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From Charge Transfer to Electron Transfer in Halogen-Bonded Complexes of Electrophilic Bromocarbons with Halide Anions†

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Experimental and computational studies of the halogen-bonded complexes, [R-Br...X⁻], of bromosubstituted electrophile, R-Br, and halide anions, X⁻, revealed that decrease of a gap between the frontier orbitals of interacting species led to reduction of the energy of the optical charge-transfer transition and to increase in the ground-state charge transfer (X⁻→R-Br) in their associates. These variations were accompanied by weakening of the intramolecular, C-Br, and strengthening of the intermolecular, Br...X⁻, bonds. In the limit of the strongest electron donor/acceptor pairs, formation of the halogen-bonded complexes was followed by the oxidation of iodide to triiodide, which took place despite the fact that the I⁻→R-Br electron-transfer step was highly endergonic and the calculated outer-sphere rate constant was negligibly small. However, the calculated barrier for the inner-sphere electron transfer accompanied by the halogen transfer, R-Br...I⁻→R[•]...Br-I[•] was nearly 24 kcal/mol lower as compared to the outer-sphere process and the rate constant of such reaction was consistent with the experimental kinetics. A dramatic decrease of the electron-transfer barriers (leading to 18-order of magnitude increase of the rate constant) was related to strong electronic coupling of the donor and acceptor within the halogen-bonded precursor complex, as well as to the lower solvent reorganization energy and the successor-complex stabilization.

Introduction

Due to complementary features of electrophilic halogens as halogen bond donors and electron-rich anions as halogen bond acceptors, halogen bonding emerged as a powerful tool for crystal engineering and molecular recognition of anionic species.[1-3] While this intermolecular bonding is most commonly related to electrostatics,[4,5] many studies pointed out that molecular-orbital interactions and charge transfer also play a significant role in the formation of halogen-bonded complexes.[6-10] It is important to note in this respect that similar electronic coupling between the π -bonded donors and acceptors results in substantial decrease or even complete elimination of the barriers for electron transfer (ET) involving planar aromatic or olefinic species in solutions and in the solid state.[11,12] Thus, the identification of the molecular-orbital component in halogen bonding suggests that in addition to controlling geometries of the intermolecular associates, this interaction affects ET processes with participation of electrophilic halogenated molecules.

Electron transfer, in particular reductive cleavage of carbon-halogen bonds, plays a major role in chemical transformations of halogen-containing compounds.[13] Saveant et al. have shown that rates of many such reactions can be accounted for in the framework of the outer-sphere Marcus theory provided that carbon-halogen bond energies and interactions between ion/radical products are taken into account ("sticky" dissociative ET model).[14,15] Still,

many redox processes of halogenated molecules are much faster than predicted by the outer-sphere ET theory and such a discrepancy suggests that they proceed *via* the inner-sphere mechanism involving strongly-bonded intermediates.[16,17]

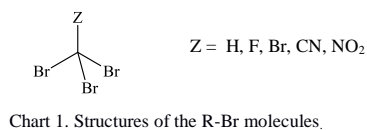
In our latest communication, this outer/inner-sphere dichotomy was illustrated for the dissociative ET reactions between the CBr₄ or CBr₃NO₂ bromocarbons with either the outer-sphere reactant decamethylferrocene (Fc*) or the halogen-bond acceptor N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD).[18] While the rates of the oxidation of Fc* calculated *via* the outer-sphere formalism agreed well with the experimental values, the analogous reactions with TMPD were many orders of magnitude faster than predicted using the same methodology. This discrepancy was related to the strong electronic coupling between the halogen-bonded reactants in the precursor [R-Br, TMPD] complexes, which lowered the ET barrier as compared to the outer-sphere pathway. Importantly, the barriers for the inner-sphere electron transfer evaluated based on the structural and spectral characteristics of the [R-Br, TMPD] associates led to the ET rate constants which were consistent with the experimental values.[18]

The attenuation of the barrier for redox-reactions due to halogen bonding has major mechanistic implications for a variety of chemical transformations potentially involving the ET step (e.g., electrophilic halogenation, halogen-atom transfer, radical polymerization).[19] Yet, transient intermediates (precursor complexes) of the ET reactions of halogenated species remain elusive, which hinder definitive analysis of the inner-sphere pathway. In a search for the systems suitable for the quantitative evaluation of the role of halogen-bonded complexes in ET reactions, we turn to the interaction between R-Br bromocarbons from Chart 1 and halide anions, X⁻.

