Russian Chemical Bulletin, International Edition, Vol. 53, No. 4, pp. 803—807, April, 2004 803

Hydrolysis of 1,2-disubstituted imidazolines in aqueous media

S. O. Bondareva,[a]* **V. V. Lisitskii,**[b] **N. I. Yakovtseva,**[b] **and Yu. I. Murinov**[a]

[a]*Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences,*
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 35 6066. E-mail: murinov@anrb.ru
[b]*Bashkir State University,*
32 ul. Frunze, 450074 Ufa, Russian Federation

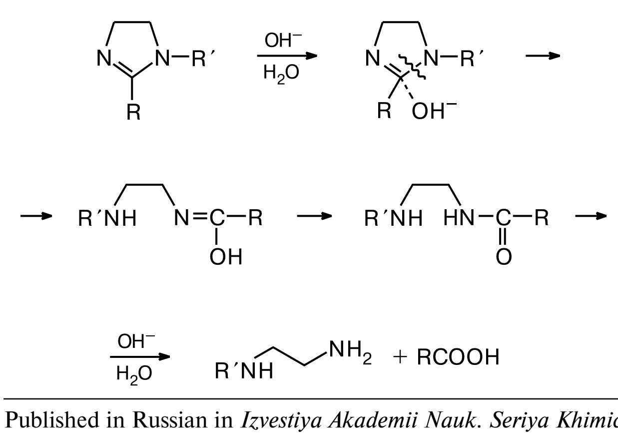
The kinetics of hydrolysis of 1,2-disubstituted imidazolines in aqueous media was studied (pH 2.0—12.5, T = 25—90 °C) by UV spectroscopy. The hydrolysis products were identified The introduction of a branched substituent into position 2 of the imidazoline ring increases the hydrolytic stability of the compounds. The effect of the pH on the hydrolysis rate of imidazolines is discussed.

Key words: substituted imidazolines, hydrolysis rate constants, hydrolysis products, protonation of imidazolines.

The use of 1,2-disubstituted imidazolines (DI) for the preparation of cation-active and ampholytic surfactants was started more than 50 years ago. Their derivatives are used today as corrosion inhibitors in processes of petroleum production, transportation, and refining. Various detergents, antistatics for polymeric materials processing, hardeners of polymeric resins, accelerators of vulcanization, and textile-auxiliary substances of many-sided design were created on the basis of DI.[1] A possibility and expediency of industrial use of DI depend, to a great extent, on their hydrolytic stability. Amphoteric DI-based surfactants were synthesized in aqueous-basic media at 40—98 °C.[2] To intensify petroleum production, highly mineralized water (sometimes sea water) is pumped into a bed or acid treatment of aquifers is used.[3] Similar factors can result in imidazoline hydrolysis.

The usual[2,4,5] scheme of hydrolysis of substituted imidazolines in aqueous-basic media (Scheme 1) suggests that the introduction of a branched substituent into the α-position to the reaction center can hinder the addition of the hydroxide ion and, hence, inhibits imidazoline hydrolysis.

Scheme 1



The purpose of this work is to study the kinetics of hydrolysis of some 1,2-disubstituted imidazolines in aqueous media in a wide pH interval and to determine the hydrolytic stability of imidazolines with an α-branched substituent in position 2 of the ring.

Experimental

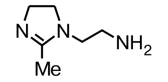
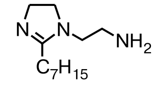
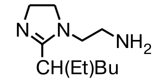
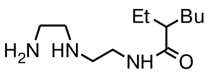
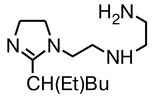
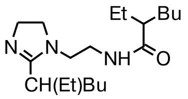
All compounds were synthesized by the condensation of anhydrous diethylenetriamine (DETA) or triethylenetetraamine with linear (acetic and octanoic) and α-branched (2-ethylhexanoic) carboxylic acids at a molar ratio of 1 : 0.9 in a nitrogen atmosphere at 200—300 °C.[6]

