# Structure, stability, and disproportionation mechanisms of organic interhalides of the cholinium series: an experimental and theoretical study

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The stability constants of acetylcholinium, carbamoylcholinium, and cholinium diiodochlorides and diiodobromides in chloroform solutions were determined and the kinetics of disproportionation of these systems in 1 : 9 $CHCl_3$—MeOH (MeCN) mixtures were studied by UV spectroscopy. A possible mechanism of mutual transformations of the polyhalides is proposed and an interrelation between the nature of the iodine-coordinating solvent and the extent of reversibility of the process is established. The electronic structures and relative stabilities of acetylcholinium iodohalides and charge-transfer complexes $S \cdot XI_2^-$ and $S \cdot I_2$ (S = MeOH, MeCN, $CHCl_3$; X = Cl, Br, I) were studied by *ab initio* RHF and MP2(full) methods in the HW+(3d) and 6-31G++(d,p) basis sets. It was found that all the solvents studied favor the decomposition of the iodohalide anions to liberate molecular iodine; however, disproportionation of $I_2$ is possible only for the $S \cdot I_2$ complexes with a high extent of charge transfer.

**Key words:** acetylcholine, choline, carbamoylcholine, iodohalides, *ab initio* quantum-chemical calculations, UV spectroscopy, stability, kinetics of disproportionation.

Extensive use of iodine-containing systems as pharmaceuticals possessing antimicrobial activity[1,2] has given an impetus to investigations on the determination of the structure and stability of iodohalides of organic cations for the structure design of bioactive compounds with different iodine retention extent. The high reactivities of molecular iodine and iodine-containing compounds have motivated a broad spectrum of studies on the kinetics, thermodynamics, and chemistry of iodine equilibria in various systems.[3] Elucidation of the electron density distribution and steric effects of substituents as well as assessment of thermodynamic and kinetic stabilities, which are necessary for comparing the structures of organic interhalides in the gas and crystalline phases and in solutions, require new research strategies involving various semiempirical and *ab initio* quantum-chemical computational schemes.

Earlier, quantum-chemical studies of the structures of polyhalides were carried out only taking isolated anions as examples in the gas phase and in the media with different dielectric constants both with inclusion of solvation effects in the framework of continuum models[4,5] and with inclusion of the solvent molecules in explicit form (by, *e.g.*, Monte Carlo simulations).[6] Large solvation effects typical of halide and polyhalide anions (in most cases, they are comparable with the stabilization energies of $XI_2^-$ complex anions[7]) make research on the behavior of these systems in solvents of different polarity topical.[8] The results of gas-phase calculations[4,5] of the stabilization energies of $XI_2^-$ anions (with respect to decomposition into $X^-$ and $I_2$) permit the interhalides to be arranged in the following series in order of increasing the relative stability: $I_3^- < BrI_2^- < ClI_2^-$. The inclusion of solvation effects using the electrostatic Born model (the medium was simulated by a dielectric continuum with $\varepsilon = 0—76$) caused no changes in the relative stabilization energies of the $XI_2^-$ complexes. Recent studies[6,9] revealed an important role of solvents that form hydrogen bonds with halide and polyhalide anions. In particular, symmetry breaking of the triiodide anions in the interactions with MeOH, water, and MeCN molecules was reported.[6] Recently, considerable attention has been given to the studies of the reactions of molecular iodine with oxygen-containing organic solvents and nitrogen-containing heterocycles, resulting in charge-transfer complexes and followed by disproportionation of the iodine molecule.[8,10] The geometric parameters and electronic structures of molecular complexes between iodine and alcohols and ethers were *ab initio* calculated at the second-order MP2(fc) level of perturbation theory in the 3-21G(d,p) basis set.[11] A spectrophotometric study of iodine complexation with macrocyclic diamines and di-*o*-methoxybenzoylthiourea in chloroform solutions was reported.[12] The stability constants of the $[(donor...I^+)I_3^-]$ complexes were evaluated

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by iterative fitting of calculated absorbances of free iodine to the experimental values obtained by the molar ratio method.

Earlier,[8] we have experimentally studied and discussed the kinetics and mechanisms of mutual transformations of iodohalide cations of different nature (tetrabutylammonium, triethylbenzylammonium, and *N*-cetylpyridinium) in the solvents, which form σ-complexes with the iodine molecule, and established that the rate constants for disproportionation depends on the nature of the solvent. We also used the results of quantum-chemical calculations of the structures of polyhalides of tetraalkylammonium[13] and alkylpyridinium[14] cations to reveal those trends in changes in the molecular stabilities, which are associated with the structural features of the cation and the nature of the anion.

In this work we studied iodohalides of acetylcholinium, carbamoylcholinium, and cholinium cations, which combine the ester and quaternary ammonium fragments. The general formula of these systems is $[Me_3N(CH_2)_2R]^+XI_2^-$, where R = OAc, X = Cl (**1**), Br (**2**), I (**3**); R = $OCONH_2$, X = Cl (**4**); R = OH, X = Cl (**5**). The stability constants of the complexes under study in chloroform solutions were determined spectrophotometrically using the function of the average iodine number. The kinetics of disproportionation reactions of the diiodohalides in the $CHCl_3$—MeOH (MeCN) systems were studied. We also carried out quantum-chemical calculations of the structures of complex acetylcholinium iodohalides, as well as anion-molecular complexes $S \cdot XI_2^-$ (S = $CHCl_3$, MeOH, MeCN) and molecular complexes of iodine with iodine-coordinating solvents differing in both the protolytic properties and polarity.

## Experimental

Acetylcholinium, carbamoylcholinium, and cholinium diiodohalides were obtained by iodination of the solutions of (i) acetylcholinium chloride and bromide and (ii) carbamoylcholinium and cholinium chlorides in MeOH with equimolar amounts of iodine dissolved in $CHCl_3$.

