Study of the solid-state hydrogen isotope exchange of L-alanine

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The solid-state reaction of isotope exchange of L-alanine (L-Ala) with spillover-hydrogen activated on a Rh(Pd)-supported catalyst was studied. The reactivity of the carbon atoms and the activation energies of isotope exchange of the hydrogen at the C(2) and C(3) atoms of the L-Ala molecule were determined using tritium NMR. The *ab initio* calculations of the activation energy of a model reaction between the alanine molecule and a hydroxonium cation were carried out. The mechanism and plausible structures of the transition states of this reaction were proposed.

Key words: isotope exchange, quantum-chemical calculations, activation energy, hydrogen spillover.

The interaction of gaseous hydrogen with metals of the platinum group results in molecular sorption, atomic chemisorption, and dissolution of hydrogen in the metal. In the case of supported catalysts such as $Pd/BaSO_4$ and Pd/Al_2O_3, the H atoms bound to the surface metal atoms can migrate to the support (spillover hydrogen, SH).[1] This activated hydrogen, located on the support surface, can enter the reactions characteristic of hydrogen on the surface of metals of the platinum group. The hydrogenation of unsaturated compounds, reduction of WO_3 to tungsten bronze, and isotope exchange in the hydroxyl groups of the inorganic supports, proceeding with participation of SH are known. Stereoselective hydrogenation of the aromatic group with the formation of an optically active compound[2] proceeds in a solid "heterogeneous catalyst—asymmetric crystals of a substituted phenol" mixture under the action of SH at room temperature. The nature of SH has not been established unambiguously up to the present despite the fact that processes using hydrogen spillover have been known for many years. According to several existing hypotheses, it is a solvated proton,[3] a proton-electron pair,[4] or an atomized hydrogen.[5] No theoretical studies using a quantum-chemical simulation of the reactions with participation of SH have been published yet.

Reaction based on applying high-temperature solid-state catalytic isotope exchange (HSCIE)[6,7] appears to be particularly efficient for the synthesis of biologically active compounds labeled by hydrogen isotopes. Intense isotope exchange between the H atoms of a solid organic compound and the activated hydrogen occurs in the solid mixture formed by a metal of the platinum group, a solid organic compound, and an inorganic support. As a rule, HSCIE proceeds to a large extent with retention of configuration of the asymmetric carbon atoms. HSCIE was the first reaction that made it possible to obtain organic compounds uniformly labeled with tritium; such compounds were inaccessible previously. The present work is dedicated to a theoretical and experimental study of the mechanism of HSCIE with tritium in alanine.

Experimental

Solid-state isotope exchange between L-alanine and tritium. A solid mixture containing 0.5 mg of L-alanine (L-Ala) ("Sigma") was placed into an ampule (10 mL). For this purpose, 25 mg of activated carbon (Norit A, "Serva") containing preliminarily supported L-Ala in a 50 : 1 ratio, and 10 mg of catalyst 5% Rh/Al_2O_3 ("Fluka") were mixed. A solid mixture obtained by coating 0.5 mg of L-Ala and 0.25 mg of rhodium(III) chloride on 5 mg of the catalyst, 5% $Pd/CaCO_3$ ("Fluka"), was also used. The ampule was evacuated and filled with gaseous tritium or a protium-tritium mixture (300 : 1) until a pressure of 100—500 Torr was reached. The reaction was carried out at 343—463 K for 20—90 min. The ampule was cooled, evacuated, and washed with hydrogen. The amino acid was desorbed with 0.1 *M* NH_4OH containing 20% of EtOH. The solution of tritium-labeled amino acid was evaporated to dryness, and then additionally evaporated twice with 20% aqueous EtOH to remove the labile tritium. The chromatographic analysis of optical isomers was performed by ligand exchange chromatography using chiral sorbents.[7] Incorporation of tritium into the amino acids was established by liquid scintillation analysis.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 757—762, April, 1997.

