

# Reactions of nucleophilic substitution involving solid organic halogen compounds under shear deformation at high pressure

A. A. Zharov, N. P. Chistotina,\* R. G. Gaziev, and I. I. Yakovleva

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,  
47 Leninsky prosp., 117913 Moscow, Russian Federation.

Fax: +7 (095) 135 5328

Under conditions of shear deformation and high pressures (SD+HP), reactions of nucleophilic substitution were studied: 1) the replacement of aliphatic halogen atom with alkaline metal halides (halo-substituted aliphatic carboxylic acids, 1-bromoadamantane); 2) the replacement of halogen atom in aromatic nucleus (halobenzoic acids, dihalobenzenes) with halogen of salt; 3) the replacement of aliphatic halogen with hydroxyl (hydrolysis in a solid phase); 4) the replacement of halogen with amino group under deformation of the samples of ammonium  $\alpha$ -halocarboxylates to give the corresponding amino acids. It was found that the exchange of the halogen atoms bonded with aliphatic carbon is most intensive in the mixtures of alkaline metal iodides with bromo-substituted acetic and propionic acids: the exchange reaction in these mixtures is observed even during grinding in the mortar. Unlike the liquid phase, under conditions of SD+HP exchange of the halogen atom of the aromatic nucleus with alkaline metal halides, proceeds successfully, and the reactivity of halides increases in the series  $\text{Na} < \text{K} < \text{Rb} < \text{Cs}$ . Under SD+HP, 1-Br-adamantane reacts with water to form 1-adamantanol. A high reactivity of the water adsorbed by the reagents is observed.

**Key words:** shear deformation, high pressure, halogen derivatives of carboxylic acids, dihalobenzenes, alkaline metal halides, ammonium salts of halogen derivatives of carboxylic acids, amino acids, halo-substituted adamantanes, adamantanol, nucleophilic substitution reaction, hydrolysis, ball mill.

There are a number of works that deal with investigation of the reactions of nucleophilic substitution: etherification,<sup>1</sup> the formation of amides from ammonium salts of acids,<sup>2-4</sup> synthesis of substituted amides, and hydrolysis of amide group.<sup>5</sup> The reactions of nucleophilic substitution in organic halogen compounds have virtually not been investigated.

The purpose of the present work is to investigate the reactivity of a series of solid organic halogen compounds in reactions of nucleophilic substitution under conditions of shear deformation at high pressure (SD+HP).

## Experimental

We investigated halogen derivatives of aliphatic acids, 1-Br-adamantane, halogen substituted benzoic acids, and dihalogen derivatives of benzene. The experiments on SD+HP were carried out in an apparatus of an anvil type<sup>6</sup> at a pressure up to 8 GPa at 293 K. The anvils were made from a VK-6 alloy with a working surface 9–10 mm in diameter. The rate of rotation of the anvils could be varied from 5 to 60° per second. The reaction products were analyzed by GC on columns with OV-225 and XE-60 stationary phases. Prior to the analysis of the halogenated acids, the latter were converted to methyl

esters with diazomethane. The products of the conversion of 1-Br-adamantane were additionally analyzed by NMR and IR spectroscopy. In the experiments with ammonium salts, the reaction mixture containing amino acids was treated by the described procedure<sup>7</sup> in order to obtain the volatile methyl esters of *N*-formylbutoxy derivatives.

## Results and Discussion

**Halide exchange in aliphatic radicals of carboxylic acids and adamantane.** The reactions in the mixtures of metal iodides with bromoacetic acid begin even when the reagents are ground in a mortar. Thus, in mixtures of  $\text{BrCH}_2\text{COOH}$  with NaI, KI, and RbI one can find 8, 7, and 1 % of  $\text{ICH}_2\text{COOH}$ , respectively. A rather high reactivity is observed for  $\beta$ -bromopropionic acid: after grinding in a mortar, 70 % of this acid is transformed to  $\beta$ -iodopropionic acid.