Imidazoline samples (Tables 1 and 2) containing at least 95% of the main substance were used. Previously described[7,8] imidazolines **1** and **2** were synthesized as model substances. To identify hydrolysis products, we also synthesized *N*-(5-amino-3-azapentyl)-2-ethylhexaneamide (**3a**), which is the most probable product of hydrolysis of compound **3**. Purity of compounds was monitored by GLC[9] on a Chrom-5 instrument (He, column 1.2 m×3 mm with 15% SE-30 on Chromaton N-AW). Electronic spectra were recorded on Specord UV—Vis and Specord M-40 spectrophotometers in a region of 50500—28000 cm^{-1} (in EtOH). IR spectra were recorded on a Specord M-80 spectrophotometer (in film). ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer (CDCl$_3$, Me$_4$Si). Potentiometric studies were carried out on an OR-211/1 pH-meter with a combined glass electrode in water (1 M KCl) using a known procedure.[10]

The content of imidazolines in a solution during hydrolysis was determined by UV spectroscopy from the intense absorption

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 767—771, April, 2004.

Table 1. Physicochemical characteristics of the synthesized compounds

Compound	Structural formula	Yield (%)	B.p. /°C (*p*/Torr)	Found/Calculated (%) C	H	N	N_{titr}	Molecular formula
1-(2-Aminoethyl)-2-methyl-4,5-dihydroimidazole (**1**)		85	110—112 (2)	56.50 56.66	10.65 10.30	—	21.05 22.03	$C_6H_{13}N_3$
1-(2-Aminoethyl)-2-heptyl-4,5-dihydroimidazole (**2**)		88	133—135 (1—2)	67.02 68.20	11.87 11.92	—	12.59 13.25	$C_{12}H_{25}N_3$
1-(2-Aminoethyl)-2-(1-ethylpentyl)-4,5-dihydroimidazole (**3**)		81	140—142 (2—3)	68.37 68.20	11.90 11.92	18.80 19.88	13.20 13.25	$C_{12}H_{25}N_3$
N-(5-Amino-3-azapentyl)-2-ethylhexaneamide (**3a**)		92	190—192 (2—3)	63.21 62.84	12.08 11.86	18.41 18.32	12.30 12.21	$C_{12}H_{27}N_3O$
1-(5-Amino-3-azapentyl)-2-(1-ethylpentyl)-4,5-dihydroimidazole (**4**)		77	182—185 (2)	65.08 66.09	11.93 11.88	20.00 22.02	15.41 16.52	$C_{14}H_{30}N_4$
1-(5-Ethyl-4-oxo-3-azanonyl)-2-(1-ethylpentyl)-4,5-dihydroimidazole (**5**)		55	210—213 (1—2)	71.76 71.17	12.08 11.65	11.93 12.45	4.39 4.15	$C_{20}H_{39}N_3O$

$\pi\rightarrow\pi^*$-band at 230—235 nm, which corresponded to the transition of the C=N bond in the heterocycle.[8] Samples were hydrolyzed in a cell, whose temperature was maintained constant, at a constant stirring velocity. The conversion of imidazolines was at least 60% in an interval of pH 7.0—9.0 and at least 90% at pH > 9.0 (hydrolysis did not virtually occur in acidic media). The pH value was monitored by an OR-211/1 pH-meter with a combined glass electrode, and a needed value was established by the addition of 0.1 *M* HCl or 0.1 *M* NaOH.

Table 2. Spectral characteristics of the synthesized compounds

Compound	UV, λ/nm (logε)	IR, ν/cm^{-1}	^{13}C NMR (δ)
1	202 (3.41), 231 (3.75)	1600 (ν(C=N)); 1016 (ν(C—N) ring); 940 (δ(Me))	164.21 (s, >C=N)
2	205 (3.30), 231.5 (3.77)	1610 (ν(C=N)); 998 (ν(C—N) ring)	168.50 (s, >C=N)
3	202 (3.20), 232.5 (3.78)	1610 (C=N); 998 (ν(C—N) ring)	170.70 (s, >C=N)
3a	204 (3.60)	1644 (ν(C=O)); 1552 (δ(NH))	176.05 (s, NHC=O)
4	204 (3.28), 236 (3.79)	1604 (ν(C=N)); 996 (ν(C—N) ring)	170.57 (s)
5	201 (3.67), 234 (3.83)	1644 (ν(C=O)); 1605 (ν(C=N)); 1552 (δ(NH)); 1000 (ν(C—N) ring)	170.43 (s, >C=N); 176.11 (s, NHC=O)

The preliminary experiment established that at the molar ratio imidazoline : water 1 : 50—1 : 150 the hydrolysis rate constants for DI were virtually unchanged. Therefore, experiments were carried out at the molar ratio imidazoline : water 1 : 120, the concentrations of imidazolines **3**, **4**, and **5** being ~0.4, ~0.3, and ~0.25 mol L^{-1}, respectively.