Tritium NMR spectroscopy. The ^3H and ^1H NMR spectra of solutions of amino acids in ^2H_2O were recorded on a Bruker AC-250 spectrometer (266.8 and 250 MHz, respectively). Tritium-labeled amino acids (50 mCi) dissolved in 500 μL of ^2H_2O were used in the measurements.[8]

Methods of Calculation. To elucidate the mechanism of the solid-state exchange between the hydrogen atoms at the C atoms of alanine and the SH atoms, quantum-chemical simulation of the reaction was used. A hydroxonium cation was considered as a model acidic center on the inorganic support. The calculations of the fragments of the potential energy surface (PES) of the interaction between the C atoms of alanine and the hydroxonium ion were carried out using the Dewar semiempirical AM1 method.[9] The geometries of the transition states and the activation energies of their formation were determined. The results obtained were refined by *ab initio* calculations according to the Hartree—Fock method[10] in the 3-21G and 6-31G* basis sets using the GAMESS program. A DEC AXP 3000-400 workstation was used in the calculations.

Results and Discussion

Experimental investigation of isotope exchange in L-alanine

Spillover tritium can migrate[11] over appreciable distances under conditions of spatial separation of the organic substance and the catalyst in HSCIE. Using this version of HSCIE, the catalyst was mechanically mixed with an inorganic support containing a preliminarily supported organic compound. There was no direct contact between the molecules of the solid organic compound and the surface of the metal of the platinum group. Therefore, the reaction of isotope exchange could only proceed in the layer of the organic compound after diffusion of the SH activated on the catalyst had occurred. Since the reaction of isotope exchange between the supported organic substance and the gaseous hydrogen isotope does not proceed in the absence of the platinum catalyst, the SH activated on the catalyst is responsible for causing the reaction under study to proceed.

To study the HSCIE reaction, L-Ala supported on activated charcoal was chosen. The molar radioactivity of the labeled amino acid obtained was determined experimentally, which made it possible to find the number of H atoms replaced by SH as a result of the HSCIE reaction. The molar radioactivity of the labeled amino acid obtained divided by the duration of the reaction allows one to estimate the rate of the reaction of isotope exchange. The isotherms of isotope replacement for a fixed composition of the solid phase at a constant hydrogen pressure were studied. The rate of the increase in the molar radioactivity in the initial stage of the reaction is only dependent on the temperature of the HSCIE reaction. The rate constant of the HSCIE reaction, expressed through the number of replaced H atoms in the molecule divided by the duration of the reaction, was determined under these conditions. The rate constant of the HSCIE reaction changes by over two orders of magnitude (Table 1) in the temperature interval between 343 and 428 K. The dependence of ln*k* on $1/T$ is shown in Fig. 1. The activation energy of the HSCIE reaction for the supported L-Ala is 15 kcal mol^{-1}.

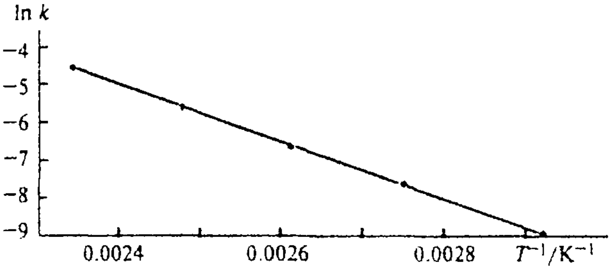


Fig. 1. Dependence of ln*k* on T^{-1} for the HSCIE reaction of L-Ala supported on charcoal. $y = -7538.6x + 13.089$, $R^2 = 0.9998$.

The reaction of solid-state catalytic hydrogenation (SCH) has been described previously.[12] For this reaction, hydrogenation and isotope exchange in the solid state have been shown to proceed simultaneously. The HSCIE and SCH reactions have similar E_a values, and their rates are in a similar way strongly dependent on the H_2 pressure. As can be seen from the data in Fig. 2, the rate of the reaction of isotope exchange in the studied pressure interval is proportional to the H_2 pressure. The kinetics of the HSCIE reaction of L-Ala at 443 K and at a pressure of 400 Torr is shown in Fig. 3. The rate of the increase in the molar radioactivity of the labeled L-Ala at the initial segment of the kinetic curve allows one to determine the rate constant of isotope exchange for the solid-state reaction. The number of tritium atoms that appear at the C(2) and C(3) atoms was found by the use of tritium NMR. The rate constants of the reaction of isotope exchange for different positions of the organic molecule (Table 2) were determined from these data. The rate of the replacement by tritium at the C—H bond at the C(3) atom at 403 K is higher than that at the C(2) atom by a factor of 7.5. The rate of isotope exchange increases as temperature increases. In this case, the rate of the exchange at the C(2) atom increases to a much larger extent. The isotope label selectively enters the methyl group of L-Ala at 403 K,