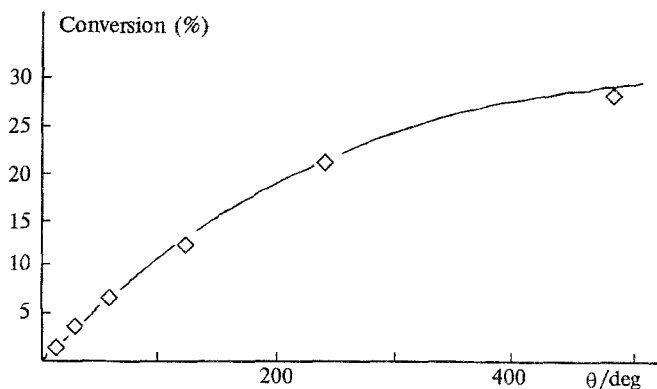
Halide exchange in halo-substituted acetic, propionic, and benzoic acids in the mixtures with various Na, K, Rb, and Cs halides was studied at a pressure up to 8 GPa at 293 K. The angles of the rotation of the anvils were up to 720°. The results obtained in this series of experiments are given in Table 1 and in Figure 1.

The data of Table 1 testify that, under conditions of SD+HP, almost all of the mixtures of halogenated acids with alkaline metal halides enter into reactions of halide exchange. The yields of the exchange products increase with increase in the value of deformation (Fig. 1) and pressure (Table 1, entries 4,5) and can rise up to >50 %. Less reactive are mixtures of the acids with Na salts (Table 1), except for the mixtures of bromoacetic acids, which easily react with NaI. The possible reason for this is the presence of water in the reaction mixture, which in this case participates in the reaction. This explanation is confirmed by the fact that the reaction in the mixtures begins even when the reagents are mixed in a mortar and proceeds during storage, while the rate of halide exchange increases together with increasing content of water in the reaction mixture. The consequence of such an exchange mechanism is the reversed order in which the reactivity of the metal halides changes, *viz.*, NaI is the most hygroscopic among the halides used, and therefore the mixtures containing this salt are the most active.

**Table 1.** Results of solid-phase exchange in mixtures of halo-substituted acetic and propionic acids and alkaline metal salts under conditions of SD+HP

Entry	Acid	Angle of rotation/deg	MHI	Yield (% of theor.)
1	ClCH <sub>2</sub> COOH	360	NaI*	0
2	«	360	NaBr	Traces
3	«	360	KBr	9.5
4	«	360	KI	12.0
5	«	240	KI	17
6	«	480	KI	38
7	ClCH <sub>2</sub> COOH	360	RbI	10.5
8	«	360	CsBr	14.5
9	«	360	CsI	12.0
10	BrCH <sub>2</sub> COOH	360	NaCl	1.5
11	«	360	NaI	61
12	«	360	KCl	13
13	«	360	KI	60
14	«	360	RbCl	30
15	«	360	RbI	50
16	«	360	CsCl	15
17	«	360	CsI	47
18	ICH <sub>2</sub> COOH	360	NaCl	2.5
19	«	360	NaBr	0
20	«	360	KCl	10.5
21	«	360	KBr	4
22	«	360	RbCl	17.5
23	«	360	CsCl	7.5
24	«	360	CsBr	7
25	ClCH <sub>2</sub> COOK	360	KI	25
26	ClCH <sub>2</sub> COOH	360	I <sub>2</sub>	4
27	BrCH <sub>2</sub> CH <sub>2</sub> COOH	360	KI	70
28	1-Br-adamantane	360	KI	19

Note. 6 GPa (for entries 5 and 6  $p = 8$  GPa), 293 K, angle of rotation of anvils 360°, content of acid in mixture 10 wt%. \* NaI was dried for three or more days in a desiccator over H<sub>2</sub>SO<sub>4</sub>.