$^1$H NMR spectra were recorded on a Bruker DPX-250 spectrometer in $CD_3OD$. The $^1$H NMR spectra of compounds **1**—**5** exhibit the following signals: a singlet from three Me groups at the quaternary N atom (δ 3.10—3.30), a multiplet from the $CH_2$ group at the N atom (δ 3.55—3.75), and a multiplet from the $CH_2$ group at the O atom (δ 4.00—4.55). The $^1$H NMR spectra of compounds **1**—**3** also exhibit a singlet from the acetyl protons (δ 2.00—2.15) while the spectrum of compound **4** exhibits a singlet from the amide protons (δ 4.60—4.70).

Electronic absorption spectra (EAS) of the chloroform solutions of the iodohalides under study were recorded on a Specord UV—VIS spectrophotometer using cells with $l$ = 1.0 cm for the spectral region 50000—30000 $cm^{-1}$ and $l$ = 5.0 cm for the spectral region 30000—140000 $cm^{-1}$. The stock solutions were the $1 \cdot 10^{-3}$ *M* solutions of (i) acetylcholinium, carbamoylcholinium, and cholinium chlorides and (ii) acetylcholinium bromide and iodide in the $CHCl_3$—MeOH (24 : 1) mixture and the $1 \cdot 10^{-3}$ *M* solution of sublimation purified iodine in $CHCl_3$. The solutions for measurements were prepared by diluting the stock solutions.

The stability constants (β) of the polyhalides of organic nitrogen-containing cations in chloroform solutions were determined using a modified spectrophotometric technique involving a shift of the equilibrium in the organic halide—iodine system.[15] At a constant concentration of the organic halide in the chloroform solution, the concentration of elemental iodine was varied from some lack to a three-fold excess. Quantitative estimate of the shift of the equilibrium (1) was obtained by measuring the absorption of free iodine in the long-wavelength region of the EAS (λ = 510 nm)

$$CtXI_2 \rightleftharpoons CtX + I_2, \quad (1)$$

where Ct are the acetylcholinium, carbamoylcholinium, and cholinium cations and X = Cl, Br, and I. The stability constants of the organic polyhalides were calculated using the function of the average iodine number

$$\bar{n}_{I_2} = \frac{C_{I_2} - [I_2]}{C_{CtX}}, \quad (2)$$

where $C_{CtX}$ and $C_{I_2}$ are the analytical concentrations of the organic halide and molecular iodine and $[I_2]$ is the equilibrium concentration of iodine.

At $0 < \bar{n}_{I_2} < 1$, the stability constants were calculated using the formula

$$\frac{\bar{n}_{I_2}}{(1 - \bar{n}_{I_2})} = \beta_1[I_2]. \quad (3)$$

The absorption spectra of the solutions of compounds **1**, **2**, **4**, and **5** in the $CHCl_3$—MeOH (MeCN) systems with the solvent ratios varied from 9 : 1 to 1 : 9 ($C = 5 \cdot 10^{-5}$ mol $L^{-1}$) were recorded on the Specord UV—VIS spectrophotometer. The rate constants for disproportionation were determined for the solutions with two concentrations, $4 \cdot 10^{-5}$ and $2 \cdot 10^{-5}$ mol $L^{-1}$. The absorbances of the solutions of compounds **1**, **2**, **4**, and **5** at λ = 367 nm were recorded at 2 min intervals over a period of 60 min using a SF-46 spectrophotometer operating in the cyclic mode. The absorbances of the solutions of the compounds under study in MeCN were measured at 2 min intervals over a period of 60 min day after day during a week.

The rate constant ($k$) for disproportionation of the interhalide ion (a first-order reaction) was calculated by the least squares method using the equation

$$\ln \frac{(A_{max} - A_0)}{(A_{max} - A_i)} = kt,$$

where $A_0$, $A_i$, and $A_{max}$ are the initial, running, and limiting values of the optical density at 367 nm, and $t$ is time. For the reversible process in acetonitrile, one has $k = k^+ + k^-$, where $k^+$ and $k^-$ are the rate constants for the direct and reverse first-order reactions.

Quantum-chemical calculations of the structures of the complexes were carried out in the Hartree—Fock approximation using the GAMESS program.[16] The basis sets employed were as

follows: HW,[17] 6-31G(d,p),[18] and two extended basis sets, 6-31G++(d,p) for H, C, and N and HW+(3d) for halogens (Cl, Br, I).[19] In some cases, optimization was performed at the second-order Møller—Plesset (MP2) level of perturbation theory. Full optimization of the geometry of the structures corresponding to the energy minima on the potential energy surface (PES) was carried out up to a gradient magnitude of $10^{-6}$ hartree Bohr$^{-1}$.

The complexation energies, $\Delta E_1$ and $\Delta E_2$, were calculated as the total energy ($E$) differences between the complexes and their constituents

$$\Delta E_1 = E(AXI_2) - E(A) - E(XI_2^-),$$

$$\Delta E_2 = E(BI_2) - E(B) - E(I_2),$$

where A = $Ct^+$, S; B = CtX, $X^-$, S·$X^-$, S.

The total energies of all the molecules, which were used for estimating the $\Delta E_1$ and $\Delta E_2$ energies, were found by full geometry optimization of particular fragments. To calculate the intracomplex interactions (binding energies $\Delta E_{1m}$ and $\Delta E_{2m}$) using the Morokuma scheme,[20] the energies of the $Ct^+$, $XI_2^-$, CtX, $I_2$, S, and S·$X^-$ fragments were calculated with fixed geometric parameters of the complexes. The extent of charge transfer due to complexation ($\Delta q$) was estimated according to Mulliken.[21] The components of the charge transfer energy in the framework of Morokuma scheme (energies of charge transfer from the iodine molecule to the solvent molecule ($E_{CT}^a$) and to the iodine molecule ($E_{CT}^k$)) were found by expansion of the total charge-transfer energy ($E_{CT}$).