Table 1. Solid-state isotope exchange of tritium for hydrogen in L-Ala supported on charcoal (a protium-tritium mixture (300 : 1) with a pressure of 400 Torr, charcoal—amino acid (50 : 1), Ph—amino acid (1 : 1))

T/K	*t* /min	*A**	Number of substituted atoms (atom mol^{-1})	ln(*k*/atom mol^{-1} min^{-1})
343	90	1.18	0.0122	−8.903
363	40	1.85	0.0191	−7.646
383	20	2.58	0.0266	−6.623
403	20	7.10	0.0731	−5.610
428	20	21.0	0.216	−4.528

* *A* — molar radioactivity/Ci mol^{-1}.

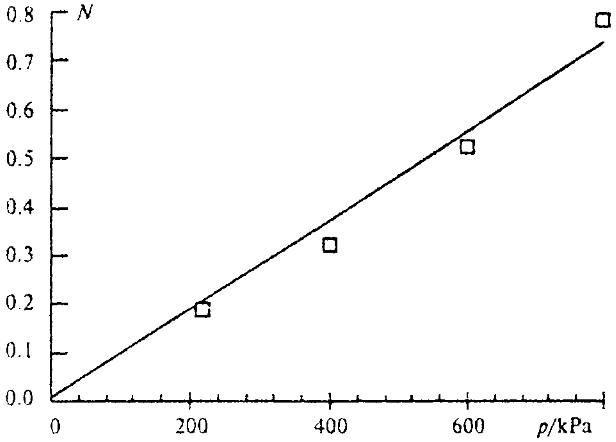


Fig. 2. Dependence of the number of hydrogen atoms incorporated into the L-Ala molecule (N) on the H_2 pressure at 443 K. $y = 0.0009x$, $R^2 = 0.9735$.

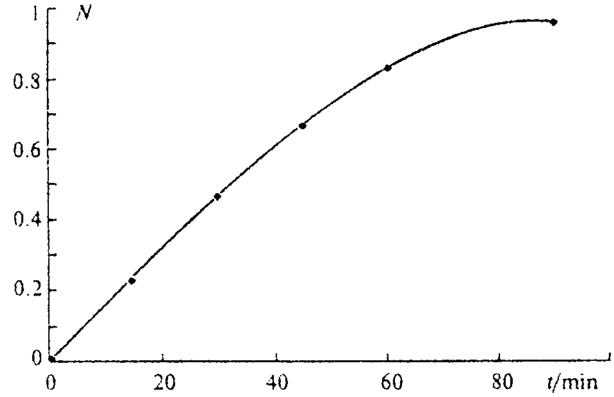


Fig. 3. The kinetics of the HSCIE reaction in L-Ala at 443 K and at an H_2 pressure of 400 Torr.

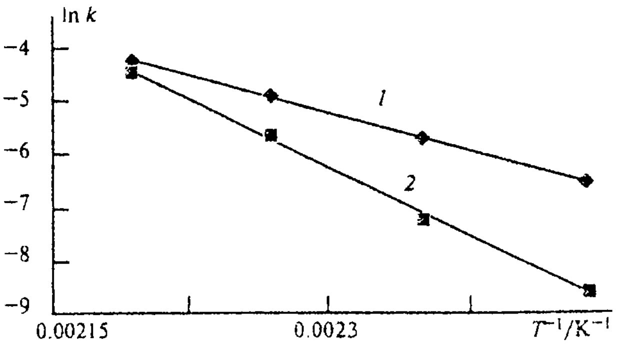


Fig. 4. Dependence of ln$k$ on T^{-1} for the reactions of high-temperature solid-state catalytic isotope exchange of the tritium atoms for hydrogen at the C(3) (*1*) and C(2) (*2*) atoms in L-Ala. *1* — $y = -7036.5x + 10.953$, $R^2 = 0.9991$; *2* — $y = -12878x + 23.357$, $R^2 = 0.9949$.

whereas uniform replacement of hydrogen by tritium for all C—H bonds of the L-Ala molecule is observed at 463 K. The dependence of ln$k$ on $1/T$ for the reaction of isotope exchange of hydrogen by tritium at the C(2) and C(3) atoms is shown in Fig. 4. The activation energy of isotope exchange in the methyl group of L-alanine is 14 kcal mol^{-1}; that for the α-position is 25.7 kcal mol^{-1}.