**Fig. 1.** Kinetics of the exchange of ClCH<sub>2</sub>COOH + KI (6 GPa, 293 K, 10 wt % of acid in KI).

The presence of water absorbed from the atmosphere is also important, though to a lesser extent, for other reaction mixtures. Thus, it was found (Table 1) that the mixtures of acids with salts react when stored in air. For example, immediately after grinding the ClCH<sub>2</sub>COOH + CsI mixture in a mortar, the yield of ICH<sub>2</sub>COOH was 0.2 %, after 4 h it was 1.4 %, and after 24 h the yield was 45 % (after 24 h storage in air, the mixture is notably moistened and turns yellow).

Of the data given in Table 1, entries 25 and 26 draw attention. The use of potassium salt (entry 25) instead of the acid dramatically enhances the intensity of the halide exchange reaction (compare entry 4). This result could be expected, because replacing a proton with K should lead to the distortion of the C—Cl bond in the acid radical and therefore to increasing the reactivity of the halide in the exchange reaction. The results of experiment 26 indicate the interaction of free iodine with chloroacetic acid to form iodoacetic acid, which is in disagreement with the conventional concepts on the reactivity of such compounds. This can be considered as an illustration of the specific influence of SD+HP on the reactivity of organic compounds.

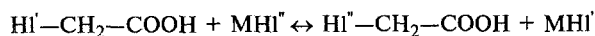
A comparison of the experiments with mixtures where the forward and back reactions take place can be done using the data given in Table 2. The yields of the forward and back reactions are close. The rates of the forward and back reactions can be estimated from the data of Table 2 using the equations for the rate of halide exchange:

$$-d[\text{R—HI}]/dx = k_1[\text{MHI}]_0 \cdot [\text{R—HI}] - k_2[\text{MHI}'] \cdot [\text{R—HI}'],$$

$$-d[\text{R—HI}]/dx = k_2[\text{MHI}]_0 \cdot [\text{R—Hal}'] - k_1[\text{MHI}'] \cdot [\text{R—HI}'],$$

where HI is halogen, R = —CH<sub>2</sub>—COOH

Since  $[\text{MHI}]_0 \gg [\text{MHI}]$ , if  $k_1$  and  $k_2$  do not differ too much, the first term of each equation is much greater than the second one, the expressions can be reduced, and after integration the equations are changed to:

**Table 2.** Comparison of the forward and back reactions:

Forward reaction			Back reaction			$k_1/k_2$
R—HI	MHI''	Yield R—HI' (%)	R—HI	MHI''	Yield R—HI' (%)	
Cl—R	NaBr	0	Br—R	NaCl	1.5	—
	KBr	9.5		KCl	13.2	0.89
	CsBr	14.6		CsCl	14.7	1.2
Cl—R	NaI	0	I—R	NaCl	2	—
	KI	12.2		KCl	10.8	1.53
	RbI	10.41		RbCl	17.7	0.8
	CsI	12.2		CsCl	7.9	2.4

$$\ln \{[\text{R—HI}^{\prime}]/[\text{R—HI}^{\prime}]_0\} = -k_1[\text{MeHI}^{\prime\prime}]_0 \cdot x,$$

$$\ln \{[\text{R—HI}^{\prime\prime}]/[\text{R—HI}^{\prime\prime}]_0\} = -k_2[\text{MHI}^{\prime}]_0 \cdot x$$

If  $[\text{MHI}^{\prime\prime}]_0$  and  $[\text{MHI}^{\prime}]_0$  are known, one can calculate the ratios of the rate constants of the forward and back reactions (see Table 2): their values only differ slightly from each other and fall within the 0.8–2.4 range.

Thus, in contrast to the liquid phase conditions, the nature of the entering halogen has little effect on nucleophilic substitution under conditions of SD+HP. The experiments with sodium salts, where a dramatic decrease in the intensity of the exchange reaction is observed, are the exceptions.

