Gas chromatography of halogenated adamantanes

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The main thermodynamic characteristics of the adsorption of haloadamantanes on graphitized thermal carbon black were determined by experimental measurements and by calculations in terms of molecular-statistic theory of adsorption. Using experimental data, the Kovac retention indices were calculated and the optimum conditions for gas-chromatographic separation of haloadamantanes on stationary phases with different polarity were elucidated. The influence of the "cage" effect in the adamantane unit on the chromatographic properties of haloadamantanes was established.

Key words: haloadamantanes, gas chromatography, adsorption, thermodynamic characteristics of adsorption, molecular statistic theory, "cage" effect, stationary phases, retention indices.

Halogenation plays an important role in the functionalization of the adamantane cage.[1] Halogen derivatives are the starting compounds or intermediates in the syntheses of most of biologically active adamantanes. The most convenient method for checking the purity of medical preparations is gas chromatography. However, data on the chromatographic behavior of haloadamantanes are scarce; this renders their analysis difficult.

The enhanced reactivity of halogenated adamantanes is known to be determined, first of all, by unusually high polarization of the C—Hal bonds and by the ease of formation of adamantyl cations, in particular, *tert*-adamantyl cations.[1,2] The specific features of electron density distribution in the adamantane nucleus are due to the so-called "cage" effect,[1—3] typical of the major part of adamantane-like structures.[4] The cage effect is also reflected in the chromatographic retention of adamantane and its derivatives under conditions of gas solid and gas liquid chromatography.[4—6]

The purpose of this work is to study the chromatographic behavior of halo-substituted adamantanes on stationary phases (SP) of different polarities and on graphitized thermal carbon black and to perform molecular-statistic calculation of the main thermodynamic characteristics of adsorption (TCA). In addition, it is of interest to study the role of the cage effect in the chromatographic retention of haloadamantanes as a function of the number and the positions of halogen atoms in the adamantane cage.

Experimental

The compounds studied in this work were synthesized at the Chair of Organic Chemistry of the Samara State Technical University. The purity of the compounds synthesized was checked by GC/MS.

The chromatographic measurements were carried out using a Tsvet-100M gas chromatograph with a flame ionization detector. Nitrogen was used as the carrier gas.

In gas solid chromatography (GSC), separation was performed on a glass micropacked column (0.7 m × 1.5 mm). The Sterling-MT graphitized thermal carbon black (GTCB) with a specific surface area of 7.6 $m^2 g^{-1}$ and a mass of 0.86 g served as the adsorbent. The adsorbent granule size was 0.18—0.25 mm. In experiments with low degrees of coverage of the GTCB surface, the substances to be analyzed were introduced in the chromatographic column from the gas phase. The values of the Henry constants (K_1) and the differential heats of adsorption ($\Delta\bar{U}_1$) were evaluated from chromatographic experiments by a known procedure.[7] The error of the experimental determination of TCA did not exceed 4%. The molecular-statistic calculation of the TCA for haloadamantanes was described previously.[7—9] The semiempirical atom—atom potential functions for intermolecular interactions (AAP) were chosen in the form of the Backinham—Corner potential.[7] The AAP parameters required for calculations were taken from the literature.[7—10] The experimental and theoretical TCA values for haloadamantanes determined in this work are listed in Table 1.

A JMS-D300 GC/MS spectrometer with a JMA-2000 computer and a HP-5890 chromatograph was used. The temperature of the ion source was 150 °C, the energy of ionizing electrons was 70 eV, the accelerating voltage was 3 kV, and the range of mass numbers was 40—400 amu.

Gas liquid chromatography (GLC) was carried out using steel packed columns (1 m × 3 mm) with Chromaton N-AW (granule size 0.125—0.160 mm) washed by HCl and containing 15% stationary phases of different polarity (PMS-100 (Russia), SE-30, OV-275, Carbowax-20M (Czechia)). The column and vaporizer temperatures were 150 and 180 °C, respectively. Solid samples were analyzed as solutions in hexane and acetone; the sample volume was 1 μL. The retention indices (RI) were

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Table 1. Experimental (I) and calculated (II) thermodynamic characteristics of adsorption of some adamantane derivatives on GTCB