The activation energy for a complex one-route reaction is determined by the activation energy of its limiting stage. For reactions with participation of SH the limiting stage can be either the stage of the transfer of activated hydrogen from the surface of the platinum metal, migration over the surface of the inorganic support, or the reaction between SH and the supported substance. For SH particles participating in interactions with different positions in the L-Ala molecule, the stages of the transfer of the activated hydrogen from the surface of the platinum metal and that of its migration over the surface of the support are common stages. The fact that different activation energies of isotope exchange are observed for different positions in the molecule may be evidence that the interaction of the spillover tritium with the organic compound is the limiting stage of the HSCIE reaction.

The isotope exchange of SH with the surface hydroxyl groups of aluminum oxide and that with the labile H atoms at the N and O atoms in supported organic compounds proceeds much faster than the reaction with the C—H bonds. Our experiments showed that the accumulation of radioactivity due to interaction with gaseous tritium in the solid mixture formed by Al_2O_3 and the catalyst Rh/Al_2O_3 at 293 K and at a pressure of 300 Torr ceases after 20 min. The tritium accumulated on Al_2O_3 is likely located in the surface hydroxyl groups, since it is readily replaced by treatment with water. In this case ~0.8 mmol of tritium is contained on the surface of 1 g of Al_2O_3. The rapid accumulation of radioactivity in a solid mixture formed by L-Ala and the catalyst ($Pd/CaCO_3$) at 293 K also mainly ceases after 20 min; in this case ~3 hydrogen atoms per mole of amino acid are replaced. All of these H atoms were probably bound to the N and O atoms, since they are easily replaced by treating the mixture with water. Un-

Table 2. Solid-state isotope exchange of tritium for hydrogen in L-Ala as a component of the solid mixture containing $Pd/CaCO_3$ and $RhCl_3$

T/K	t /min	A*	Number of tritium atoms (atom mol^{-1})		ln(k/atom mol^{-1} min^{-1})	
			C(2)	C(3)	C(2)	C(3)
403	60	8	0.012	0.270	−8.517	−6.502
423	40	12	0.028	0.401	−7.264	−5.708
443	30	23	0.110	0.675	−5.608	−4.893
463	20	31	0.230	0.846	−4.465	−4.262

* A — molar radioactivity/Ci mol^{-1}.

der these conditions, isotope exchange of the H atoms at the C(2) and C(3) atoms was less than 0.01%. The transfer of tritium from the surface of the platinum metal and its migration over the surface of Al_2O_3 are fast stages compared to the isotope exchange in the HSCIE reaction.

The activation energy of the reaction of isotope exchange in L-Ala supported on charcoal appeared to be close to the E_a value of isotope exchange in the methyl group of L-Ala. This might be associated with the fact that the isotope exchange in L-Ala supported on charcoal was carried out at 428 K and lower temperatures, *i.e.*, under conditions when isotope exchange occurs predominantly in the methyl group of the amino acid. The similar values of E_a for the HSCIE reaction in a solid mixture of the amino acid with the catalyst and the amino acid preliminarily supported on charcoal can be evidence for the reaction proceeding with participation of spillover tritium activated on the catalyst in both cases. The HSCIE reaction is characterized by retention of configuration of the C atoms in the isotope exchange of hydrogen by tritium. Thus, the replacement of hydrogen with tritium at the C(2) atom is 23 %, while the content of the D-isomer does not exceed 2 % in the sample of L-Ala obtained at 463 K.

Quantum-chemical simulation of isotope exchange in L-alanine

The reactivity of H atoms in the solid organic substance was studied using tritium NMR of the products of the HSCIE reaction. The H atoms of the CH_3 group in the alanine and valine molecules were shown to be the most reactive.[13] The H atoms at the secondary and tertiary C atoms enter the reaction to a much lesser extent. The use of thermal atomization of gaseous tritium for obtaining tritium-labeled organic compounds is known.[14] It has been suggested that activated tritium reacts as a radical particle in a two-stage mechanism of the reaction of isotope exchange. Since in this case a radical of the organic compound is formed as an intermediate, the reactivity of different positions must be determined by the stability of the radicals formed at these positions. The radical at the tertiary C atom is more stable than those at the primary or secondary C atoms. Therefore, the H atom at the tertiary C atom reacts more readily with radicals. Were the spillover tritium to participate in the HSCIE reaction as a radical particle, one would expect that the methyl groups in alanine and valine would be less reactive than the other groups of these amino acids. The observed character of the distribution of isotope atoms in the labeled amino acid allows one to assume that SH in the HSCIE reaction does not react as a radical particle. Therefore, the hypothesis that SH has a protonic character can be considered as more reasonable.