**Exchange of halogen bonded with phenyl ring.** The substitution of halogen in benzene ring was studied under conditions of SD+HP for halo-substituted benzoic acids and dihalo-derivatives of benzene. Unlike the reactions with halo-aliphatic derivatives, no reaction products were found when the reagents were mixed in a mortar or when storing the reaction mixtures. The main results of the experiments at SD+HP are given in Table 3. All of the reaction mixtures enter the reactions of halide exchange at SD+HP. It should be noted that, in contrast to alkyl halides, such exchange does not occur in a liquid phase. Thus, control experiments showed that a mixture of *para*-, *ortho*-, and *meta*-bromobenzoic acids and NaI does not enter the exchange reaction when stored for 5 h in boiling acetone (15 wt % of NaI, sensitivity of analysis  $\approx$  0.03 % of the conversion). Similarly to alkyl halides, the lowest yield of the exchange products was observed in the experiments with sodium salts. However, the reactivity of the other salts is not much higher, unlike the experiments with aliphatic com-

**Table 3.** Exchange of halogens in halobenzoic acids and halobenzenes with alkaline metal halides under conditions of SD+HP

Entry	Reagent	Salt	Pressure /HPa	Concentration of reagent (wt %)	Yield (% of theor.)
1	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> COOH	NaI	6	10	0.6
2		KI	6	10	2.3
3		RbI	6	10	1.15
4		CsI	6	10	1.4
5	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> COOH	KI	6	10	0.63
6	<i>p</i> -IC <sub>6</sub> H <sub>4</sub> COOH	NaCl	6	10	0.4
7		KCl	6	10	0.5
8		RbCl	6	10	2.1
9		CsCl	6	10	2.4
10	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> COOH	KI	1.5	10	0.065
11		KI	3	10	0.12
12		KI	4	10	0.27
13		KI	5	10	1.36
14		KI	6	10	3.73
15	<i>o</i> -BrC <sub>6</sub> H <sub>4</sub> COOH	KI	6	10	1.65
16	<i>m</i> -BrC <sub>6</sub> H <sub>4</sub> COOH	KI	6	10	1.07
17	<i>p</i> -IC <sub>6</sub> H <sub>4</sub> COOH	KBr	6	10	5.1
18	<i>o</i> -IC <sub>6</sub> H <sub>4</sub> COOH	KBr	6	10	2.6
19	<i>m</i> -IC <sub>6</sub> H <sub>4</sub> COOH	KBr	6	10	3.1
20	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> Br	KI	4	1	0.65/0.03*
21		KI	5	1	2.3/0.65
22		KI	6	1	5.6/4.3
23	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> I	KI	6	1	8.9
24		KI	6	1	0.95**

Note. 293 K, angle of rotation of anvils 360°. \* Yield *p*-BrC<sub>6</sub>H<sub>4</sub>I /Yield *p*-IC<sub>6</sub>H<sub>4</sub>I. \*\*  $T = 195$  K.

pounds. As follows from the data of Table 3, the yields of the forward (entries 1–4) and back (entries 5–8) reactions do not differ significantly (not more than a twofold difference), as in the case of alkyl halides. The dependence of the yields of the products on pressure and temperature is illustrated by entries 10–14, 20–22, and 23–24. At the same deformation value, the conversions of the reaction mixtures increase with increasing pressure and temperature. The evaluations of the volume of activation and energy of activation are  $\Delta V^\ddagger = -2.3 \text{ cm}^3 \text{ mol}^{-1}$  and  $\Delta E^\ddagger = -3.3 \text{ cm}^3 \text{ mol}^{-1}$  for the experiment series 10–14 and 20–22, respectively, and  $E_a = 11 \text{ kJ mol}^{-1}$ . These values are not high, which is characteristic of SD+HP processes.

