, 30]. The attempts to use other catalyst instead of potassium carbonate, such as diazabicyclo[2.2.2]octane (DABCO) and zinc chloride have been made but their presence caused extension of the reaction time without reducing the occurrence of additional processes [29].



Scheme L

where: R = -H, $-CH_3$.



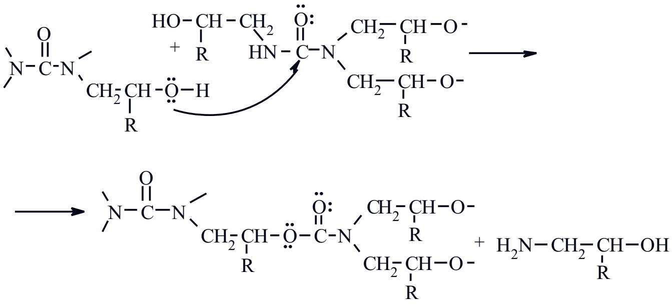
Scheme M

where: R = -H, $-CH_3$.

The mass balance and spectral analysis showed that the expected reaction (Scheme L) is accompanied by side processes:

— incorporation of carbonate groups in the product structure (Scheme M),

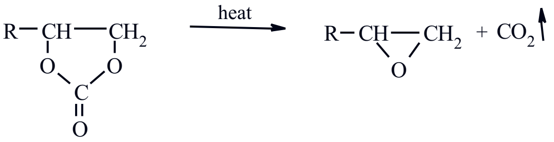
— condensation of forming hydroxyalkyl urea derivatives (Scheme N).



Scheme N

where: R = -H, $-CH_3$.

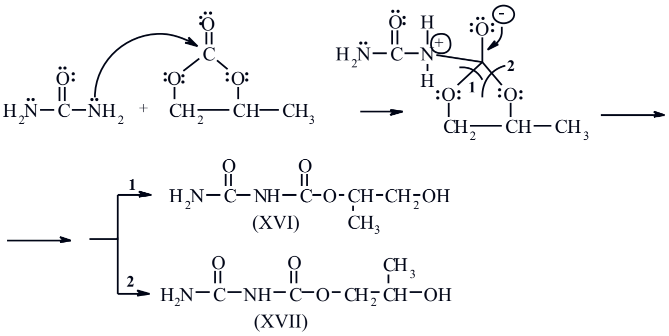
During the reaction with alkylene carbonates a part of them may decompose to carbon dioxide and alkylene oxide [31] according to Scheme O.



Scheme O

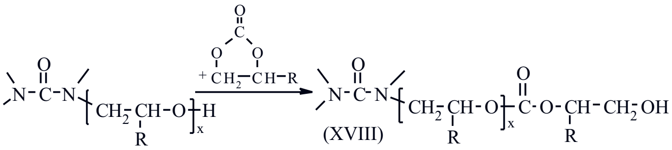
where: R = -H, $-CH_3$.

A mass balance of the urea reaction with alkylene carbonates performed assuming that all the amount of alkylene carbonate reacted with urea with carbon dioxide evolution, showed that the mass of the products is slightly greater or equal to the calculated one. This fact suggests the presence of carbonate groups in the product's structure. This conclusion has been confirmed by spectral analysis. In ^{1}H NMR spectrum of the products of urea reaction with EC the signal at 4.2 ppm from protons of methylene group in the ester structure has been observed. Moreover in the spectra, for the products obtained at molar ratio of reagents equal to 1:1, the signal at 6.4 ppm, characteristic for primary amide groups protons of N-substituted by acceptor group urea derivatives [32], and the signal at 7.5 ppm coming from protons of imide's groups (allophanates) [formula (XV) in Scheme M] [29] has been noted. During the reaction of urea with EC a product with built-in carbonate group is formed as a result of carbonate ring opening from the less substituted side, according to the route 1 shown in Scheme P.



