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Mechanism of Formation and Molecular Structure of α-Halothioacetones

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Abstract — The mechanism of formation of α-halo thioketones in reactions of haloacetones with H_2S in the presence of HCl was studied by quantum-chemical methods. The cause of failure in attempted preparation of iodo thioketone by this procedure was elucidated. The stereoelectronic structure and capability for 1,3-prototropic rearrangements of α-halothioacetones were studied.

Previously we have developed procedures for preparing α-halo thioketones and studied their diverse transformations [1–9]. The only method of their synthesis is reaction of haloacetone with H_2S in the presence of HCl at low temperatures (–70°C) in the absence of solvent.

$$MeC(=O)CH_2X + H_2S \xrightarrow[-70°C]{HCl} MeC(=S)CH_2X,$$

$$X = F, Cl, Br.$$

With iodoacetone (X = I), the reaction occurs differently, yielding hexane-2,5-dithione [4]. 1-Iodo-2-propanethione can be prepared by reaction of bromothioacetone with NaI in acetone at 70°C [5]. However, attempts to perform similar exchange with chloro- and fluorothioacetone in acetone failed.

Proceeding with these studies, we performed a quantum-chemical analysis of the critical points on the potential surface of formation of α-halothioacetones, studied their stereoelectronic structure, and examined their capability for intramolecular 1,3-prototropic rearrangements. The potential surface of the reaction of α-haloacetones with H_2S and HCl was studied using the GAUSSIAN 98 program package with the aim to determine elementary steps of the reaction, estimate the relative thermodynamic stability of prereaction complexes and reaction products, and localize transition states. Taking into account a wide spectrum of the atomic numbers of halogens, the calculations for predicting the topological properties of the systems in the configuration region of the reaction were performed by the B3LYP hybrid density functional method using the LANL2DZ basis in the Extra-Basis approximation [10–13]. Complete optimization of the geometries of the molecular systems corresponding to the transition states (λ 1, where λ is the number of negative eigenvalues of the Hesse matrix in the given stationary point [14]) and energy minima (λ 0) on the potential surface was performed to the value of 10^{-5} au bohr^{-1}. When analyzing flat areas of the potential surface in studies of conformationally labile states such as prereaction complexes, we set the limiting values at 10^{-6} au bohr^{-1}. The structures corresponding to the energy minima on the potential surface were identified by moving along the gradient line from a saddle point to the neighboring critical point, starting with a small shift along the transition vector. This allowed us to find the gradient reaction pathway correctly.

The main energetic and geometric characteristics of the starting compounds (as isolated molecules) are given in Table 1. According to the calculations, the most stable rotation states in haloacetones (except fluoroacetone) are the *gauche* states (relative mutual arrangement of the heteroatoms). The extent to which the halogen atom deviates from the plane of the molecular core grows with increasing atomic number of the halogen. The *trans* state is the most stable for fluoroacetone.

Examination of the potential surfaces for the reactions of H_2S with haloacetones in the presence of HCl allowed us to determine the most probable mechanism of formation of halothioacetones. The first reaction step is the 1,3-prototropic rearrangement in haloacetone (enolization) involving HCl as mediator (Scheme 1).

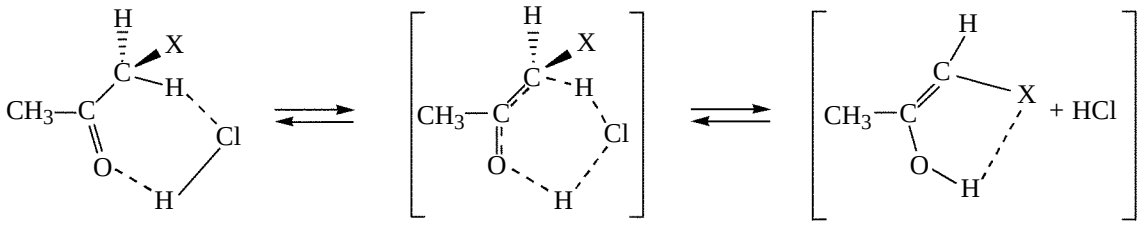
In this case, the activation barrier is considerably lower than in pure intramolecular 1,3-shift (for example, the activation energy at X = F in the absence of the mediator molecule is 183 kJ mol^{-1}, and in its presence it is 93.9 kJ mol^{-1}, Table 2). The stabiliza-