Results and Discussion

Identification of hydrolysis products. Hydrolysis products (HP) of imidazolines isolated from working solutions were studied by GLC, IR spectroscopy, and ^{13}C NMR spectroscopy. The chromatogram of the HP of imidazoline **3** exhibits a small peak of non-hydrolyzed imidazoline, which is eluted first, followed by two rather intense peaks with very close retention times (Fig. 1). The retention times of these peaks coincide with the elution time of compound **3a**. Analysis of the chromatogram shows that the HP of imidazolime **3** also contain minor amounts of acylated imidazoline **5** and bisacylated DETA. It is likely that imidazoline **5** is primarily present as an amine admixture in the hydrolyzed samples of imidazoline **3** and is partially hydrolyzed during experiment to form bisacylated DETA.

The data of IR spectroscopy (Table 3) indicate the amide structure of the HP. The IR spectra of the HP are virtually identical with the IR spectrum of individual amide

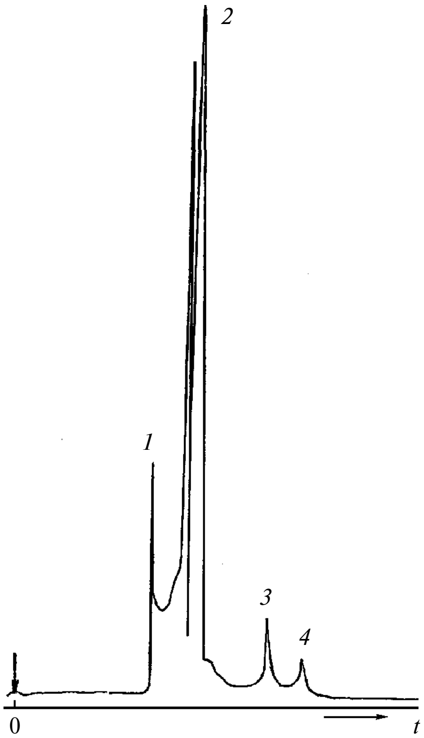


Fig. 1. Chromatogram of the hydrolysis products of imidazoline **3**: non-hydrolyzed imidazoline **3** (*1*), monoacylated DETA (**3a**) (*2*), monoacylated imidazoline **5** (*3*), and bisacylated DETA (*4*); vertical arrow corresponds to the moment of sample injection.

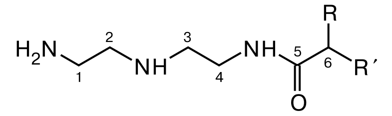
3a but differ from the latter by a noticeable broadening of the bands.

The ^{13}C NMR spectra confirm the amide structure of the HP (Table 4), and the downfield signal of the sp^2-hybridized C atom of the amide group (C(5)) is the most characteristic. The most part of signals in the spectra of the HP are duplicated by less intense signals, which differ from the main signals by ~0.2 ppm. It is most likely that some isomeric amide is formed as an admixture along with the main product, which agrees with the published data.[11] For example, a scheme of alkaline hydrolysis of 1,2-disubstituted imidazolines was proposed (Scheme 2). Reaction *a* was proved to be the main process, whereas the product of reaction *b* is formed only in insignificant amounts.

Table 3. Characteristic frequencies of vibrations of molecules of the hydrolysis products of imidazolines in the IR region