Further experiments showed that the conversion of the reagents increases when decreasing the starting concentration of the organic compound, being also dependent on the method of mixing the starting reaction mixture. The reproducibility of the results was also improved when the concentration of the halo-derivative was decreased. Reasonable reproducibility was obtained for mixtures containing 1 % of an organic reagent mixed with other reagents on a vibrational mill, which is commonly used for the preparation of samples for IR spectroscopy. The degrees of conversion of the mixtures of isomeric benzoic acids with various alkali metal halides at different rotation angles of the anvil are given in Table 4.

As for halide exchange in halo-substituted benzoic acids, the degree of conversion increases with increasing deformation value (see Table 4). The influence of the nature of the salt cation is clearly revealed, *viz.*, the reactivity increases in the order of  $\text{NaI} < \text{KI} < \text{RbI} < \text{CsI}$ , *i.e.*, in parallel with the size of cation. The reactivity of *para*-substituted benzoic acids is always higher than that of *ortho*- and *meta*-substituted acids (see also Table 3, entries 2,5, and 14–19).

**Replacement of halogen with hydroxyl group.** This substitution was studied using the reactions of 1-Br-adamantane with Li and K hydroxides and with water. It was found that under conditions of SD+HP the hydrolysis of 1-Br-adamantane occurs. Adamantanol (AdOH) was also found to be formed in the reaction of halogen exchange in the mixture of Br-adamantane with KI. The results of the experiments are given in Table 5.

Considering the data of Table 5, one can note that the yield of 1-adamantanol under conditions of SD+HP is virtually independent of the basicity of the reagent, because the yields of the alcohol are nearly the same for the reaction mixtures with solid hydroxides and the experiment with moistened 1-Br-adamantane. The replacement of bromine with hydroxyl group occurs even in the absence of alkali. The water contained in the reagents due to absorption from air is enough for the reaction (entries 4 and 5).

The high reactivity of the absorbed water under conditions of SD+HP was already mentioned in the literature.<sup>4,5</sup> It is the hydrolysis of polymer molecules by absorbed water that is the reason for the formation of unexpected products such as free  $\beta$ -alanine.

A threefold increase in the yield of 1-adamantanol in experiment 5 relative to that of experiment 4 is most probably due both to the increased humidity of KBr and the greater value of the shear stress for this salt (it is 1.15-fold greater than that for KI).

**Replacement of halogen with amino group.** The possibility of replacing halogen with an amino group under SD+HP has been reported previously.<sup>8</sup> In this work, a mixture of chloroacetic acid with ammonia carbonate was used. After the experiment, the sample was treated with ninhydrin, and a coloring indicating the formation of glycine was observed. The purpose of this work is to study the replacement of halogen with an amino group under deformation of the ammonia salts of halogen-

**Table 4.** Conversions of bromobenzoic acids in reactions with alkaline metal halides at different angles of rotation of anvils ( $\theta$ )

Salt	$\theta$ /deg	Yield (%)		
		<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> COOH	<i>o</i> -BrC <sub>6</sub> H <sub>4</sub> COOH	<i>m</i> -BrC <sub>6</sub> H <sub>4</sub> COOH
NaI	360	1.1	1.3	0.7
	720	3.5	3.6	1.6
KI	180	14.2	6.8	4.9
	360	32.1	13.7	13.9
	720	45.2	17.0	20.2
RbI	180	20.9	12	8.3
	360	46.8	22.5	23.0
	720	57.2	24.4	27.3
CsI	180	26.4	18.4	9.2
	360	49.6	31.3	22.4
	720	60.9	38.5	32.6

*Note.* Concentration of each acid 1 wt %, 6 GPa.

**Table 5.** Reactions of hydrolysis of 1-Br-adamantane under conditions of SD+HP

Entry	Reagent	Yield AdOH (%)
1	LiOH	6.1
2	KOH	4.4
3	H <sub>2</sub> O	4.7
4	KI *	2.3(19)**
5	KBr *	6.3

Note. 8 GPa, 293 K, angle of rotation of anvils 360°, molar composition of starting mixture 1-Br-adamantane : reagent 1 : 10.