Table 1. Total energies (E_{tot}, au),[a] dipole moments (μ, D), zero-point harmonic vibration energies (*ZPE*, au), lowest harmonic frequencies (ω, cm^{-1}), C–X bond lengths (*d*, Å), and angles by which the X atoms deviate from the molecular core plain (φ, deg),[b] calculated by the B3LYP/LANL2DZ ExtraBasis method for the molecules of haloacetones $MeC(=O)CH_2X$, H_2S, and HCl

Structure (symmetry)	$-E_{tot}$	μ	*ZPE*	ω_i	*d*	φ
X = F (C_s)	292.36641	1.05	0.07698	71	1.449	0.0
X = Cl (C_1)	207.46384	1.71	0.07572	44	1.882	32.3
X = Br (C_1)	205.68318	2.94	0.07520	50	2.044	69.2
X = I (C_1)	203.90496	3.04	0.07493	68	2.214	75.7
H_2S (C_{2v})	11.28978	1.75	0.01424	1213	–	–
HCl (C_∞)	15.53953	1.80	0.00617	2710	–	–

[a] 1 au = 2622.9897 kJ mol^{-1}. [b] Counting from the *trans* arrangement of the heteroatoms.

Scheme 1.



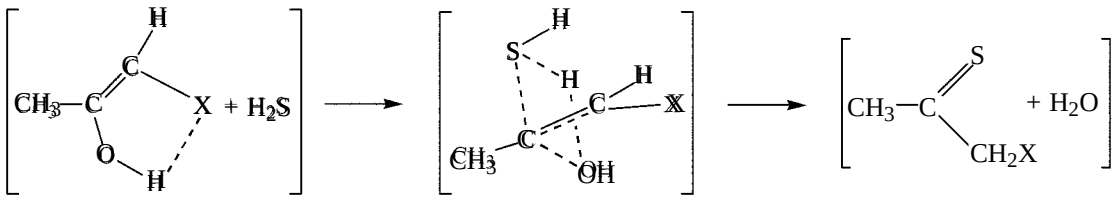
Ia–Id **IIa–IId** **IIIa–IIId**

X = F (**a**), Cl (**b**), Br (**c**), I (**d**).

tion energy of prereaction bimolecular complexes **Ia**–**Id** relative to isolated fragments [without taking into account zero-point harmonic vibration energy (*ZPE*)] decreases with increasing atomic number of halogen (38.3, 33.1, 32.9, and 29.5 kJ mol^{-1}, respectively). With *ZPE* taken into account, these values decrease to 27.6, 26.9, 26.2, and 23.1 kJ mol^{-1}, respectively (Tables 1, 2), the stability of bimolecular complex **III** relative to transition state **II** increases, and the activation energy of the transitions **I** → **III** decreases by the value within 2–5 kJ mol^{-1}.

In the next step, H_2S reacts with the active enol form of haloacetone (Scheme 2).

Scheme 2.



IVa–IVd **Va–Vd** **VIa–VId**

The activation energies of this process at X = F, Cl, Br, and I are 230.3, 232.5, 237.7, and 241.1 kJ mol^{-1}, respectively (Table 3). The dissociation energies of the C–X bonds (459.8, 320.6, and 259.2 kJ mol^{-1} for X = F, Cl, and Br, respectively [15]) are higher than the activation energies of the **IV** → **VI** transformations, whereas the dissociation energy of the C–I bond (192.3 kJ mol^{-1}) is lower. Furthermore, in contrast to haloacetones with X = F, Cl, and Br, in associates of iodoacetone with HCl coordination of HCl