## Results and Discussion

The results of the spectrophotometric study of the stabilities of compounds **1**—**5** in chloroform solutions (lgβ = 3.91, 4.39, 5.35, 3.09, and 3.06, respectively) indicate a regular increase in the stabilities of acetylcholinium iodohalides **1**—**3** in order $I_2Cl^- < I_2Br^- < I_3^-$. Among diiodochlorides **1**, **4**, and **5**, acetylcholinium diiodochloride is the most stable compound (lgβ = 3.91), which points to a significant effect of the cation structure on the ability of these systems to retain molecular iodine.

The kinetics of disproportionation of organic diiodobromides and diiodochlorides in solvents were studied by measuring the EAS of the solutions of the compounds **1**, **2**, **4**, and **5** in the $CHCl_3$—MeOH (MeCN) systems with different solvent ratios.

The EAS of the solutions of compound **1** in the $CHCl_3$—MeOH mixture at different solvent ratios are shown in Fig. 1. As the content of MeOH in the mixture increases, the absorption bands of the molecular complex of iodine with MeOH and of the triiodide ion appear at 460 nm and in the region 367 nm, respectively. In the MeCN—$CHCl_3$ mixture, an increase in the MeCN concentration causes an increase in the absorption in the region 367 nm, which is due to the formation of the triiodide anion.

The spectral changes observed for the $CHCl_3$—iodine-coordinating solvent system are related to the disproportionation of the $I_2$ constituent of the anion under the action of the polar solvent, which forms a σ-complex with elemental iodine[8,11]:

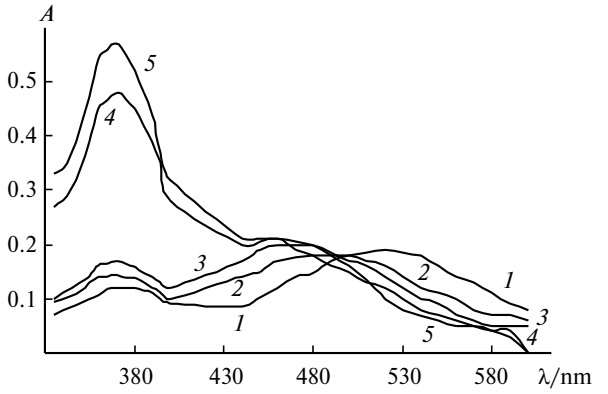


**Fig. 1.** Electronic absorption spectra of solutions of compound **1** in the $CHCl_3$—MeOH mixture ($C = 4 \cdot 10^{-5}$ mol L$^{-1}$): $CHCl_3$ : MeOH = 9 : 1 (*1*), 7 : 3 (*2*), 5 : 5 (*3*), 3 : 7 (*4*), and 1 : 9 (*5*).

$$I_2X^- + S \longrightarrow X^-\cdot S + I_2\cdot S, \quad (4)$$

$$I_2\cdot S \longrightarrow [I^-...I^+]\cdot S, \quad (5)$$

$$[I^-...I^+]\cdot S + I_2X^-\cdot S \longrightarrow I_3^-\cdot S + XI\cdot S, \quad (6)$$

where S = MeOH or MeCN. The EAS of the end products of the disproportionation of acetylcholinium diiodochloride **1** is shown in Fig. 2 (curve *8*). Transformation of the diiodochloride ion with time (see Fig. 2, curves *1*—*7*) is accompanied by hyperchromism of the absorption bands of the triiodide ion in the region 367 nm. The absorption spectrum of compound **1** in the $CHCl_3$—MeOH (1 : 9) system is identical to that of acetylcholinium triiodide (see Fig. 2, curve *9*). We established that the dispropor-

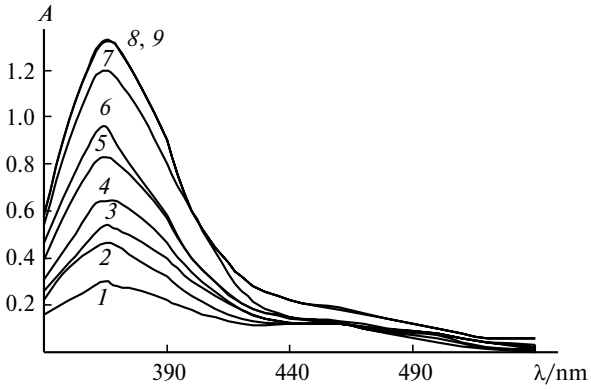


**Fig. 2.** Electronic absorption spectra of solutions of compound **1** ($C = 4 \cdot 10^{-5}$ mol L$^{-1}$, $l = 5$ cm) in the $CHCl_3$—MeOH (1 : 9) mixture recorded after 1 (*1*), 24 (*2*), 48 (*3*), 72 (*4*), 96 (*5*), 120 (*6*), 144 (*7*), and 168 h (*8*). The EAS of acetylcholinium triiodide was recorded 1 h after sample preparation ($C = 2 \cdot 10^{-5}$ mol L$^{-1}$, $l = 5$ cm) (curve *9*).