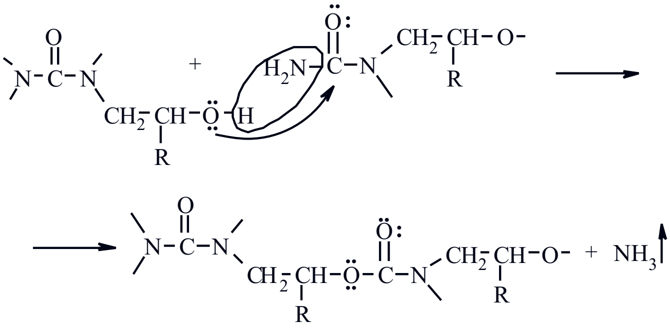
Scheme P

In ^{1}H NMR spectrum of the products of urea reaction with PC a doublet at 1.25 ppm and multiplet at 4.5 ppm are observed. The above signals are derived from protons of methylene and methine groups in the structure given by formula (XVI) in Scheme P, respectively. No signal at about 4.2 ppm (derived from protons of methylene group in the ester structure) excludes the possibility of the second way of carbonate ring opening with the formation of product described by formula (XVII) in Scheme P [30]. With an excess of alkylene carbonate, the carbonate groups can be incorporated into the product structure not only at the nitrogen atom of urea, but also, as it is shown in Scheme Q, into the oxyalkylene chain [formula (XVIII), $x \geq 1$], but in the case of the products of urea reaction with PC only methine groups are present at carbonate group.



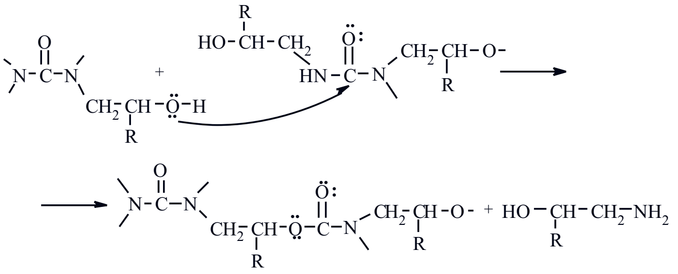
Scheme Q

where: x = 0, R = -H, $-CH_3$.



Scheme R

where: R = -H, $-CH_3$.



Scheme S

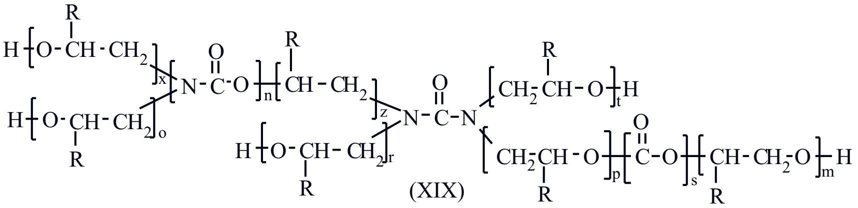
where: R = -H, -CH_3.

Formed hydroxyalkyl derivatives of urea can react together forming carbamate group with separation of:

— ammonia, in a reaction with primary amide group (Scheme R),

— aminoalcohol (2-aminoethanol in a reaction with EC or 1-aminopropan-2-ol in a reaction with PC), during a reaction with secondary amide group (Scheme S).

A general structure of the product can be represented by the formula (XIX).

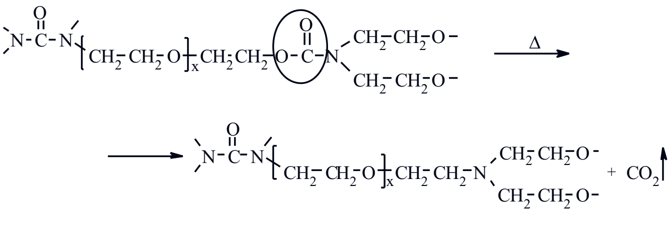


(XIX)

where: $n \geq 0$, $s \leq 1$, $z \geq 1$, $p \geq 0$, R = -H, -CH_3.

The presence of carbonate and carbamate groups in the structure of hydroxyalkyl derivatives of urea has been confirmed by the analysis of ^{1}H NMR spectrum of urea derivative obtained at starting molar ratio of the reagents equal to 1:12 [31], taken before and after heating at 200 °C (*i.e.* under condition of carbonate [33] and carbamate [34] groups decomposition).

Initially, after 4 h of heating, in ^{1}H NMR spectrum of the reaction mixture obtained with the participation of EC only decrease of the signal at 4.2 ppm derived from the protons of methylene group in the structure -(CO)O-CH_2- (of carbonate and carbamate) is observed without the appearance of new signals. This indicates a loss of carbonate groups situated at amide groups [formula (XX), z = 0] and/or in ethoxy chain [formula (XX), $z \geq 1$] according to Scheme T.



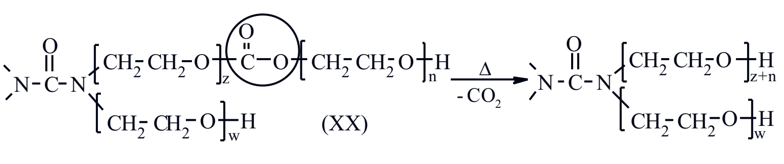
Scheme U

where: x = 0.