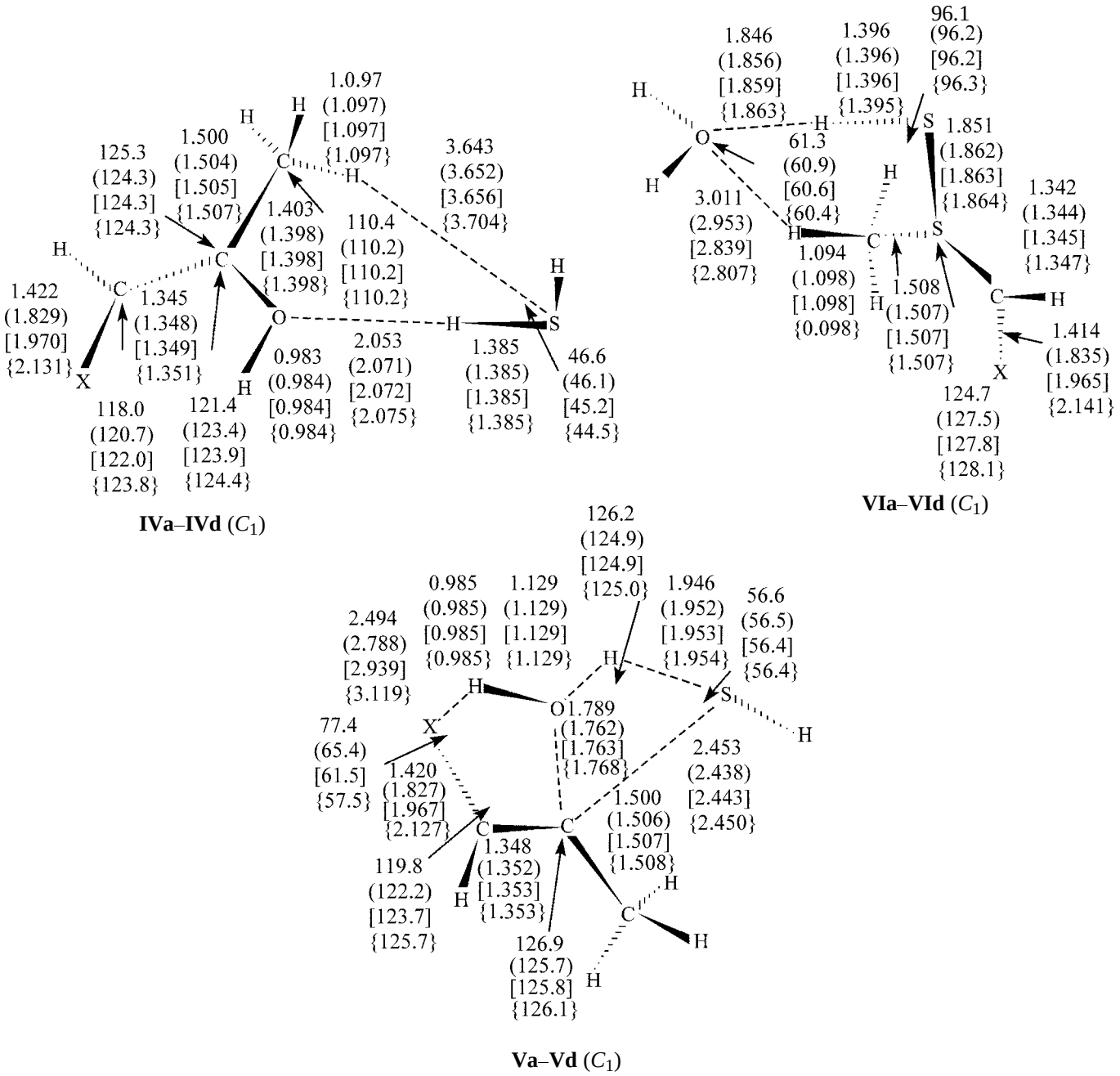


Fig. 1. Geometric characteristics (bond lengths, Å; bond angles, deg) of structures **IVa**–**IVd** and **VIa**–**VId** corresponding to the minima and of transition states **Va**–**Vd** corresponding to saddle points on the potential surface of the reaction MC(OH)CHX + H_2S → MeC(SH)CHX + H_2O. The figures for structures **b, c, d** are given in parentheses, brackets, and braces, respectively.

with the ionized iodine atom and formation of the intermolecular hydrogen bond are the most favorable. Therefore, the pathway of the reaction of iodoacetone with H_2S in the presence of HCl differs from that of the reactions involving the other haloacetones [4]. With the *ZPE* corrections taken into account (Table 3), the activation energies of the **IV** → **VI** transformations decrease by the values within 2–3 kJ mol^{-1}, and the relative stability of the prereaction complexes increases by 3–6 kJ mol^{-1}, in contrast to the **I** → **III** reaction. The main structural characteristics of bimolecular complexes **IV** and **VI** and of transition states **V** are given in Fig. 1.