\* Content of water in the mixture components (%): KI, 0.24; KBr, 0.35; Br-Ad, 0.67 wt %. \*\* In brackets the yield of 1-adamantane is given.

**Table 6.** Formation of amino acids from ammonium salts of halo-substituted carboxylic acids under conditions of SD+HP

Ammonium salt of an acid	<i>p</i> /GPa	Amino acid	Yield of amino acid (% of theor.)
$\alpha$ -Br-propionic	5	$\alpha$ -Alanine	1.35
$\alpha$ -Br-hydrocinnamic	5	$\alpha$ -Phenylalanine	0.95
$\alpha$ -Br-phenylacetic	5	Phenylglycine	4.60
Chloroacetic	6	Glycine	1.05
Bromoacetic	6	Glycine	0.75
Iodoacetic	6	Glycine	0.60

Note. 293 K, angle of rotation of anvils 360°.

containing amino acids. The starting compounds, conditions of the experiments, and yields of amino acids are given in Table 6.

The data given in Table 6 indicate that ammonia salts of  $\alpha$ -halogen substituted carboxylic acids are able

to react under conditions of SD+HP to form  $\alpha$ -amino acids, *viz.*,  $\alpha$ -alanine,  $\alpha$ -phenylalanine, phenylglycine, and glycine. The reactivity of the halogen (Br) at the  $\alpha$ -carbon atom can change by an order of magnitude depending on the nature of the radical and is the highest in the case of the salt of  $\alpha$ -Br-phenylacetic acid. The ammonia salts of  $\alpha$ -Br-substituted acids may be put in the following order according to their increasing reactivity: Br-acetic acid <  $\alpha$ -Br-hydrocinnamic acid <  $\alpha$ -Br-propionic acid <  $\alpha$ -phenylacetic acid.

The highest reactivity of ammonium  $\alpha$ -Br-phenylacetate seems to be explained by the "rigidity" of the molecule of this salt, which is caused by the close disposition of the phenyl ring and the carboxyl group. According to the experimental data accumulated in the chemistry of deformational processes, rigid molecules usually show an increased reactivity under conditions of SD+HP.

The investigation of ammonium halo acetates showed that the yield of glycine in the reaction with iodoacetic acid is 1.75-times lower than that for chloroacetic acid. This fact shows that the reaction at SD+HP differs from the chemical process in the liquid phase, because it is known that in a solution iodine exchanges most readily due to its high polarizability, bromine is less reactive, and the least reactive is chlorine. Under conditions of the solid phase, the chloro-derivatives of amino acids most readily enter the reaction of the replacement of halogen with amino group.

**Experiments using a ball mill.** High reactivity of some mixtures of halogen containing compounds with alkaline metal halides found at SD+HP gave rise to a series of experiments with the use of a ball eccentric mill, where the SD+HP conditions appear when the balls are encountering and slipping.

A principal feasibility of the exchange reactions between the halogen bonded with aliphatic carbon atom and the halide of alkaline metal salt was reported previ-

**Table 7.** Conditions of the experiments and yields of the products of halo-substitution reactions upon treatment of the reagents in a ball mill

Entry	Reaction mixture	Composition of reac. mixture /mol : mol	Time of experiment /h	Product	Yield (% of theor.)
1	ClCH <sub>2</sub> COOH + KI	10*	0.85	ICH <sub>2</sub> COOH	26.0
2	1-Br-adamantane + KI	1:10	0.7	1-I-adamantane AdOH	70.0 15.5
3	Hexylchloride + KI	10*	0.7	Hexyliodide	Traces
4	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> COOH + KI	10*	3.	<i>o</i> -IC <sub>6</sub> H <sub>4</sub> COOH	0.06
5	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> COOH + KI	10*	1.5	<i>p</i> -IC <sub>6</sub> H <sub>4</sub> COOH	2.6
6	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> Br+KI	1*	2	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> I <i>p</i> -IC <sub>6</sub> H <sub>4</sub> I	17.7 5.1
7	1-Br-adamantane + LiOH	1:10	0.7	AdOH	2.1
8	1-Br-adamantane + H <sub>2</sub> O	1:1	0.7	AdOH	2.8
9	1-Br-adamantane + KBr	1:10	0.7	AdOH	8.5