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Such a choice is related to the fact that halogen-bonded associates between Br⁻ anions and R-Br molecules from Chart 1, as well as between Cl⁻ and I⁻ anions and CBr₄ were reported earlier.[7,10,20] Furthermore, variations of energies of the highest occupied molecular orbitals (HOMO) of halide anions and the lowest unoccupied molecular orbital (LUMO) of R-Br bromocarbons[10,21] allows to modulate free energies of electron transfer between these reactants and therefore control viability of redox processes with their participation. In fact, the switch from the formation of intermolecular complexes to redox reactions was observed earlier in the systems involving halide anions and various π -acceptors. For example, while Br⁻ anions formed charge-transfer complexes with tetracyanoethylene (TCNE), iodide salts were used as a reducing agent for synthesis of the TCNE^{•-} anion-radicals.[22,23] In comparison, the weaker π -acceptors, e.g. tetracyanopyrazine, formed charge-transfer complexes with Cl⁻, Br⁻, and I⁻ anions.[22] Recently, the reversible formations of intermolecular complexes or irreversible redox reactions were observed in the solutions containing various anions and electrophilic naphthalenediimide or hexaazatriphenylene derivatives.[24,25] However, while the inner-sphere pathway was suggested in one of these works,[25] the intermediates of the ET reactions in these systems were not characterized, which precluded quantitative verification of the proposed mechanism.

In the current work, we intend to show that variation of the HOMO/LUMO energies (and, thus, redox-potentials) of interacting halide anions and R-Br bromocarbons results in the gradual transition from the reversible formation of the halogen-bonded (charge-transfer) complexes to irreversible electron-transfer reactions. Our main goal is to demonstrate that halogen-bonded complexes represent critical intermediates which facilitate redox processes between halogenated electrophiles and (sterically-accessible) electron-rich species.

Results and Discussion

UV-Vis spectral measurements of complex formation between bromocarbons and halides. Addition of chloride or iodide salts to solutions of R-Br bromocarbons led to the appearance of new UV-Vis absorption bands which were not present in the spectra of the separate components (similar spectral changes in the systems with bromide anions were reported earlier[10]). The dependencies of intensity of these new bands on concentrations of reagents, temperature and time indicated that they are related to the reversible formation of 1:1 [R-Br, X⁻] complexes followed (in some cases) by irreversible redox processes.

For example, addition of (Bu₄N)I to a solution of CBr₃F in dichloromethane resulted in instantaneous appearance of the absorption band at $\lambda_{\max} = 312$ nm (Figure 1). This band was persistent and its intensity grew with increasing concentration of iodide at constant concentration of CBr₃F (or vice versa). The variation of concentration of the Bu₄N⁺ counter-ions did not affect the UV-Vis spectra and essentially the same results were obtained with (Pr₄N)I salts. The dependence of the absorption intensity on the molar ratio of iodide and CBr₃F in the solutions in which the sum of their concentrations was constant (Job's method) showed clear peak at 1:1 ratio of reagents. All these data pointed out that appearance of this absorption band is related to the formation of [CBr₃F, I⁻] complex (eq 1):

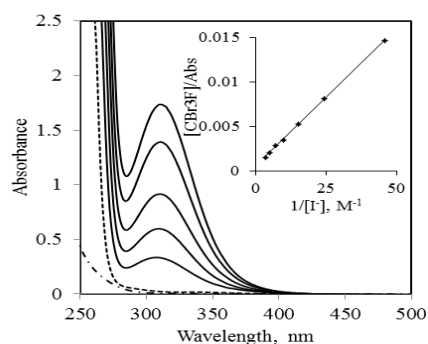
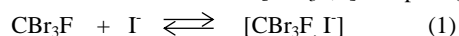


Figure 1. Spectral changes resulting from the addition of (Bu₄N)I to a 4.8 mM solution of CBr₃F in CH₂Cl₂ (19 °C) showing rise of the band at $\lambda_{\max} = 312$ nm of [CBr₃F, I⁻] complex. Concentration of (Bu₄N)I (solid lines, from the bottom to the top): 22 mM, 41 mM, 66 mM, 101 mM and 138 mM. Dashed and dot-dashed lines correspond to the separate solutions of (Bu₄N)I and CBr₃F, respectively. Insert: Benesi-Hildebrand treatment of the absorption data at $\lambda = 312$ nm.