Table 2. Total energies (E_{tot}, au), relative energies (ΔE, kJ mol^{-1}), numbers of negative eigenvalues of the Hessian (λ), zero-point harmonic vibration energies (*ZPE*, au), and imaginary or lowest harmonic frequencies [($i\omega/\omega_1$), cm^{-1}], calculated by the B3LYP/LANL2DZ ExtraBasis method for structures **I**–**III**

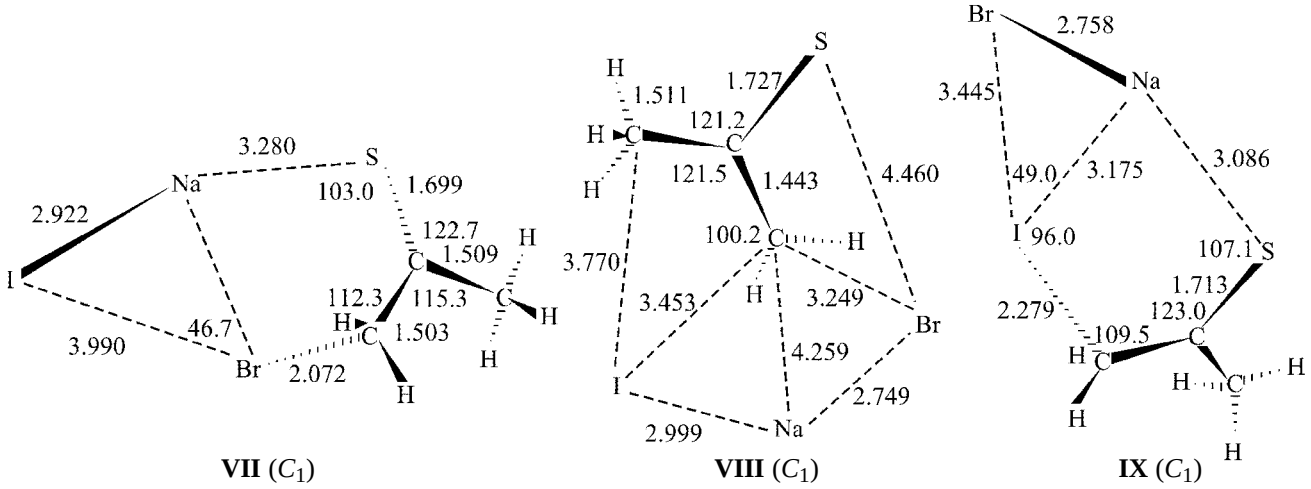
Structure (symmetry)	$-E_{tot}$	ΔE	λ	*ZPE*	$i\omega/\omega_1$
Ia (C_s)	307.91882	0	0	0.08551	38
IIa (C_1)	307.88302	93.9	1	0.08354	*i*789
IIIa (C_s)	307.89624	59.2	0	0.08475	18
Ib (C_1)	223.01598	0	0	0.08423	31
IIb (C_1)	222.97882	97.5	1	0.08259	*i*733
IIIb (C_s)	222.99227	62.2	0	0.08305	14
Ic (C_1)	221.23526	0	0	0.08384	28
IIc (C_1)	221.19373	108.9	1	0.08197	*i*463
IIIc (C_s)	221.21630	63.2	0	0.08236	20
Id (C_1)	219.45801	0	0	0.08353	24
IId (C_1)	219.41639	109.2	1	0.08164	*i*417
IIId (C_s)	219.43185	68.6	0	0.08213	17

Table 3. Total energies (E_{tot}, au), relative energies (ΔE, kJ mol^{-1}), numbers of negative eigenvalues of the Hessian (λ), zero-point harmonic vibration energies (*ZPE*, au), and imaginary or lowest harmonic frequencies [($i\omega/\omega_1$), cm^{-1}], calculated by the B3LYP/LANL2DZ ExtraBasis method for structures **IV**–**VI**