Compound	ΔT/K	Constant of the equation[a]		$-\Delta\bar{U}_1$/kJ mol^{-1}				$\ln K_1$ (423 K)/cm^3 m^{-2}			
		I		I	II			I	II		
		$-A$	B		1[b]	2[c]	3[d]		1[b]	2[c]	3[d]
Adamantane	333—433	11.37	4925.00	41.0	40.6	40.9	—	0.48	0.44	0.48	—
1-Chloroadamantane	393—473	11.23	5424.59	45.1	44.8	45.0	45.2	1.59	1.48	1.52	1.59
2-Chloroadamantane	393—473	11.31	5448.64	45.3	44.9	45.2	—	1.57	1.51	1.56	—
1,3-Dichloroadamantane	393—473	11.93	6367.24	52.9	50.4	52.5	53.0	3.12	2.88	2.93	3.11
1-Bromoadamantane	393—473	11.48	5689.20	47.3	47.7	47.9	48.1	1.97	1.89	1.94	1.97
2-Bromoadamantane	393—473	11.57	5721.51	47.6	47.5	47.7	—	1.96	1.92	1.96	—
1,3-Dibromoadamantane	393—473	—	—	—	58.6	58.8	59.1	—	3.75	3.80	3.86

[a] The constants of the equation $\ln K_1 = A + B/T$.

[b] Without corrections for the cage effect.

[c] With a correction for the cage effect introduced in the AAP of the cage C atoms ($\beta = 1.02$).

[d] With a correction introduced in the AAP of the Hal atom in the bridgehead position ($\beta_{Cl} = 1.04$; $\beta_{Br} = 1.015$).

calculated by a known method[11] (the error of experimental determination of the RI was 6—10 i.u.).

Results and Discussion

The K_1 and $\Delta\bar{U}_1$ values of some chloro- and bromo-substituted adamantanes, both experimental and determined by the molecular-statistic method, listed in Table 1 demonstrate the similarity of the thermodynamic characteristics of adsorption for 1- and 2-haloadamantanes; therefore, these compounds cannot be separated in a column with GTCB. Nevertheless, according to GC/MS analysis, the 2-isomer is eluted ahead of the 1-isomer, although the differences between the TCA values are slight. This order of elution is opposite to that established previously[4] for adamantanol and aminoadamantane isomers. Apparently, the inversion of the order of elution of the 1- and 2-isomers on passing to chloro- and bromoadamantanes is due to the different influence of OH or NH_2 groups, on the one hand, and Hal atoms, on the other hand, on the electron density distribution in the molecules. Since the nonequivalent adsorption behavior of the atoms can be estimated quantitatively in terms of the molecular-statistic theory of adsorption,[7,9,10] in this study we calculated the thermodynamic characteristics of adsorption of haloadamantanes.

The parameters of the potential function of intermolecular interaction are sensitive to the state of the electronic shells of the atom in the adsorbing molecule.[7] Therefore, atoms of the same element can be adsorbed differently. This allows the use of atom—atom potentials to study the influence of various intramolecular interactions on the behavior of organic compounds subjected to chromatography. The atom—atom potentials of halogen atoms attached to an aromatic ring have been calculated;[8—10] it was demonstrated that these parameters are suitable only for a rough estimation of the heats of adsorption of molecules of the corresponding aliphatic derivatives.[12] In calculations of the TCA for polyhalo-substituted benzene and naphthalene derivatives, the AAP parameters of the halogen atoms do not exhibit additivity, which is related to the so-called "*ortho*" and "*ortho—ortho*" effects.[9,10,13] Thus, depending on the specific features of electron density distribution in the adsorbed molecule, caused by changes in the nearest neighboring atoms and the valence states of the atoms in the molecule, the AAP parameters of halogen atoms can be appreciably dissimilar.[4,9,10,13]

The attempt to describe the adsorption of haloadamantanes using the known parameters of the atom—atom potentials for halogens, carbon, and hydrogen provides results that do not coincide with the experimental TCA values (see Table 1). The values of the Henry constant K_1 for 1-isomers prove to be lower than the corresponding K_1 values for 2-isomers, thus conflicting with the order of elution of compounds observed experimentally. Previously,[4—6] it has been found that the cage effect occurring inside the adamantane unit accounts for the nonequivalent properties of the bridging and bridgehead carbon atoms in the adamantane framework. After introduction of the β correction (1.02) in the AAP parameters of the bridgehead carbon atoms, the experimental and calculated TCA values for 2-chloro- and 2-bromoadamantanes lies within the experimental error. However, in the case of 1-chloro- and 1-bromoadamantanes, the difference between the calculated and experimental TCA values exceeds the error of gas-chromatographic measurements, and the theoretical order of elution of the isomers still differs from the experimental one.