**Table 1.** Rate constants ($k$) for disproportionation of organic iodohalides **1**, **2**, **4**, and **5** in MeOH and MeCN

| Compound | $C\cdot10^5$ /mol L$^{-1}$ | MeOH | | MeCN | | |
|---|---|---|---|---|---|---|
| | | $k\cdot10^3$ /min$^{-1}$ | ρ | $k^-\cdot10^4$ /min$^{-1}$ | $k^+\cdot10^5$ /min$^{-1}$ | ρ |
| **1** | 4 | 0.32±0.002 | 0.999 | 1.40 | 9.52 | 0.93 |
| | 2 | 0.29±0.001 | 0.999 | 1.81 | 9.94 | 0.90 |
| **2** | 4 | 0.22±0.014 | 0.991 | 2.30 | 53.0 | 0.97 |
| | 2 | 0.34±0.012 | 0.987 | 1.56 | 6.24 | 0.96 |
| **4** | 4 | 1.09±0.014 | 0.999 | 3.90 | 9.00 | 0.97 |
| | 2 | 1.02±0.010 | 0.999 | 2.54 | 38.1 | 0.97 |
| **5** | 4 | 2.02±0.008 | 0.999 | 0.11 | 2.03 | 0.96 |
| | 2 | 2.01±0.006 | 0.999 | 0.14 | 2.17 | 0.95 |

*Note.* $C$ is the solution concentration, ρ is the linear correlation coefficient, and $k = k^+ + k^-$ ($k^+$ and $k^-$ are the rate constants for the direct and reverse first-order reactions).

tionation of iodohalides in MeOH is a first-order reaction, whereas the disproportionation in MeCN is a reversible first-order reaction.

The $k$ values are listed in Table 1.

The starting point of the quantum-chemical study was to analyze the energy characteristics and geometric parameters of complexes **1**—**3** calculated using two basis sets, 6-31G(d,p) for H, C, N, and O and HW+(3d) for Cl, Br, and I (Fig. 3, Tables 2 and 3). Analysis of the stabilization energies ($\Delta E_2$) and CtX...$I_2$ interaction ener-

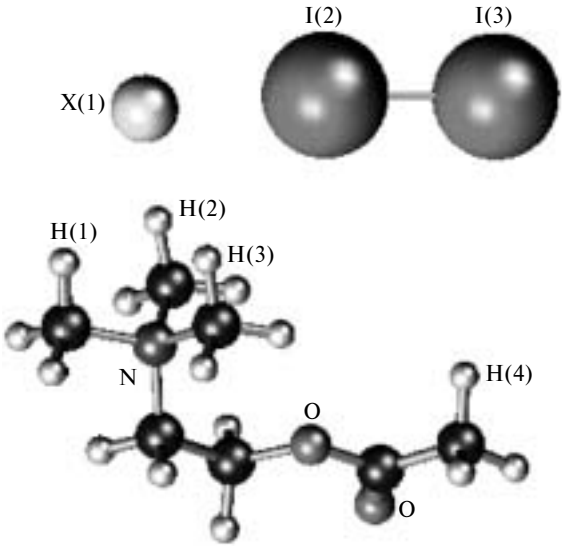


**Fig. 3.** Atomic arrangement schemes for compounds **1**—**3** (X = Cl, Br, I) obtained from RHF calculations with the 6-31G(d,p) basis set for H, C, N, and O and the HW+(3d) basis set for Cl, Br, and I.

**Table 2.** Energy characteristics (complexation energies, $\Delta E_1$ and $\Delta E_2$, and binding energies, $\Delta E_{1m}$ and $\Delta E_{2m}$) and geometric parameters (bond lengths ($r$) and bond angles X(1)—I(2)—I(3) ($a$)) of $[Me_3N(CH_2)_2OAc]^+XI_2^-$ (X = Cl, Br, I) complexes obtained from RHF calculations with the 6-31G(d,p) basis set for H, C, N, and O and the HW+(3d) basis set for Cl, Br, and I

| X | $-\Delta E_1$ | $-\Delta E_{1m}$ | $-\Delta E_2$ | $-\Delta E_{2m}$ | $r$/Å | | | | | | $a$ /deg | $\Delta q$ $(XI_2^-)$* | $-q(I_2)$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | kcal mol$^{-1}$ | | | | H(1)—X(1) | H(2)—X(1) | H(3)—X(1) | H(4)—I(3) | X(1)—I(2) | I(2)—I(3) | | | |
| Cl | 70.84 | 74.52 | 11.39 | 13.27 | 2.724 | 2.561 | 2.592 | 4.429 | 2.922 | 2.762 | 175.23 | 0.0480 | 0.0863 |
| Br | 68.88 | 71.73 | 10.47 | 12.39 | 2.943 | 2.778 | 2.810 | 4.014 | 3.098 | 2.770 | 174.90 | 0.0382 | 0.0452 |
| I | 66.30 | 68.31 | 9.94 | 12.41 | 3.219 | 3.055 | 3.100 | 3.746 | 3.255 | 2.794 | 174.88 | 0.0347 | 0.0982 |

* The extent of charge transfer according to Mulliken was calculated by the formula $\Delta q(XI_2^-) = 1 + q(XI_2^-)_{complex}$.
** The total Mulliken charge of the $I_2$ constituent of the complex.

**Table 3.** Expansion of the binding energies ($\Delta E_{1m}$) in the $[Me_3N(CH_2)_2OAc]^+XI_2^-$ (X = Cl, Br, I) systems using the Kitaura—Morokuma scheme[20] according to RHF/HW calculations

| X | $-E_{ES}$ | $E_{EX}$ | $-E_{PL}$ | $-E_{CT}{}^a$ | $-E_{CT}{}^k$ | $-E_{MIX}$ | $-\Delta E_{1m}$ |
|---|---|---|---|---|---|---|---|
| | kcal mol$^{-1}$ | | | | | | |
| Cl | 74.99 | 10.28 (11.06) | 4.92 | 4.18 (3.69) | 0.31 (0.16) | 1.91 (0.40) | 76.04 (73.10) |
| Br | 72.36 | 9.70 (10.23) | 3.84 | 3.36 (3.00) | 0.25 (0.10) | 1.37 (0.45) | 71.47 (69.52) |
| I | 68.91 | 8.88 (9.22) | 2.84 | 2.60 (2.44) | 0.22 (0.04) | 0.80 (0.31) | 66.48 (65.31) |