To prove this hypothesis, a quantum-chemical calculation of the interaction between a proton and the amino acid was carried out.[13] The energies of the proton affinity for different C atoms in the alanine and valine molecules were calculated. The existence of a correlation between proton affinity and reactivity in the HSCIE reaction was shown. Activated hydrogen exhibits the properties of an electrophilic particle. A proton is known to react with methane in the gaseous phase to yield a complex ion containing a five-coordinated C atom. In the methonium ion formed, two H atoms (with lengthened C—H bonds) approach each other to a distance that allows for the formation of a bond between them.[15] The *ab initio* quantum-chemical calculations showed the possibility of the synchronous transfer of an H atom between interacting molecules in the interaction of methane with the hydroxonium ion.[16] In this case, a transition state with a five-coordinated C atom that has a geometry similar to that of the previously described methonium ion is formed. The activation energy of this isotope exchange at one catalytic center is 21 kcal mol^{-1}. The transition state of this reaction is additionally stabilized at the expense of the formation of a bond between the exchanging hydrogen ions. This mechanism of synchronous isotope exchange seems to be more probable than that of synchronous transfer with participation of two catalytic centers.[17—19] The exchanging hydrogen atom in the transition state attacks the C—H bond from the side of the replaced H atom. The proposed mechanism is in good agreement with the observed retention of configuration of the C atom in the HSCIE reaction.[6]

At moderate temperatures the proton is covalently bonded to one or two electronegative atoms. In the latter case a hydrogen bond is formed. The transfer of the proton in the solid or over a surface containing bound water and hydroxyl groups can occur *via* a "relay" mechanism. The activation energy of such a transfer is 4.8 kcal mol^{-1}.[20] It is also assumed that in the case of spillover the proton and its pertinent electron can move individually over the surface. Both electronic and ionic conductivity have been found to exist in studies of spillover over the surface of an inorganic support.[4] In order for the processes involving SH to occur fast at moderate temperatures, the presence of cocatalysts is necessary. The rate constant was shown to be dependent on the proton affinity of the cocatalyst.[3] The cocatalysts participate in proton transport. The coefficient of diffusion of SH over the surface of an inorganic support can change by ten orders of magnitude if the mechanism of SH transport and the temperature of the process changes.[21] The spillover of hydrogen is accelerated in the presence of steam at moderate temperatures.[4,22]

The water molecules adsorbed on the surface, the surface OH groups, and the O atoms of the inorganic support can participate in SH transport. The interaction between the H_3O^+ ion and the organic compound was considered to be a model for the solid-state reaction of isotope exchange. The mechanism of electrophilic substitution at the saturated C atom with synchronous

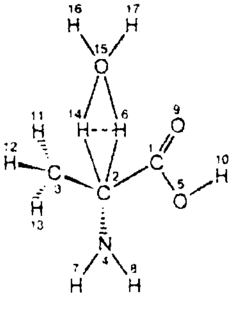
Table 3. Results of the AM1 calculations of geometric parameters (bond lengths, bond and dihedral angles) for the transition state of the reaction of isotope exchange of hydrogen between the C(2) atom of alanine and the hydroxonium ion (structure **1**)

Bond	R/Å	Bond	R/Å
1—2	1.55	14—4	2.24
2—3	1.55	14—9	2.81
2—4	1.38	15—16	0.96
1—5	1.34	15—17	0.96
1—9	1.23	16—9	3.85
2—15	3.36	**Angle**	**φ/deg**
3—15	4.03		
1—15	4.00	6—2—14	33.4
4—7	1.00	6—15—14	21.5
5—10	0.98	6—14—2	73.3
4—8	1.00	1—2—3	107.5
3—11	1.12	1—2—4	116.0
3—12	1.12	1—5—10	110.0
3—13	1.12	2—1—9	124.7
2—6	1.36	2—1—5	112.7
2—14	1.36	16—15—17	104.2
6—15	2.11	2—6—14—15	−180.0
14—15	2.08	1—2—6—9	11.4
6—14	0.78	2—1—5—10	177.5
6—9	2.32	3—2—1—9	95.4
6—4	2.17	4—2—1—9	−132.0