It is known that the bridgehead carbon atoms of the adamantane framework can interact additionally with each other to bring about delocalization of electron density over the entire cage.[14,15] Correspondingly, the atoms of α-substituents experience pronounced influence of the adamantane cage, which is reflected on their polarizability.[16] Thus, the specific features of the physicochemical properties,[16—18] reactivity,[1—3] and chromatographic behavior[4—6] of 1- and 2-substituted adamantanes are, apparently, related to the fact that the cage effect influences the properties of 1- and 2-substituents in different manners.

The fact that the experimental and calculated TCA values for 2-haloadamantanes are brought into agreement after the introduction of corrections for the nonequivalent adsorption poroperties of the bridgehead and bridging carbon atoms of the cage indicates that 2-substituents do not experience direct cage effect. In the case of 1-derivatives, agreement between the experimental and calculated results can be attained only by applying an additional correction for the AAP parameters of the Hal atoms in the bridgehead positions. Using the algorithm of determination of the correction β known from the literature,[4,7,10] it was shown that a satisfactory agreement between experimental and calculated TCA values is attained when the AAP parameters of chlorine and bromine atoms have been increased by factors of 1.04 and 1.015, respectively.

The dipole moment of a molecule (μ/D) is inversely proportional to its polarizability (α/cm^3); thus, the more polar is the molecule, the less pronounced should be the dependence of molecular polarizability on intramolecular interactions. Apparently, with an increase in the polarization, the required adjustment decreases. Since the 1-bromoadamantane molecule is more polar (μ = 2.49 D) than the 1-chloroadamantane molecule (μ = 2.32 D),[16] the role of the cage effect in the AAP parameters of the chlorine atom in 1-chloroadamantane is more significant than that for the bromine atom in 1-bromoadamantane.

The possibility of using the refined AAP parameters of chlorine atoms in 1-chloroadamantane for the calculation of TCA of the 1,3-dichloroadamantane molecule can serve as a criterion for the validity of the correction β proposed. As follows from the data of Table 1, the calculated TCA values for the 1,3-dichloroadamantane molecule found using the AAP of a chlorine atom refined in this study coincide to within the experimental error with the K_1 and $\Delta\bar{U}_1$ values determined experimentally.

Despite the additivity of the AAP parameters of chlorine and bromine in the molecules of 1,3-haloderivatives, the increments of the heat of adsorption introduced by each atom individually are markedly different (Table 2). Apparently, these differences are not related to the electronic structure of adamantane but stem from the arrangement of the adamantane cage on the GTCB surface.[7] The increments of the heats of adsorption for halo-derivatives of the aliphatic series vary in a similar way[7] (see Table 2). Unlike the increments for halo-substituted adamantanes, the increments of the heats of adsorption of the halogen atoms for the series of planar chloro- and bromobenzene molecules are constant and are equal to 9 and 11 kJ mol^{-1}, respectively.[8—10] A similar situation is found for ethane derivatives. Note that the increments of the adsorption heats found in this study for the halogen atoms in the 1- and 2-isomers are virtually equal.

Table 2. Contributions of the halogen atoms to the heat of adsorption of halogenated adamantanes, benzene, and ethane on GTCB

Adamantane		Benzene[a]		Ethane[b]	
Halogen	$\Delta(-\bar{U}_1)$ /kJ mol^{-1}	Halogen	$\Delta(-\bar{U}_1)$ /kJ mol^{-1}	Halogen	$\Delta(-\bar{U}_1)$ /kJ mol^{-1}
Cl(1)	4.1	Cl(1)	9	Cl(1)	5.6
Cl(2)	4.3	Cl(1,4)	9	Cl(1,2)	6.4
Cl(1,3)	7.8	Br(1)	11	Br(1)	7.7
Br(1)	6.3	Br(1,4)	11	Br(1,2)	9.5
Br(2)	6.5				
Br(1,3)[c]	11.8				

[a] The data were taken from Refs. 9, 10.

[b] The data were taken from Ref. 7.

[c] For 1,3-dibromoadamantane, the calculated value $\Delta\bar{U}_1$ = 59.1 kJ mol^{-1} was used.