*Note.* Because of the slow convergence of iterative procedures for extended basis sets when using the Kitaura—Morokuma approximation, the expansion of the binding energies was obtained from the RHF/HW calculations for the geometries found by optimizations in the 6-31G(d,p) basis set for H, C, and N and the HW+(3d) basis set for Cl, Br, and I; the values corrected for the basis set superposition error are given in parentheses. $E_{ES}$ is the elecrtrostatic energy, $E_{EX}$ is the exchange repulsion energy, $E_{PL}$ is the polarization energy, $E_{CT}{}^a$ and $E_{CT}{}^k$ are the energies of charge transfer from the iodine molecule to the solvent molecule and to the iodine molecule, respectively, and $E_{MIX}$ is the higher-order interaction energy.

gies ($\Delta E_{2m}$) allowed the compounds under study to be arranged in the following series of relative stabilities (with respect to the anion): $ClI_2 > BrI_2 > I_3$, which is similar to the series of the gas-phase stabilities of isolated anions. However, these results contradict the experimental series obtained for the chloroform solutions, namely, $ClI_2 < BrI_2 < I_3$.[14] This makes the studies on the solvation effect topical. Recently,[22] we have studied the arrangement of the solvent molecules within the first solvation shell of (i) isolated polyhalide anions of different nature and (ii) their complexes with a number of organic cations. It was shown that chloroform reverses the relative stability series determined for the gas phase.

In this work the stabilities of iodohalide ions in various solvents were studied by quantum-chemical methods. The overall process was as follows

$$XI_2^- + n\,S \rightleftharpoons X^- \cdot nS + I_2, \qquad (7)$$

where S = MeOH, MeCN, $CHCl_3$; $n$ = 1—6.

We began with the calculations of anion-molecular complexes $S \cdot XI_2^-$. The results obtained for the most stable configurations of the complexes are shown in Fig. 4 and listed in Table 4. As can be seen, the $\Delta E_1$ and $\Delta E_{1m}$ values point to nearly identical effects of solvents on the iodohalide anion. However, analysis of the $\Delta E_2$ and $\Delta E_{2m}$ values showed that reversal of the relative stability series found for the gas phase is possible only for chloroform solutions. This effect is apparently due to the specific coordination of the iodohalide anion to the H atom of the CH unit of the solvent (see Fig. 4, *d*).

Then we studied the reaction (7), which involves a successive accumulation of solvent molecules in the first solvation shell of the halide ion (Table 5). A comparative analysis of the results obtained showed that the solvent molecules and the iodine molecule do compete for the halide anion. What is more, accumulation of the solvent molecules favors reversal of the relative stability series typical of the gas phase (see Table 5). Analogously, we have recently shown[22] that accumulation of the solvent