Table 4. Results of the Hartree—Fock and AM1 calculations of geometric parameters (bond lengths, bond and dihedral angles) for the transition state of the reaction of isotope exchange of hydrogen between the C(3) atom of alanine and the hydroxonium ion (structure **2**)

Bond	R/Å		Angle	φ/deg	
	AM1	3-21G		AM1	3-21G
1—2	1.53	1.52	1—2—3	106.3	107.3
2—3	1.54	1.52	1—2—4	113.1	105.7
2—4	1.44	1.47	1—5—10	110.5	115.4
1—5	1.34	1.33	5—1—9	121.0	125.6
1—9	1.24	1.21	5—1—2	115.2	111.4
3—15	3.30	2.85	9—1—2	123.7	122.9
2—6	1.14	1.08	3—2—4	110.7	106.9
4—7	1.00	1.01	2—4—7	111.8	113.8
4—8	1.00	1.01	2—4—8	113.0	113.0
5—10	0.98	0.97	6—2—1	107.5	110.2
3—11	1.43	1.21	2—3—12	112.1	113.2
3—12	1.12	1.09	2—3—13	112.7	114.1
3—13	1.13	1.08	2—3—11	111.8	112.9
3—14	1.32	1.23	2—3—14	103.6	100.1
11—14	0.87	0.90	11—3—14	36.6	43.5
9—11	2.07	2.19	3—11—9	96.3	142.1
9—14	2.81	2.60	3—11—14	64.7	69.7
4—11	3.05	2.99	11—15—14	22.4	29.5
4—14	2.77	2.38	15—11—14	82.3	72.4
11—15	2.02	1.80	3—15—16	128.6	137.8
14—15	2.08	1.75	3—15—17	126.3	110.9
15—16	0.96	0.97	16—15—17	104.4	111.2
15—17	0.96	0.97	9—15—10	1.5	2.0
			2—1—5—10	−179.2	−178.2
			3—2—4—7	−101.9	−71.5
			3—2—4—8	132.7	161.1
			9—1—2—3	−12.2	−6.9
			5—1—2—3	168.3	176.8
			1—9—11—3	29.5	19.3
			3—11—14—15	180.0	−179.1
			3—11—14—9	−70.8	−94.1

proton exchange was investigated. Formation of transition states similar to those observed for isotope exchange in methane is possible if the H_3O^+ ion and the C atoms of alanine approach each other. The geometry of the transition states for the reaction of isotope exchange of hydrogen at the C(2) and C(3) atoms (structures **1** and **2**, respectively) is shown below.



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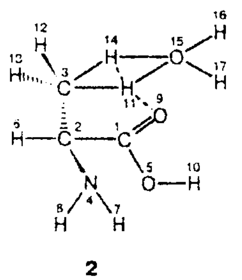

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The results of the calculations are given in Table 3 and Table 4. Using the Dewar semiempirical AM1 method, the activation energy of isotope exchange of the hydrogen at the α-carbon atom of alanine was determined to be 21 kcal mol^{-1}, while isotope exchange in the methyl group occurs with an activation energy of merely 11 kcal mol^{-1}. The cause of this stabilization of the transition state at the C(3) atom might be the interaction of the H(11) atom with the carbonyl oxygen O(9). Such interaction is not realized for the transition state at the C(2) atom. Good agreement is observed between the E_a values calculated using the quantum-chemical simulation and those experimentally measured for the HSCIE reaction. This may be evidence for the validity of the proposed mechanism of the HSCIE reaction.

Thus, the interaction between SH and the organic compound has been shown to be the stage that determines the rate of the HSCIE reaction. A mechanism of solid-state hydrogen isotope exchange with participation of positively charged hydroxonium ions interacting with the C—H bonds of organic compounds has been suggested. The isotope exchange is in agreement with the mechanism of electrophilic substitution at the saturated C atom with the formation of a transition state that includes a five-coordinated C atom. A model explaining the observed reactivity and the retention of configuration of asymmetric atoms in the molecules of tritium-labeled amino acids obtained from the HSCIE reaction has been proposed.

This work was financially supported by the International Science Foundation (Grant N6A000) and the Russian Foundation for Basic Research (Project Nos. 94-03-09015 and 96-03-34443).

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Received April 23, 1996;
in revised form November 12, 1996