The attention is drawn by the observed difference in the order of elution of isomeric adamantanols, aminoadamantanes, and haloadamantanes on GTCB. In the case of derivatives with electron-donating groups, (OH and NH_2), the 1-isomer is the first to be eluted, while in the case of derivatives with electron-withdrawing groups (Cl, Br), this is the 2-isomer.[4] This might be due to the fact that the decrease in the electron density on the oxygen and nitrogen atoms in 1-adamantanol and 1-aminoadamantane induced by the cage effect attenuates the polarizability of these molecules and weakens the holdup on GTCB. Conversely, the halogen atoms, which exhibit electron-donating properties, carry a higher electron density when occur in position 1 than in position 2. This is indicated by the data on chemical shifts in the ^{1}H NMR spectra of the compounds in question.[3,19] Like an aromatic system, the adamantane nucleus can act as either an electron donor or an electron acceptor, depending on the electronic structure of substituents.[5,19]

Data on the chromatographic retention of haloadamantanes on stationary phases of different polarity are scarce. Therefore, we studied the chromatographic properties of this group of compounds under conditions of GLC.

Table 3 lists the retention indices (*I*) found in this study. The retention indices of all the compounds considered were found to increase on passing from nonpolar (SE-30, PMS-100) to polar (OV-275, Carbowax-20M) stationary phases. Unlike adsorption on GTCB, in the adsorption on GLC sorbents, 2-halo-derivatives are retained more strongly than 1-halo-derivatives.

It is known[4—6] that the main contribution to the chromatographic retention of adamantane derivatives under GLC conditions is made by the bulky adamantyl fragment. Chromatographic behavior of adamantyl-con-

Table 3. Retention indices (I) of halo-substituted adamantanes on stationary phases with different polarity at 423 K

Compound	I/i.u.			
	SE-30	PMS-100	OV-275	«Carbowax-20M»
Adamantane	1120	1138	1283	1325
1-Methyladamantane	1140	—	—	1315
2-Methyladamantane	1200	—	—	1407
1-Chloroadamantane	1300	1321	1570	1691
2-Chloroadamantane	1345	1369	1610	1741
1,3-Dichloroadamantane	1453	1474	1833	2013
1,3,5-Trichloroadamantane	1582	1642	2067	2311
1-Chloromethyladamantane*	1409	—	—	1800
1-Bromoadamantane	1389	1417	1675	1817
2-Bromoadamantane	1433	1460	1719	1869
1,3-Dibromoadamantane	1590	1631	1987	2264
1,3,5-Tribromoadamantane	1779	1829	2273	2659
1-Bromomethyladamantane*	1494	—	—	1925

* The data were taken from Ref. 5.

Table 4. Increments (I) of the retention indices for the halogen atoms and the methyl group in adamantanes for various SP

Compound	I/i.u.			
	SE-30	PMS-100	OV-275	«Carbowax-20M»
1-Methyladamantane	20	—	—	−10
2-Methyladamantane	80	—	—	82
1-Chloroadamantane	180	183	287	366
2-Chloroadamantane	225	231	327	416
1,3-Dichloroadamantane	153	173	263	322
1,3,5-Trichloroadamantane	129	148	234	298
1-Chloromethyladamantane	269	—	—	485
1-Bromoadamantane	269	279	392	492
2-Bromoadamantane	313	322	436	544
1,3-Dibromoadamantane	201	214	312	447
1,3,5-Tribromoadamantane	189	198	286	395
1-Bromomethyladamantane	354	—	—	610

taining compounds is largely determined by the position of the substituent in the adamantyl cage. Being involved in weak interactions with the molecules of a polar SP, the adamantyl fragment substituted in the bridgehead positions behaves similarly to aromatic systems.[5,6] When adamantane derivatives contain substituents at the bridging atoms, the adamantane cage, like other bulky hydrocarbon groups,[5] shields the functional group. Table 4 gives the calculated increments of the retention indices for halogen atoms on different stationary phases. It can be seen that for nonpolar SP (SE-30 and PMS-100), the increments for the halogen atoms in the 1- and 2-derivatives are intermediate between those for aromatic[20,21] and aliphatic[22] halo-containing molecules. The increments for aromatic and aliphatic halo-derivatives on polar stationary phases, OV-275 and Carbowax-20M, vary in a similar way.