A continuation of heating (up to 10 h) causes farther reduction of the signal at 4.2 ppm and the simultaneous appearance of the signal at 2.6 ppm originated from protons of methylene group in the amine $C\underline{H_2}$-N structure [29]. Then the carbamate groups resulting from condensation are decomposed with the formation of tertiary amine structure in the reaction shown in Scheme U.

A similar change has been observed analyzing ^{1}H NMR spectra of the products of urea reaction with PC, but after 4 h of heating a signal at about 2.4 ppm [30] was observed.

Condensation of urea hydroxyalkyl derivatives can also be confirmed by the presence of oxazolidinones in their composition (GC-MS and GC analysis). A maximum amount of *N*-(2-hydroxyethyl)oxazolidinone in the product of urea reaction with EC equals to 5 wt. % at 8 molar excess of EC relative to urea, and decreases to 1 wt. % at a greater excess of EC in the starting reaction mixture. During the reaction of urea with PC the participation of condensation process is smaller and the content



Scheme T

where: x = 1.

of *N*-(2-hydroxypropyl)-5-methyloxazolidinone is about 1 wt. %.

Condensation of hydroxyethyl derivatives of urea is limited to a partial dimerization only (confirmed by MALDI-ToF spectroscopy). The products obtained at 8- and 12-molar excess of EC are composed of oligomers containing respectively up to 15 and 17 oxyethylene units per 1 mole of urea and 10 moles of oxyethylene groups per 1 mol of dimer [29]. The molar mass of the product obtained at 12-molar excess of EC equals to about 350 g/mol (by GPC), which also confirms a small content of dimers. A similar situation is in the case of the products of urea reaction with an excess of PC (M_w = 385 g/mol).

The reactions of urea with alkylene carbonates are accompanied by formation of carbodiimides due to dehydratation of *N,N'*-disubstituted urea derivatives [35] according to Scheme V.

$$R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R \xrightarrow{\text{heat}} R{-}N{=}C{=}N{-}R + H_2O$$

Scheme V

where: R = alkyl or hydroxyalkyl group.

The fact is confirmed by an intensive band at 2157 cm^{-1}, characteristic for valence vibration of N=C=N bonds occurring in the IR spectra of the products.

The above process disappears at 2-molar excess of PC [30] and 4-molar excess of EC [29].

Moreover, during the reaction of urea with alkylene carbonates ammonium carbamate is formed (identified using IR spectroscopy by comparison with the standard method), which disappears at 4-molar excess of EC [29], but does not depend on PC excess [30].

The hydroxyalkylation reactions of urea with alkylene carbonates are also accompanied by formation of polyglycols. In the products of urea reaction with EC tetraethylene glycol in quantities not exceeding 4 wt. % is present [29]. In turn, among the products of urea reaction with PC, dipropylene (DPG) and tripropylene (TRIPG) glycols are present, which quantities do not exceed 10 wt. %. Propylene glycol is not present among the products of the reactions and the content of DPG decreases, whereas the content of TRIPG increases with an increase in PC excess [30].

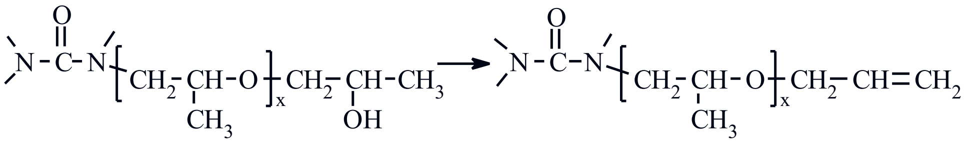
During the reaction of urea with PC at 4 and bigger molar excess of PC, as it is shown in Scheme W, a partial dehydratation of the terminal hydroxypropyl groups takes place with the formation of allyl groups (the presence of low intensity multiplets within the range of 4.9—6.1 ppm in ^{1}H NMR spectra of the products, spectroscopy MALDI-ToF) [30].

The products of urea reaction with alkylene carbonates exhibit high thermal stability. Two peaks are observed on the DTG curve of the products of urea reaction with EC. The first peak at 220 °C originates from carbonate and carbamate groups decomposition (the peak disappears after annealing of the product at 200 °C [29] and the second one at 350 °C originates from decomposition of carbamide groups [29]. With an increase of EC excess in reaction with urea the first peak moves towards higher temperatures and at 16-molar excess of EC practically only one peak at 350 °C is observed on the DTG curve [29]. From the above it can be concluded that contribution of carbonate and carbamate groups in the product decreases with an increase of EC excess. On the DTG curve of the products of urea reaction with PC only one peak at 260 °C is observed, which means simultaneous decomposition of carbamide, carbonate and carbamate groups [30].