Lowering temperature of a dichloromethane solution at constant concentrations of CBr₃F and iodide resulted in reversible increase of intensity of the absorption band at 312 nm (Figure 2). Quantitative analysis of the dependence of intensity of the absorption band on concentrations of the reagents afforded formation constant and extinction coefficient of the [CBr₃F, I⁻] complex of $K = 1.6 \text{ M}^{-1}$ and $\epsilon = 2.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The treatment of the temperature dependence of absorption (Van't Hoff graph) afforded an enthalpy and entropy of the [CBr₃F, I⁻] complex formation of $\Delta H = 2.4 \text{ kcal M}^{-1}$ and $\Delta S = -8.0 \text{ cal M}^{-1} \text{ K}^{-1}$.

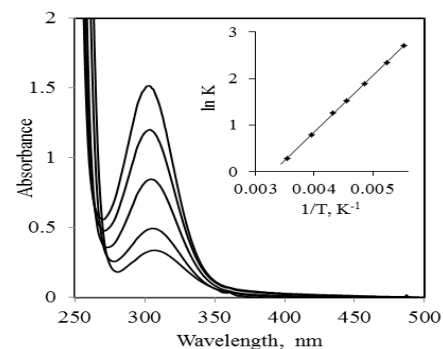


Figure 2. Temperature modulation of the reversible formation of the [CBr₃F, I⁻] complex (solid lines, from the bottom to the top): 253 K, 232 K, 206 K, 191 K, 181 K. Insert: Van't Hoff plot for the [CBr₃F, I⁻] complex formation.

Spectral and thermodynamic characteristics of the [CBr₃F, I⁻] complex formed in acetonitrile were close to the corresponding values in dichloromethane (see Figure S1 and Table S1 in ESI), in agreement with the recently reported minor solvent dependence of halogen bonding.[9]

Spectral changes resulting from the mixing of Cl⁻ anions with the R-Br bromocarbons from Chart 1, as well as mixing of I⁻ anions with CBr₄ or CHBr₃ were similar to that taking place in the solutions containing CBr₃F and iodide (see Figures S2 – S5 and Table S1 in ESI). In all these cases, addition of a halide salt to a solution of bromocarbon resulted in instantaneous appearance of new (persistent) absorption bands in the 230 – 350 nm range (note that similar bands which appeared upon addition of iodide to a solution CBr₃NO₂ or CBr₃CN were more or less persistent only at low temperature, *vide infra*). The dependencies of intensities of these bands on concentrations of components indicated that they are related to the reversible formation of the 1:1 complexes (eq 2):



The absorption band maxima for the [R-Br, X⁻] complexes (together with the extinction coefficients) and equilibria constants of their formation are summarized in Table 1.

Table 1. Spectral characteristics and formation constants of the [R-Br, X⁻] complexes.^a

R-Br	E_{LUMO}^c	[R-Br, Cl ⁻]		[R-Br, Br ⁻] ^b		[R-Br, I ⁻]	
		λ_{max} (nm)	K	λ_{max} (nm)	K	λ_{max} (nm)	K
CBR ₃ H	0.0756	<230 ^d	-	259(1.0)	0.3	294	0.4
CBR ₃ F	0.0613	247(1.1)	1.0	269(1.2)	1.0	312(2.0)	1.6
CBR ₃ CN	0.0559	261(0.7)	6.8	286 (1.1)	9.9	325 ^e	-
CBR ₄	0.0465	265(0.6) ^f	3.0 ^f	292 (1.0)	2.8	345(1.3) ^f	3.2 ^f
CBR ₃ NO ₂	0.0473	246, 297sh	6.7	267, 320sh	8.5	298, 360sh ^e	-

a) λ_{max} in nm, ϵ in $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and K in M^{-1} measured at 292 K in CH_2Cl_2 . b) Ref. 10. c) MP2/6-311+G(d,p) calculations with SCI PCM solvation (see Experimental). HOMO energies of Cl⁻, Br⁻ and I⁻ anions resulted from the analogous computations are -0.3140, -0.2913, and -0.2693 Ha, respectively. d) The band maximum is overshadowed by absorption of components and solvent. e) Measured at 185 K (*vide infra*). f) From ref. 20.