Note. The temperature was 350 K; the vibration frequency and amplitude were 15 Hz and 100 mm, respectively. \* Wt % of organic reagent in the starting mixture.

ously.<sup>9</sup> In this work, the reaction of *N*-Bromethylphthalimide with the alkaline metal halogenides during the treatment of solid reagents in a gear mill was studied.

The results of a solid-phase exchange of halogens in the mixtures of halobenzoic acids or halobenzenes and alkaline metal salts during the treatment in a ball mill are given in Table 7. The most reactive is bromine bonded to aliphatic hydrocarbon moiety (1-Bradamantane). The treatment of this compound in a ball mill with KI resulted in the yield of 1-I-adamantane up to 70 %. Halobenzoic acids, especially *o*-Cl-benzoic acid (entry 4), exhibit a low reactivity. The hydrolysis of the organic halogen compounds in a ball mill proceeds to a considerable extent (entries 7,8) similarly to the SD+HP conditions. The role of water contained in the reagents is very significant in this process. This is confirmed by rather high yields of AdOH found in the experiments 2 and 9.

Thus, the results of the investigations indicate that, under conditions of SD+HP, solid halogen containing compounds of different types are capable of entering into the reactions of nucleophilic substitution that can be either typical or untypical of these compounds under conditions of a liquid phase. The exchange of halogens in the aromatic compounds with the participation of solid alkaline metal salts is an example of the reactions that do not occur or are difficult to carry out under common conditions.

Our results confirm the above-mentioned proposal about an unusually high activity of the water absorbed by the reagents under SD+HP conditions in the hydrolysis reactions.

In the processes of transformation of solid reagents, the regularities characteristic of the SD+HP conditions

are observed, viz., the degree of conversion depends on the value of SD and is sensitive to the shear stress of the reaction mixture. The data obtained in the SD+HP experiments indicate a rather high reactivity of the halogen-containing compounds (the time of the experiment can be only several seconds), which significantly exceeds the reactivity of the same compounds in liquid media.

## References

1. I. I. Yakovleva, A. A. Zharov, and V. M. Zhulin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2174 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 1968 (Engl. Transl.)].
2. A. A. Zharov, M. A. Alimov, N. P. Chistotina, and I. I. Yakovleva, *Th. dokl. VI Mezhd. konf. po organ. sintesu (IUPAC) [Abstracts of VI International Conf. on Organic Synthesis (IUPAC)]*, Moscow, 1986, A-101 (in Russian).
3. N. P. Chistotina and A. A. Zharov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2289 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 2103 (Engl. Transl.)].
4. A. A. Zharov and N. P. Chistotina, *Dokl. Akad. Nauk SSSR*, 1989, **306**, 650 [*Dokl. Chem.*, 1989, **306** (Engl. Transl.)].
5. N. P. Chistotina and A. A. Zharov, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 1197 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 944 (Engl. Transl.)].
6. N. P. Chistotina and A. A. Zharov, *Pribory i tekhnika eksperimenta [Instruments and Techniques of Experiments]*, 1974, No. 2, 229 (in Russian).
7. M. Makita, S. Yamamoto, and Yu. Tsudako, *Clin. Chim. Acta*, 1978, **88**, 305.
8. A. B. Solov'eva, V. A. Zhorin, and N. S. Enikolopyan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 717 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1977, **26**, No 3 (Engl. Transl.)].
9. A. V. Dushkin, E. V. Nagovitsyna, V. V. Boldyrev, and A. G. Druganov, *Sibirskii Khim. Zh., Izv. Sib. Otdel. Akad. Nauk SSSR*, 1991, No 5, 75 (in Russian).

Received October 24, 1994