SP	Halo-derivatives			
	aromatic		aliphatic	
	Cl	Br	Cl	Br
Non-polar	165	240	260	350
Polar	270	385	150	575

The increments for the halogen atoms in 1-substituted adamantanes are closer to the corresponding values for the halogen atoms in aromatic derivatives, while those in 2-substituted adamantanes are more similar to those found for aliphatic halo-derivatives. Apparently, it is due to this fact that retention of 1-haloadamantanes on the sorbent is weaker than the retention of the corresponding 2-derivatives.

Upon the insertion of a methylene unit between the halogen atom and the 1-adamantyl group, the retention indices on both polar and nonpolar SP substantially increase (by 105—110 i.u). The contribution of the methylene unit to the retention is found to be comparable with the contribution of the CH_2 group in the series of aliphatic monohalo-substituted hydrocarbons on the same stationary phases (95—100 i.u.), while the increment for the halogen atom is equal to the contribution of halogen atoms in the corresponding 1-haloderivatives. In the case of nonpolar SP (SE-30), the contribution of the methylene unit to the retention of 1-methyladamantane is 20 i.u.[5] The decrease in the contribution of the CH_2 group is related to the cage effect on the α-carbon atom, which decreases the electron density at the neighboring atoms[1,3,19] and, hence, weakens the dispersion interactions with the SP molecules. The contribution of the methylene unit (35 i.u.) to the retention of 1-ethyladamantane proves to be much lower than the contribution of the Me group (110 i.u.).[5] Thus, the increase in the retention index (105—110 i.u.) observed on passing from 1-halo-derivatives to the corresponding 1-halomethyl derivative appears to be due to the increase in the increment for the halogen atom rather than to the contribution of the CH_2 group. Assuming that the increment for the methylene unit is 20 i.u., we find that the contributions of the chlorine and bromine atoms to 1-halomethyl derivatives are 269 and 354 i.u., respectively (see Table 4). The increments of the retention indices for the halogen atoms in molecules with a bridging methylene group are equal to those for the halogen atoms in aliphatic derivatives to within the experimental error. The reason is apparently that the "cage" effect does not influence directly the halogen atom in 1-halomethyladamantanes. Thus, the retention indices of 1- and 2-haloadamantanes on nonpolar SP can be calculated in terms of the additive scheme with allowance for the cage effect in the adamantane unit. The retention indices on polar SP exhibit the same pattern of variation (see Table 3).

The introduction of a methylene unit in the bridgehead position of the adamantane molecule results in a decrease in the RI by 10 i.u. for the adsorption on a polar SP (Carbowax-20M); this is associated with the influence of the cage effect on the α-carbon atom (see Table 4).

The same value for the increment of the CH_2 group is found for 1-halomethyladamantanes. If the contribution of the adamantane fragment to the retention of halomethyladamantanes by a sorbent is taken to be equal to its contribution in adamantane, the increment for the halogen atom in 1-halomethyladamantanes on polar SP proves to be somewhat higher (by 35 i.u. for chloro and bromo derivatives) than the increments for the halogen atoms in the corresponding aliphatic derivatives. Conversely, if the increments for the halogen atoms in halomethyladamantanes and aliphatic halo derivatives (1-chloromethyladamantane and 1-bromomethyladamantane) are taken to be equal, the contribution of the adamantane fragment to the retention proves 35 i.u. greater than that in 1-haloadamantanes. Apparently, this is a result of additional specific interaction of the adamantane nucleus with polar molecules of the stationary phase.

The increase in the contribution of the adamantane cage to the retention on polar SP in 1-halomethyladamantanes with respect to 1-haloadamantanes appears to be related to the introduction of the methylene unit, which attenuates the deforming influence of the halogen atom on the electronic shell of the adamantyl nucleus and, hence, increases its polarizability.[21] The retention of hydrocarbon fragments on various SP depends on their polarizability.[5,6] Thus, the retention indices of haloadamantanes on polar stationary phases can be calculated in terms of the additive scheme that takes into account the additional specific interaction of the adamantane cage with the SP molecules caused by the enhanced electron density within the adamantane unit.[1,3,19]

Thus, an increase in the number of halogen atoms in the bridgehead positions of the adamantane cage entails a decrease in the contribution of the halogen atom to the retention on both polar and nonpolar SP. A similar dependence is observed for the corresponding aliphatic[22] and aromatic[21] adamantane derivatives.

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