Because of the numerous side processes during reaction of urea with alkylene carbonates, such as incorporation of carbonate groups into the products' structure, condensation of hydroxyalkylated derivatives of urea and polyglycols formation, it was decided to apply *N,N'*-bis(2-hydroxyalkyl)urea derivatives expecting elimination or reduction of the described processes. The derivatives of [*N,N'*-bis(2-hydroxyethyl)urea (BHEU) and *N,N'*-bis(2-hydroxypropyl)-urea (BHPU)] were obtained in the reaction of urea transamination by proper aminoalcohols according to Scheme X.

A known, general method [36] of urea hydroxyalkyl derivatives synthesis has been applied and optimized for BHEU and BHPU [37].

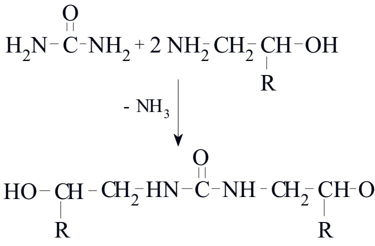
Previously reported products were of resin forms and were characterized by hydroxyl numbers only. A method of BHEU synthesis in crystalline form, described in [38] did not lead to the desired derivative. In the mentioned work BHEU and BHPU were obtained with high efficiency, purified by crystallization (melting temperatures



$$\rangle N{-}\overset{O}{\overset{\|}{C}}{-}N\langle\left[CH_2{-}\underset{CH_3}{CH}{-}O\right]_x CH_2{-}\underset{OH}{CH}{-}CH_3 \longrightarrow \rangle N{-}\overset{O}{\overset{\|}{C}}{-}N\langle\left[CH_2{-}\underset{CH_3}{CH}{-}O\right]_x CH_2{-}CH{=}CH_2$$

Scheme W

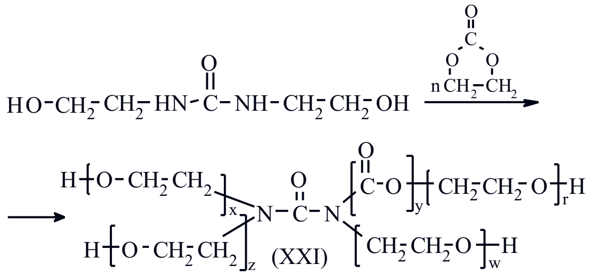
where: x = 1.



$$H_2N-\overset{O}{\overset{\|}{C}}-NH_2 + 2\,NH_2-CH_2-\underset{R}{\underset{|}{CH}}-OH \xrightarrow{-NH_3} HO-\underset{R}{\underset{|}{CH}}-CH_2-HN-\overset{O}{\overset{\|}{C}}-NH-CH_2-\underset{R}{\underset{|}{CH}}-OH$$

Scheme X

where: R = -H, $-CH_3$.



Scheme Y

where: n = x + z + r + w.

were $t_{m\,BHEU}$ = 82 °C, and $t_{m\,BHPU}$ = 94 °C) and characterized by instrumental methods [37].

The reactions of *N,N'*-bis(2-hydroxyalkyl)ureas with alkylene carbonates were conducted at starting molar ratios of the reagents such that the oxyalkylene units excess in relation to urea was identical as compared to the reaction of urea with alkylene carbonates. The reactions were similar to the reaction of urea with alkylene carbonates [29, 39]. Only a slightly larger content of carbonate groups in the product structures has been observed (using ^{1}H NMR spectroscopy and mass balance).

An analysis of ^{1}H NMR spectrum of urea derivative obtained at 6-molar excess of BHEU, registered before and after annealing at 200 °C has shown that after 4 h of annealing the intensity of the signal at 4.2 ppm, originating from protons of methylene groups in the (CO)O-CH_2- structure decreases (decomposition of carbonate and/or carbamate groups) with simultaneous appearance of a signal at about 2.6 ppm, originating from protons of methylene groups in the $\underline{CH_2}$-N- structure of amine (decomposition of carbamate groups) [39]. Changes in the area of individual signals point to the simultaneous decomposition of carbonate and carbamate groups, which has been fully explained in [39]. A contribution of carbamate groups formed by dimerization of hydroxyethyl urea derivatives (confirmed by MALDI-ToF spectroscopy), estimated based on the content of *N*-(2-hydroxyethyl)-oxazolidinone in the reaction mixture (GC), is comparable to the content of the groups in the products of urea reaction with a proper excess of EC. A similar situation is in the case of the content of *N*-(2-hydroxypropyl)-5-methyloxazolidinone in the products of BHPU reaction with PC and urea reaction with PC [30].