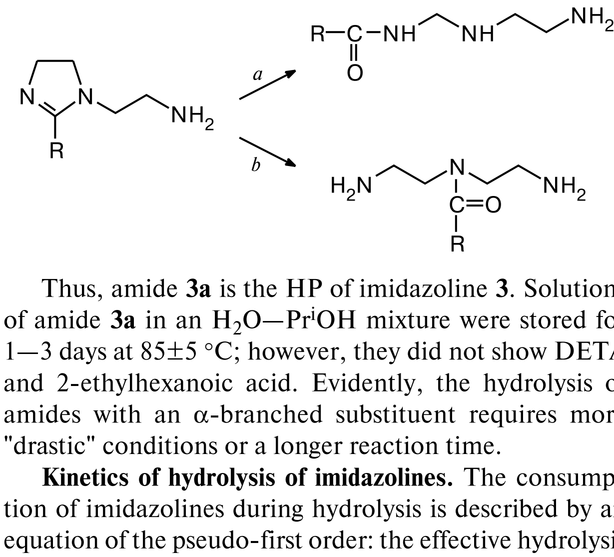
Type of vibrations	ν/cm^{-1}			
	HP-**1**	HP-**2**	HP-**3**	**3a**
$\nu(NH_2)$	3296	3300, 3190 sh	3296, 3190 sh	3288
Overtone $\nu(C=O)$	3100 w	3080 w	3060 w	3060
$\nu(C=O)$ (I amide band)	1660 sh, 1648	1660 sh, 1640	1638 br	1640
$\delta(NH)$ (II amide band)	1568	1560	1552 br	1560
$\delta(NH)$ out-of-plane	725 br	728 br	740 br	740

Table 4. ^{13}C NMR spectra of the hydrolysis products of imidazolines



Atom	δ_C		
	HP-**2**	HP-**3**	**3a**
C(1)	37.48 (w), 37.65	40.33 (w), 40.55	38.71
C(2)	39.62	42.01	41.32
C(3)	42.05	44.12	48.57
C(4)	52.24	52.38 (w), 52.54	51.50
C(5)	173.45 (w), 173.64	177.41, 177.60	176.05
C(6)	49.13 (w), 49.30	50.03 (w), 50.22	49.34

Scheme 2

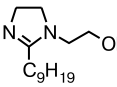
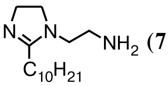


Thus, amide **3a** is the HP of imidazoline **3**. Solutions of amide **3a** in an H_2O—Pr^{i}OH mixture were stored for 1—3 days at 85±5 °C; however, they did not show DETA and 2-ethylhexanoic acid. Evidently, the hydrolysis of amides with an α-branched substituent requires more "drastic" conditions or a longer reaction time.

Kinetics of hydrolysis of imidazolines. The consumption of imidazolines during hydrolysis is described by an equation of the pseudo-first order: the effective hydrolysis constants of DI with linear (**1**, **2**) and α-branched alkyl substituents in position 2 of the imidazoline ring (**3—5**) are given in Table 5. The published data for their closest analogs, *viz*., 1-(2-hydroxyethyl)-2-nonylimidazoline (**6**) and 1-(2-aminoethyl)-2-decylimidazoline (**7**), are given for comparison.

As expected, the introduction of a branched substituent into the α-position to the reaction center substantially inhibits the hydrolysis rate. For example, at 90 °C and pH 12.4, sample **2** is completely hydrolyzed already within 12—15 min, whereas its isomer (sample **3**) is hydrolyzed only within 5—6 h, *i.e.*, the hydrolysis rate slowed down

Table 5. Effective hydrolysis constants (k_{eff}) of imidazolines in an aqueous medium at different temperatures (25—90 °C), pH 12.4

Compound	$k_{\mathrm{eff}} \cdot 10^5/\mathrm{s}^{-1}$			
	25 °C	50 °C	75 °C	90 °C
1^a	21.8±2.6	—	—	—
2^a	20.0±2.3	—	—	500±85
3^a	0.37±0.02	2.8±0.1	7.8±0.6	20.8±1.4
4^a	—	—	—	20±1.4
$5^{a,b}$	0.67±0.02	7.2±0.1	15±1.5	37±2
 **(6)**^{c}	—	~31	—	—
 (**7**)^d	~56^e	~290	—	—

[a] This work.
[b] In an H_2O—Pr^{i}OH mixture.
[c] See Ref. 4.
[d] See Ref. 11.
[e] T = 30 °C.

Table 6. Activation parameters of hydrolysis of imidazolines at pH ≈ 12

Compound	$\log(A/\mathrm{s}^{-1})$	E_A/kJ mol^{-1}
$2^{a,b}$	4.1	44.6
3^b	4.1	53.8
5^b	4.4	54.6
$6^{c,d}$	2.6	39.2
$7^{a,c,d}$	8	67

[a] The parameters were estimated from two values of effective hydrolysis constants measured at two temperatures.
[b] This work.
[c] The values were calculated from the experimental data presented.
[d] See Refs. 4 and 11.

by at least 25 times. Comparison of the experimental hydrolysis rate constants (k) with the published data (taking into account minor differences in the temperature, pH, and concentrations) also gives a difference of 10—50 times.