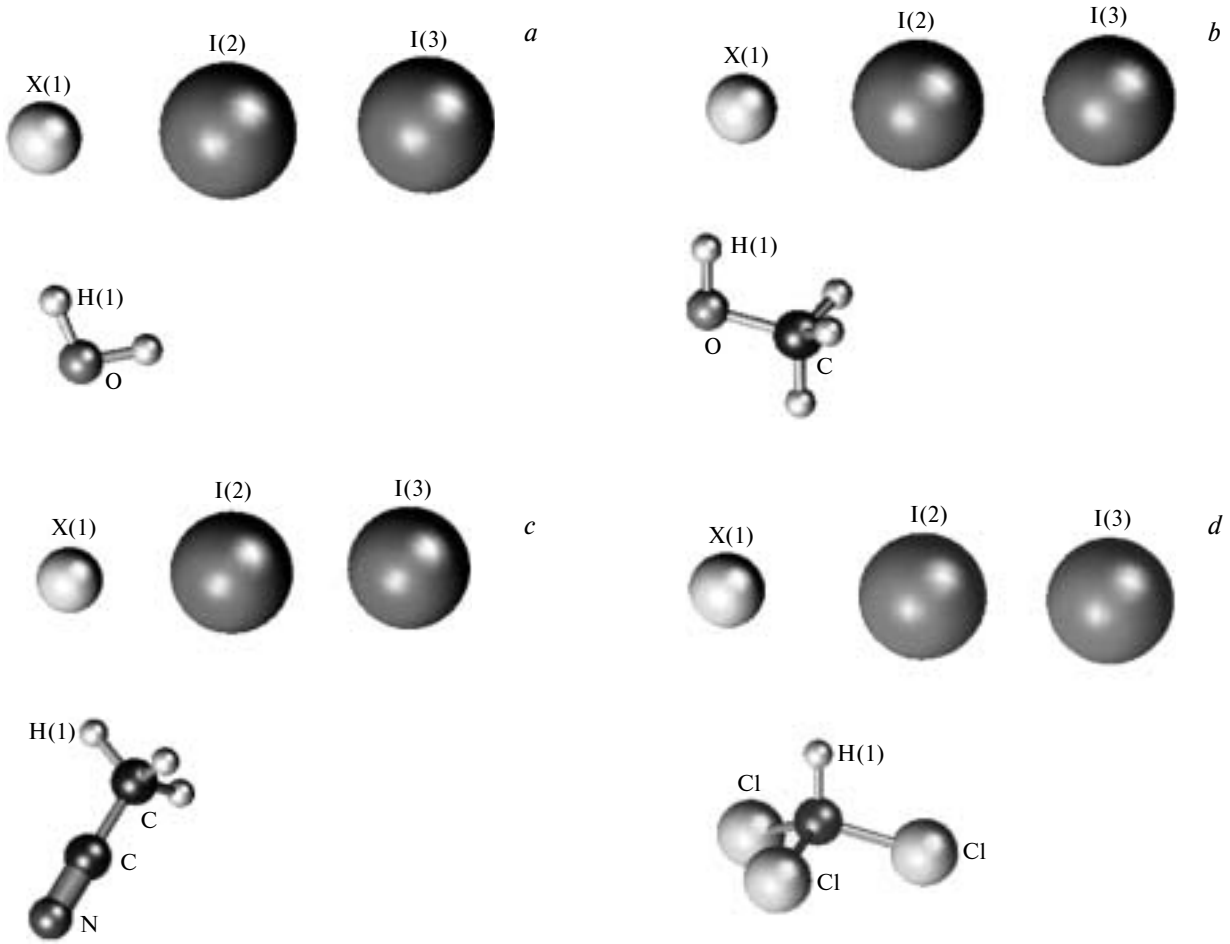


**Fig. 4.** Atomic arrangement in anionic complexes $H_2O \cdot XI_2^-$ (*a*), $MeOH \cdot XI_2^-$ (*b*), $MeCN \cdot XI_2^-$ (*c*), and $CHCl_3 \cdot XI_2^-$ (*d*) (X = Cl, Br, I) calculated by the RHF method with the 6-31G++(d,p) basis set for H, C, N, and O and the HW+(3d) basis set for Cl, Br, and I with inclusion of electron correlation at the MP2 level of perturbation theory.

**Table 4.** Energy characteristics (complexation energies, $\Delta E_1$ and $\Delta E_2$, and binding energies, $\Delta E_{1m}$, $\Delta E_{2m}$) and geometric parameters (bond lengths ($r$) and bond angles ($a$)) of $S \cdot XI_2^-$ (S = MeOH, MeCN, $CHCl_3$; X = Cl, Br, I) complexes obtained from RHF calculations with the 6-31G++(d,p) basis set for H, C, N, and O and the HW+(3d) basis set for Cl, Br, and I with inclusion of electron correlation at the MP2 level of perturbation theory

| S | X | $-\Delta E_1$ | $-\Delta E_{1m}$ | $-\Delta E_2$ | $-\Delta E_{2m}$ | $-E_{CT}$ | $r$/Å | | | $\Delta r$/Å | $a$/deg |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | kcal mol$^{-1}$ | | | | | X(1)—I(2) | I(2)—I(3) | X(1)—H(1) | Y—H(1) | Y—H(1)—X(1) |
| MeOH | Cl | 10.25 | 10.56 | 30.56 | 34.78 | 2.08 | 2.672 | 2.898 | 2.332 | 0.0100 | 165.87 |
| | Br | 9.23 | 9.45 | 28.87 | 33.87 | 1.59 | 2.829 | 2.924 | 2.558 | 0.0080 | 164.43 |
| | I | 8.21 | 8.36 | 28.07 | 34.11 | 1.16 | 3.011 | 2.954 | 2.829 | 0.0070 | 161.47 |
| MeCN | Cl | 10.03 | 10.12 | 32.82 | 37.62 | 1.30 | 2.652 | 2.913 | 2.654 | 0.0010 | 150.80 |
| | Br | 9.53 | 9.60 | 30.80 | 36.46 | 0.88 | 2.811 | 2.939 | 2.928 | 0.0010 | 149.15 |
| | I | 9.13 | 9.19 | 29.61 | 35.29 | 0.61 | 2.995 | 2.968 | 3.208 | 0.0009 | 146.95 |
| $CHCl_3$ | Cl | 11.24 | 11.52 | 29.32 | 33.71 | — | 2.680 | 2.893 | 2.324 | 0.0070 | 171.70 |
| | Br | 9.21 | 9.44 | 26.76 | 33.57 | — | 2.832 | 2.921 | 2.609 | 0.0040 | 160.23 |
| | I | 9.59 | 9.70 | 27.36 | 34.84 | — | 3.009 | 2.954 | 2.926 | 0.0020 | 152.05 |
| — | Cl | — | — | 35.86 | 41.01 | — | 2.632 | 2.936 | — | — | — |
| | Br | — | — | 32.78 | 38.83 | — | 2.795 | 2.959 | — | — | — |
| | I | — | — | 30.89 | 37.96 | — | 2.985 | 2.985 | — | — | — |

*Note.* The $\Delta r$ values were calculated as the Y—H (Y = C, O) bond length difference between the complex and the isolated solvent molecule. Because of the slow convergence of the iterative process for extended basis sets when using the Kitaura—Morokuma scheme, the expansion of the binding energies was obtained from RHF calculations with the HW basis set for the geometries found by optimizations at the MP2 level of perturbation theory using the extended basis sets, 6-31G++(d,p) for H, C, and N and HW+(3d) for Cl, Br, and I.

**Table 5.** Energy effects ($\Delta E$) of reaction (7) and complexation energies ($\Delta E_1$) of anions with the solvent ($X^- \cdot nS$) according to RHF/HW calculations

| $n$ | X | $\Delta E$/kcal mol$^{-1}$ | | | $-\Delta E_1$/kcal mol$^{-1}$ | | |
|---|---|---|---|---|---|---|---|
| | | $CHCl_3$ | MeOH | MeCN | $CHCl_3$ | MeOH | MeCN |
| 1 | Cl | 16.61 | 22.96 | 26.36 | 23.61 | 17.26 | 13.86 |
| | Br | 15.42 | 20.82 | 22.59 | 18.73 | 13.34 | 11.56 |
| | I | 14.45 | 18.79 | 19.14 | 14.23 | 9.94 | 9.54 |
| 2 | Cl | −1.93 | 2.38 | 14.02 | 42.15 | 37.84 | 26.20 |
| | Br | 0.017 | 1.92 | 12.08 | 34.14 | 32.23 | 22.07 |
| | I | 2.24 | 1.16 | 10.30 | 26.44 | 27.51 | 18.37 |
| 3 | Cl | −16.23 | −17.43 | 3.48 | 56.45 | 57.65 | 36.73 |
| | Br | −12.20 | 15.89 | 3.01 | 46.35 | 50.04 | 31.15 |
| | I | −7.94 | −14.52 | 2.56 | 36.62 | 43.19 | 26.12 |
| 4 | Cl | −26.21 | — | −4.87 | 66.43 | — | 45.09 |
| | Br | −21.62 | — | −4.28 | 55.77 | — | 38.44 |
| | I | −16.04 | — | −3.72 | 44.72 | — | 32.40 |
| 5 | Cl | −35.69 | — | −12.49 | 75.91 | — | 52.71 |
| | Br | −29.86 | — | −10.98 | 64.01 | — | 45.14 |
| | I | −23.24 | — | −9.59 | 51.91 | — | 38.27 |
| 6 | Cl | −41.19 | — | −18.23 | 81.41 | — | 58.45 |
| | Br | −35.78 | — | −16.08 | 69.93 | — | 50.24 |
| | I | −28.84 | — | −14.11 | 57.52 | — | 42.79 |