Structure (symmetry)	$-E_{tot}$	ΔE	λ	*ZPE*	$i\omega/\omega_1$
IVa (C_s)	303.64394	0	0	0.09310	17
Va (C_1)	303.55613	230.3	1	0.09204	*i*493
VIa (C_s)	303.64703	–8.1	0	0.09474	30
IVb (C_1)	218.74337	0	0	0.09186	14
Vb (C_1)	218.65473	232.5	1	0.09092	*i*482
VIb (C_s)	218.74410	–1.9	0	0.09288	33
IVc (C_1)	216.96309	0	0	0.09130	12
Vc (C_1)	216.87247	237.7	1	0.09040	*i*483
VIc (C_s)	216.96157	1.7	0	0.09303	32
IVd (C_1)	215.18440	0	0	0.09095	11
Vd (C_1)	215.09258	241.1	1	0.09001	*i*486
VId (C_s)	215.18377	1.6	0	0.09260	24

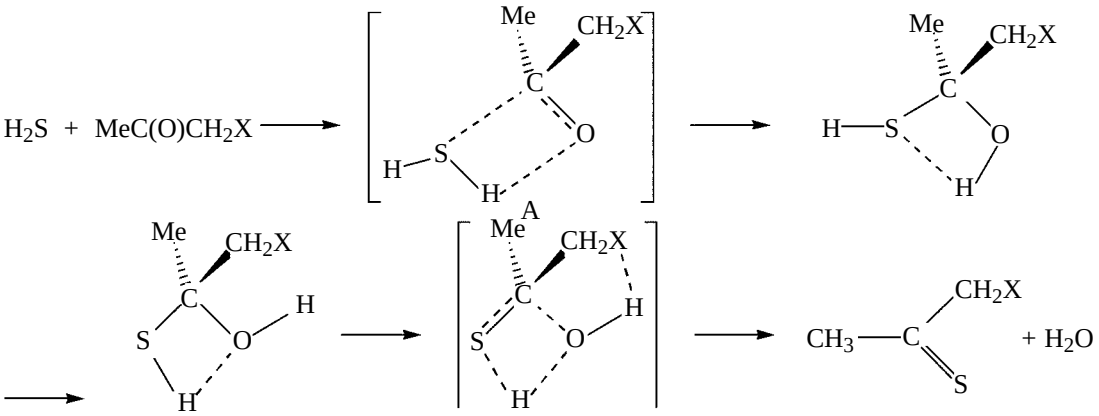
The reaction pathway involving formation of four-membered transition state A, followed by intramolecular autoprotonation with elimination of water (similar mechanism was considered in [7]), is less favorable than the above-considered route by 85–115 kJ mol^{-1}.

One of the factors responsible for the successful preparation of iodothioacetone by the reaction of bromothioacetone with NaI and failed attempts to perform the similar reactions with fluoro- and chlorothioacetone is unfavorable thermodynamics of the system bimolecular complex → product [$MeC(S)CH_2X$ + NaI → $MeC(S)CH_2I$ + NaX] in the case of X = F or Cl and favorable thermodynamics at X = Br. The calculations predict the higher stability of the prereaction complexes with X = F and Cl (by 33.4 and 2.4 kJ mol^{-1}, respectively) and, on the contrary, the higher stability of the reaction products with X = Br (ΔH 19.5 kJ mol^{-1}). The activation energy of the substitution is 104.5 kJ mol^{-1} with X = Br, and in going to Cl and F it increases (to 123.6 and 175.4 kJ mol^{-1}, respectively). The structural characteristics of bimolecular complexes **VII** and **IX** and of transition state **VIII** for the substitution reaction at X = Br are given in Fig. 2.

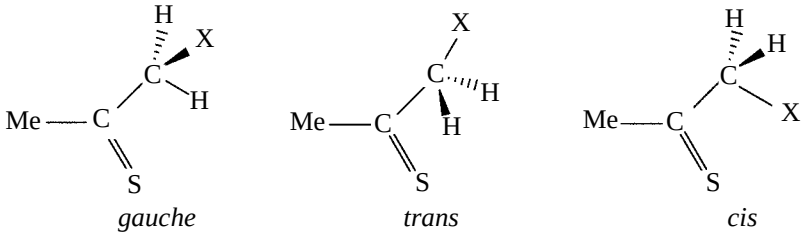


VII (C_1) **VIII** (C_1) **IX** (C_1)

Fig. 2. Geometric characteristics (bond lengths, Å; bond angles, deg) of bimolecular structures [$MeC(S)CH_2Br$ + NaI] (**VII**) and [$MeC(S)CH_2I$ + NaBr] (**IX**) corresponding to the minima and of transition state **VIII** corresponding to the saddle point on the potential surface of the reaction [$MeC(S)CH_2Br$ + NaI → $MeC(S)CH_2I$ + NaBr].