The activation parameters of hydrolysis of 1,2-disubstituted imidazolines with a branched substituent in position 2 of the imidazoline ring (Table 6) were determined from the temperature dependence of ln$k$ (Fig. 2). The published data of imidazolines with linear substituents are given in Table 6 for comparison.

In our opinion, the hydrolysis of DI in acidic media is studied in less detail: the commonly accepted scheme for acid hydrolysis is absent, and published data are poorly generalized. For example, it has been reported[5,12] that in acidic media (pH ≈ 1—2) solutions of imidazolines are stable during at least 6 months. However, an almost 100% conversion is observed[13] on heating 1,2-di- and 2-monosubstituted imidazolines for 6 h at 140 °C and pH ≈ 0—1. Therefore, it can be assumed that comparatively drastic conditions are needed to decompose the imidazoline structure in acidic media.

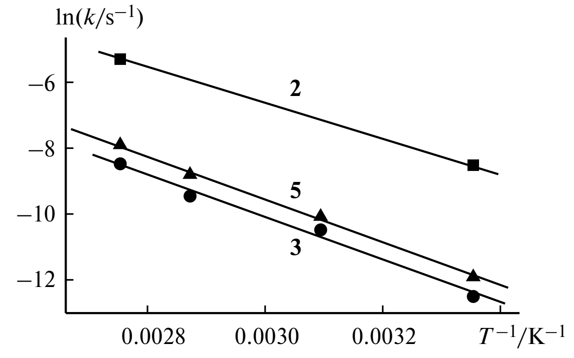
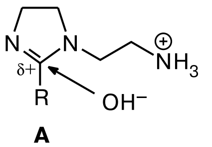
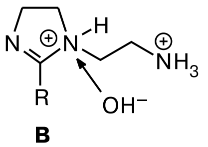


Fig. 2. Temperature dependence of the hydrolysis rate constant (k) for the hydrolysis of 1,2-disubstituted imidazolines with α-branched (**3**, **5**) and linear (**2**) alkyl substituents.

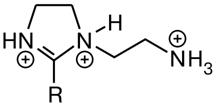
The influence of the pH on the hydrolysis of DI was studied for compound **3** in an interval of pH 2.0—12.7 at 70 and 90 °C. The plot of log$k$ *vs.* pH is presented in Fig. 3, *a*. Two rectilinear regions with the inflection point at pH ≈ 10 are well seen, and the distribution curves for the protonated forms of compound **3** in water are given for comparison (see Fig. 3, *b*). They were calculated from the previously[6] determined stepwise protonation constants of imidazoline **3**. The inflection point in the plot (see Fig. 3, *a*) approximately corresponds to the maximum content of imidazoline protonated at the primary amino group. With an increase in the pH, the equilibrium shifts toward the formation of the non-protonated form of DI; the tangent slope close to 1 indicates the first order of the reaction with respect to the hydroxide ion.[14] Hydrolysis is not virtually observed at pH < 6. However, the content of DI protonated at the tertiary N atom in the imidazoline ring is maximum at these pH values. It is most likely that the positive charge on the N atom (structure **B**) prevents