*Note.* $\Delta E = E(X^- \cdot nS) + E(I_2) - E(XI_2^-) - nE(S)$, where $E$ is the total energy. Since the total energy differences between particular conformers of the $X^- \cdot nS$ systems ($n > 3$, S = MeOH) can be obtained only from higher-level computations[19] and lie beyond the accuracy of the approximation employed in this work, the calculations were carried out only up to $n = 3$.

molecules within the first solvation shell of the $X^-$ ions provides a considerable energy gain. Such an approach with inclusion of solvation of the halide ion only (it should be noted that solvation of the iodine molecule was ignored) allowed the relative stabilities of iodohalides ($ClI_2^-$, $BrI_2^-$, $I_3^-$) to be calculated for the same solvent. This strategy is supported by some data,[6,9] which point to the key role of solvation of the $X^-$ ions during the formation of $XI_2^-$ ions. It is this factor that seems to be responsible for reversal of the relative stability series in non-aqueous solvents.[7] Based on the results of calculations performed in the framework of the polarizable continuum model, we have shown[22] that, in contrast to chloroform, the solvation energies of interhalide complexes in a polar medium (water) become comparable with the binding energies of X...I in $CtXI_2$, which causes subsequent decomposition of interhalides. It was emphasized that the nature of both the solvents and the anions is of crucial importance for transformations of iodohalides. Based on the scheme of transformations of the $XI_2^-$ anions (see above) and on the experimental data on the stability and kinetics of disproportionation of organic iodohalides, two main stages of their decomposition were established. These are the cleavage of the X...I bond in the complex and the transformation of molecular iodine into the triiodide anion *via* the formation of the $S \cdot I_2$ molecular complex. In this work we carried out a quantum-chemical study of the energy characteristics of first stage of disproportionation in order to reveal the role of the coordinating iodide anion in the

overall decomposition of the iodohalide. The results of calculations for $n = 1$ (Eq. (7)) unambiguously indicate that the process is hardly probable, the decomposition of the diiodochloride anion having the lowest probability. As the number of solvent molecules increases, the decomposition (7) proceeds with a considerable energy gain. What is more, the relative stability series of the anions is reverted ($ClI_2^- < BrI_2^- < I_3^-$), which is in agreement with the experimental values of the stability constants.

Next, we performed a quantum-chemical study of several neutral complexes $S \cdot I_2$. It was shown that disproportionation of the iodine constituent of the complex is responsible for the overall decomposition of the iodohalide (Tables 6, 7, and Fig. 5). Analysis of the energies of the interactions within the $S \cdot I_2$ molecular complexes provides an explanation for disproportionation of organic iodohalides in solvents of different polarity (Eqs. (4)—(6)). A comparison of the $\Delta E_2$ ($\Delta E_{2m}$) energies and the

**Table 6.** Energy characteristics (complexation energies ($\Delta E_1$) and binding energies ($\Delta E_{1m}$)) and geometric parameters (bond lengths ($r$) and bond angles ($a$)) of $S \cdot I_2$ (S = MeOH, MeCN, $CHCl_3$) complexes obtained from RHF calculations with the 6-31G++(d,p) basis set for H, C, N, and O and the HW+(3d) basis set for Cl, Br, and I with inclusion of electron correlation at the MP2 level of perturbation theory

| S | $-\Delta E_1$ | $-\Delta E_{1m}$ | $-\Delta q(I_2)$* | $r$/Å | | $a$/deg |
|---|---|---|---|---|---|---|
| | kcal mol$^{-1}$ | | | I(1)—I(2) | I(1)—Y | Y—I(1)—I(2) |
| MeOH | 7.04 | 7.15 | 0.0587 | 2.720 | 2.809 | 178.22 |
| MeCN | 6.39 | 6.44 | 0.0783 | 2.721 | 2.922 | 179.99 |
| $CHCl_3$ ($C_{3v}$) | 3.97 | 3.97 | 0.0007 | 2.705 | 3.918 | 82.95 |
| $CHCl_3$ ($C_1$) | 4.26 | 4.28 | 0.0104 | 2.708 | 3.511 | 96.63 |

* The extent of charge transfer according to Mulliken was calculated by the formula $\Delta q(I_2) = q(I(1)) + q(I(2))$.