During reactions of *N,N'*-bis(2-hydroxyalkyl)ureas with alkylene carbonates a subsequent reactions of hydroxyl groups occur more easily then the reactions of secondary amide groups with carbonates and only at 3.5—4-molar excess of alkylene carbonate the protons of amide groups in the structure of the products formed fully disappear (stated using ^{1}H NMR spectroscopy) [39].

The influence of the kind of catalyst on the structure of the products obtained has been investigated on the example of urea reaction with 3.5-molar excess of EC presented in Scheme Y. Besides potassium carbonate, diazabicyclo[2.2.2]octane (DABCO) and tetrabutylammonium hydroxide were applied as catalysts [39]. In the presence of DABCO secondary amide groups do not practically occur in the product structure given by formula (XXI), where y = 0; x, z, w, r ≥ 1, but the signal at about 7 ppm characteristic for the protons of secondary amide groups is present for the structure specified as formula (XXI), where x = 0; y = 1; z, w, r ≥ 1 [39].

An application of tetrabutylammonium hydroxide causes that the product contains in its structure secondary amide groups without and with built-in carbonate group (signals at 6,15 and 7 ppm) [39]. In turn an application of potassium carbonate as a catalyst results in a total disappearance of secondary amide groups in the product structure [39]. Therefore it can be concluded that both DABCO and tetrabutylammonium hydroxide are more conductive to subsequent reactions of hydroxyl groups with EC than to the reactions of amide groups with EC.

The reactions of BHEU with EC are accompanied by the formation of a small amount of by-product, which is tetraethylene glycol. The by-product is formed during the reaction with the participation of tetrabutylammonium hydroxide (50 % aqueous solution) as a catalyst (about 10 wt. %) or by applying potassium carbonate and 6 or more molar excess of EC (about 4 wt. %) [40].

The products of BHPU reaction with PC are accompanied by di- and tripropylene glycols which total amount increases slightly with the increase of PC excess and reaches 7 wt. % [30].

Allyl groups are also present in the structure of the products of BHPU reaction with PC (stated using ^{1}H NMR spectroscopy and MALDI-ToF spectrometry) [30].

The products of BHEU reaction with 6- and 10-molar excess of EC are a mixture of oligomers containing from 10 to 12 oxyethylene units per 1 mole of urea and up to 5 oxyethylene units per one mole of dimer [39], that is slightly fewer oxyethylene units than in derivatives obtained with the participation of urea and the same excess of EC [29]. In turn, the products obtained at 6-molar excess of PC relative to BHPU consist of oligomers containing up to 11 oxypropylene units per one urea mole [30], *i.e.* more than a corresponding hydroxyethoxy derivatives of urea. The molar masses of the products obtained in reactions of *N,N'*-bis(2-hydroxyalkyl)ureas with alkylene carbonates are slightly smaller (*ca.* 15 %) as compared to the molar masses of the products obtained with the participation of the urea and the analogical excess of EC and PC. The molar masses are 300 and 320 g/mole for the product of BHEU and BHPU reaction with 10-molar excess of EC and PC, respectively.

The use of *N*,*N*′-bis(2-hydroxyalkyl)ureas in reactions with alkylene carbonates helped to avoid formation of carbamate and eliminated formation of carbodiimides. Moreover, the formation of polyglycols has been reduced, particularly in reactions with PC [30].

A thermal stability of *N*,*N*′-bis(2-hydroxyalkyl)ureas reaction products with alkylene carbonates is similar, and even higher as compared with that for reaction products of urea with alkylene carbonates, and the maximum decomposition temperature is within the range of 240—350 °C. On the DTG curve of the products obtained in reaction with BHEU and EC the first peak is observed at 240 °C and the second one at 350 °C [39].

The maximum decomposition temperature of the products of BHPU reaction with PC is within the range of 270—300 °C [30].

Thermal stability of reaction products of urea with alkylene carbonates is higher as compared with that of the products of parabanic acid hydroxyalkylation by alkylene carbonates. Therefore, the presence of carbamide groups in the structure of the above products determines their high thermal stability.

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