A



B



C

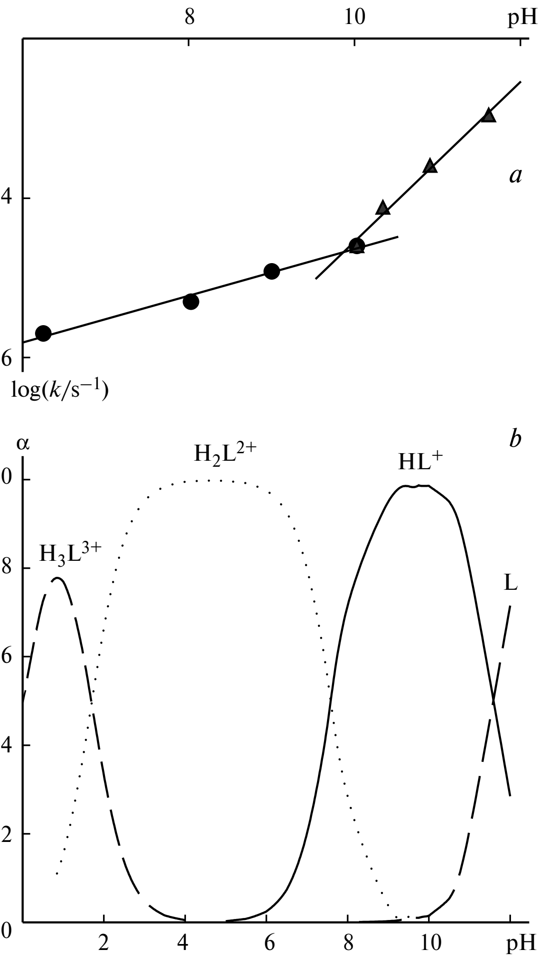


Fig. 3. Effect of the pH on the hydrolysis rate of imidazoline **3** at 90 °C (*a*) and the distribution of the protonated forms of compound **3** in the 3—HCl—H_2O system for different pH at 25 °C (*b*); α is the molar fraction.

hydrolysis *via* Scheme 1, because the partially positive charge on the C atom is not formed in this case (**A**).

No protonation of the imidazoline molecule at the sp^2-hybridized N atom (structure **C**) was observed under the comparatively mild conditions chosen. In this case, the presence of two like charges in the ring can result in the decomposition of the imidazoline structure and, most likely, causes the hydrolysis of imidazolines in acidic media.

References

1. P. S. Belov, V. I. Frolov, and B. E. Chistyakov, *Novye poverkhnostno-aktivnye veshchestva na osnove zameshchennykh imidazolinov* [*New Surfactants Based on Substituted Imidazolines*], TsNIITEneftekhim, Moscow, 1975, 54 pp. (in Russian).
2. B. S. Kolomiets, V. K. German, and V. V. Suchkov, *Zh. Prikl. Khim.*, 1978, 2758 [*J. Appl. Chem. USSR*, 1978 (Engl. Transl.)].
3. V. A. Antipov and V. I. Levashova, *Neftekhimiya*, 2002, **6**, 475 [*Petroleum Chemistry*, 2002, **6** (Engl. Transl.)].
4. B. S. Kolomiets, V. K. German, and V. V. Suchkov, *Zh. Prikl. Khim.*, 1978, 1141 [*J. Appl. Chem. USSR*, 1978 (Engl. Transl.)].
5. V. P. Kasperchik, G. I. Sergeev, and V. S. Soldatov, *Dokl. Akad. Nauk BSSR* [*Rev. Acad. Sci. Belorussian Acad. Sci.*], 1988, **7**, 621 (in Russian).
6. S. O. Bondareva, Yu. I. Murinov, and L. V. Spirikhin, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 2041 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 2007].
7. V. V. Krut´, Author´s Abstract, Ph. D. (Chem.) Thesis, Moscow, 1967, 23 pp. (in Russian).
8. P. A. Perov, V. V. Krut´, G. A. Tember, and N. T. Gerasimova, *Zh. Prikl. Spektrosk.*, 1980, 309 [*J. Appl. Spectr.*, 1980, No. 2 (Engl. Transl.)].
9. G. I. Batukova, V. D. Davydov, and N. S. Rodimushkina, *Zh. Anal. Khim.*, 1977, 1462 [*J. Anal. Chem. USSR*, 1977, No. 7 (Engl. Transl.)].
10. F. R. Hartley, C. Burgess, and R. M. Alcock, *Solution Equilibria*, Ellis Horwood, New York—Chichester—Brisbane—Toronto, 1980.
11. A. Savignac, T. Kabbage, P. Dupin, and M. Calmon, *J. Heterocycl. Chem.*, 1978, **15**, 897.
12. R. B. Martin, A. Parcell, *J. Am. Chem. Soc.*, 1961, **83**, 4834.
13. B. S. Kolomiets, V. K. German, and V. V. Suchkov, *Zh. Prikl. Khim.*, 1978, 2119 [*J. Appl. Chem. USSR*, 1978 (Engl. Transl.)].
14. N. M. Emanuel´ and D. G. Knorre, *Kurs khimicheskoi kinetiki* [*The Course of Chemical Kinetics*], Vysshaya Shkola, Moscow, 1984, 463 pp. (in Russian).

Received July 30, 2003;
in revised form December 9, 2003