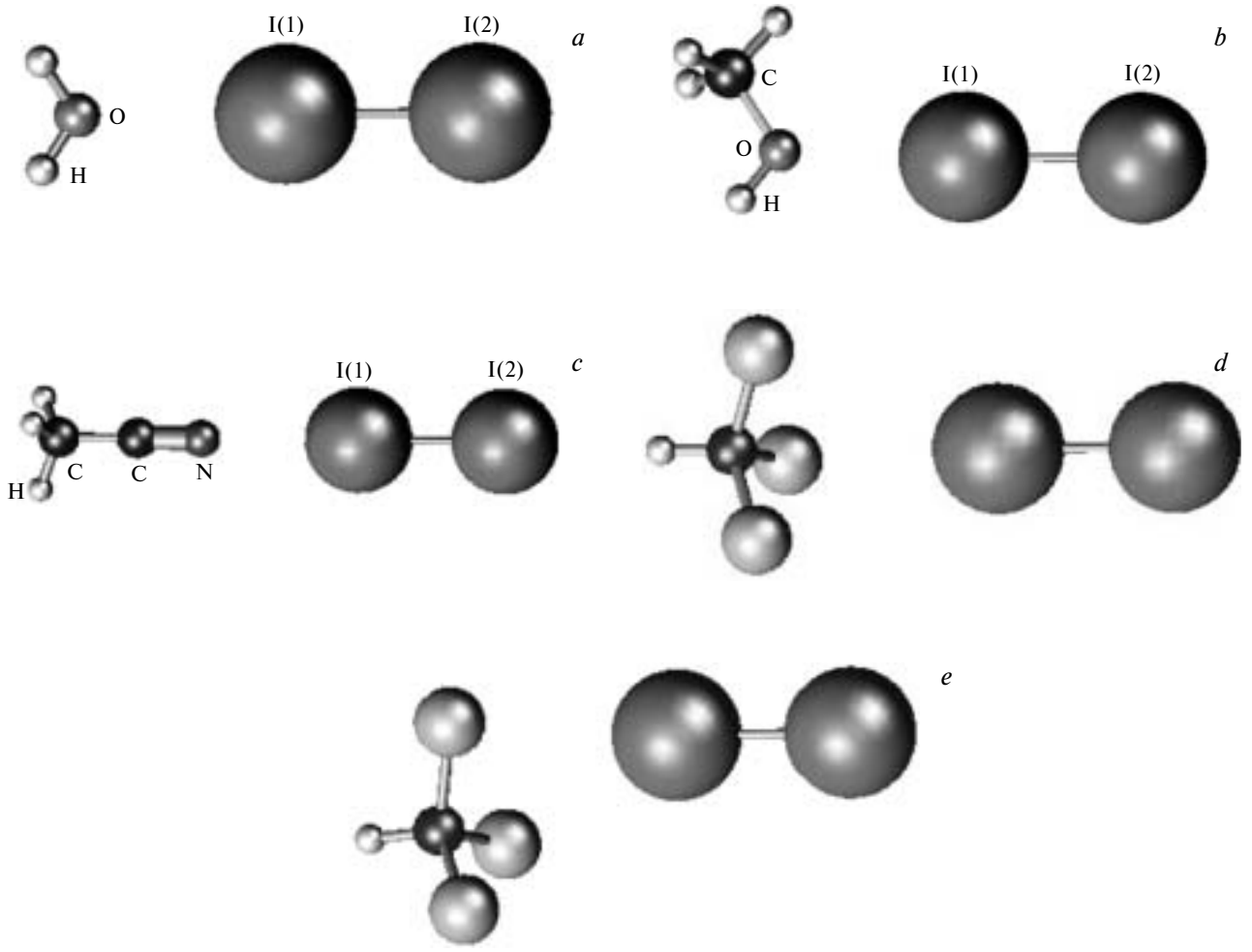


**Fig. 5.** Atomic arrangement in neutral complexes $H_2O \cdot I_2$ (*a*), $MeOH \cdot I_2$ (*b*), $MeCN \cdot I_2$ (*c*), $CHCl_3 \cdot I_2$ ($C_{3v}$) (*d*), and $CHCl_3 \cdot I_2$ ($C_1$) (*e*) obtained from RHF calculations with the 6-31G++(d,p) basis set for H, C, N, and O and the HW+(3d) basis set for Cl, Br, and I with inclusion of electron correlation at the MP2 level of perturbation theory.

**Table 7.** Expansion of the binding energies ($\Delta E_{1m}$) in the $S \cdot I_2$ (S = MeOH, MeCN) systems using the Kitaura—Morokuma scheme[20] according to RHF calculations with the 6-31G(d,p) basis set for H, C, N, and O and the HW+(3d) basis set for Cl, Br, and I

| S | $-E_{ES}$ | $E_{EX}$ | $-E_{PL}$ | $-E_{CT}{}^{a}$ | $-E_{CT}{}^{k}$ | $E_{MIX}$ | $-\Delta E_{1m}$ |
|---|---|---|---|---|---|---|---|
| | kcal mol$^{-1}$ | | | | | | |
| MeOH | 11.45 | 12.13 (12.18) | 2.88 | 1.82 (1.77) | 2.64 (2.46) | 2.73 (3.02) | 3.93 (3.36) |
| MeCN | 8.77 | 10.57 (10.60) | 2.53 | 1.80 (1.67) | 2.68 (2.64) | 2.45 (2.70) | 2.77 (2.31) |

*Note*. For notations, see Table 3. The values corrected for the basis set superposition error are given in parentheses.

charge-transfer energies (according to Mulliken or in the framework of Morokuma scheme) in the $MeOH \cdot I_2$, $MeCN \cdot I_2$, and $CHCl_3 \cdot I_2$ solvates (see Tables 6 and 7) points that complexes with a large extent of charge transfer $S \rightarrow I_2$ can be formed only for MeOH and MeCN. The results of (analogous) earlier calculations[11] of the equilibrium geometric parameters and atomic charges of I in the molecular complexes of $I_2$ with oxygen-containing solvents are in qualitative agreement with our results obtained in the 6-31G(d,p) basis set.

Thus, using a correlation between the results of *ab initio* calculations of the structures **1**—**3** and complexes $S \cdot XI_2^-$ and $S \cdot I_2$ and the experimental stability estimates for a number of organic iodohalides, we established the determining role of solvents in stabilizing the anionic structures. It was found that all the solvents studied favor the decomposition of the iodohalide anions to liberate molecular iodine; however, disproportionation of $I_2$ following Eqs. (4)—(6) is possible only for the $S \cdot I_2$ complexes with a high extent of charge transfer.

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