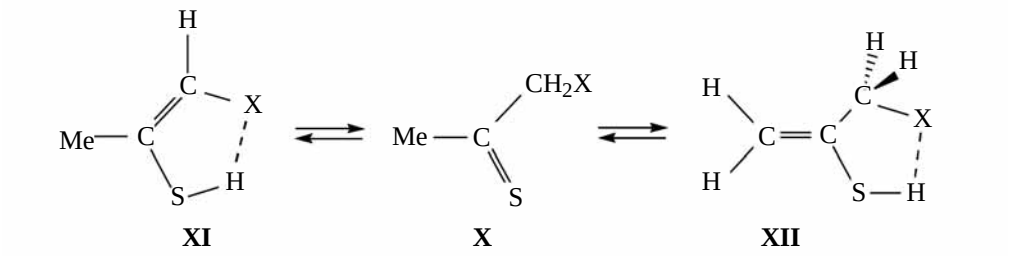
Thioketones can exist in the gas phase in the form of three rotational conformers with *cis*, *trans*, and *gauche* orientation of the heteroatoms; the activation barriers separating these conformers exceed 25 kJ mol^{-1}. This suggests that the conformers can be spectroscopically distinguishable in solution. An exception is fluorothioacetone, for which the calculation predicts existence in the gas phase of the *cis* and *trans* rotamers only.



X = F, Cl, Br, I.

The most stable is the *gauche* stationary state (for fluorothioacetone, *trans* state); its polarity, as judged from the dipole moments, grows with increasing atomic number of halogen (0.68, 1.82, 2.26, 2.58 D). The degree of orthogonality, or the angle by which the heteroatom X deviates from the molecular core plane, and, correspondingly, the extent of interaction of the halogen lone electron pair with the π orbital of the C=S band are maximal with X = I (φ 76° counting from the *trans* form). As the halogen atomic number decreases, the XCCS fragment becomes more planar (φ 62°, 45°, 0°). The *trans* conformations, which are the next in stability, appear to be the least polar owing to opposite orientation of the dipoles of the heteroatoms. The difference between the relative energies of the *gauche* and *trans* conformations (kJ mol^{-1}) grows in the order F (0.0) < Cl (10.3) < Br (14.6) < I (20.4). The order of polarity variation remains virtually the same (I > Br > Cl $\approx$ F), but the differences between the dipole moments become less pronounced (1.00, 0.73, 0.69, 0.68 D). The stability of the *cis* states relative to the *gauche* states is still lower (except X = I) owing to enhancement of unfavorable dipole–dipole interactions; the relative energies amount to 15.2, 16.0, 18.2, and 20.3 kJ mol^{-1} for X = F, Cl, Br, and I, respectively. The *cis* states are the most polar, and the order of polarity variation in the halogen series becomes reverse: fluorothioacetone appears to be the most polar (4.49 D), and iodothioacetone, the least polar (3.72 D). The fact that the *gauche* and *trans* conformations substantially differ in the polarity from the *cis* conformations suggests that the *cis* conformations of α-halo thioketones can be stabilized in highly polar solvents, with an increase in their populations.

Halothioacetones can potentially exist in three tautomeric prototropic forms **X**–**XII**; their relative stability decreases in the order **X** > **XI** > **XII**, irrespective of particular halogen. The relative energies of tautomers **X**–**XII** with X = F, Cl, Br, and I are, respectively, 0, 45.3, and 51.8; 0, 48.8, and 52.9; 0, 50.2, and 54.0; and 0, 52.7, and 56.6 kJ mol^{-1}.



XI **X** **XII**

X = F, Cl, Br, I.

The mechanism of **X** → **XII** transformations involves as the limiting step 1,3-prototropic shift (its activation energy lies within 160–195 kJ mol^{-1}, decreasing with an increase in the atomic number of halogen), followed by low-barrier (activation energy 40–60 kJ mol^{-1}) rotational transformation into the structure stabilized by formation of a five-membered pseudo-chelate ring. Similarly, the **X** → **XI** rearrangement involves 1,3-prototropic shift (its activation energy is 145–170 kJ mol^{-1}, decreasing with an increase in the atomic number of halogen), followed by low-barrier formation of a five-membered pseudo-chelate heteroring additionally stabilized by the allyl fragment.

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