On a whole, spectral and thermodynamic characteristics of the [R-Br, X⁻] complexes are in the same range as the values established earlier for the molecular donor/acceptor complexes.[6] Most notably, the graph in Figure 3 demonstrates a clear correlation between the energies of the electronic transition in the [R-Br, X⁻] complexes and the differences of energies of the LUMO of the R-Br electrophile and the HOMO of the halide anion. The intense absorption bands in the UV-Vis spectra of the [R-Br, X⁻] complexes and the Mulliken correlation of their energies point out that orbital (charge-transfer) interaction plays a significant role in the formation of these associates.[26]

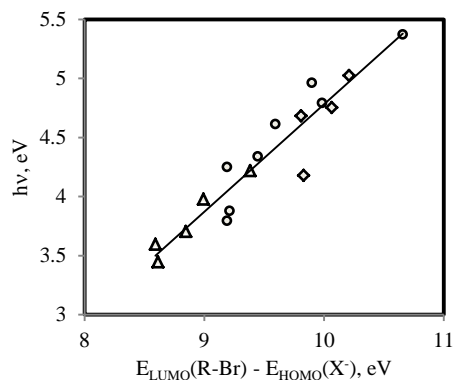


Figure 3. Mulliken correlation between the energies of the (lowest-energy) absorption bands and the difference of the frontier orbital energies of the interacting species for the [R-Br, X⁻] complexes where X⁻ = Br⁻(○), Cl⁻(◻) and I⁻(△).

Structural features of the R-Br/X⁻ associates. X-ray measurements of the co-crystals formed by bromocarbons with tetrapropylammonium salts of Cl⁻ or I⁻ anions revealed infinite networks formed by 3:3 coordination of R-Br molecules and halides and separated by Pr₄N⁺ counterions. As in the analogous complexes with bromide anions,[10] these networks demonstrate two distinct architectures, i.e. twisted 2D-layers consisting of chair-like hexagonal cells formed by three R-Br molecules and three anions, and zigzag ladders consisting of tetragonal cells formed by pairs of electrophiles and pairs of halides (Figure 4 and Figure S6 in ESI). Notably, the Br...X⁻ contacts within the R-Br/X⁻ networks were much shorter than the sum of the corresponding van der Waals radii (Table 2) and C-Br...X angles were close to 180 deg (Table S2), as typical for halogen bonding.

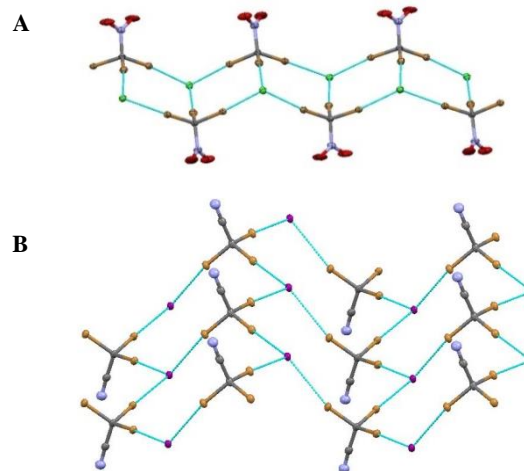


Figure 4. Infinite networks in the (Pr₄N)X-R-Br co-crystals formed by halogen bonds (light blue lines) between (A) CBR₃NO₂ and Cl⁻ anions and (B) CBR₃CN and I⁻ anions.

Table 2. Halogen bond length, $d_{\text{Br}\cdots\text{X}}$, and charge transfer, Δq , in R-Br...X⁻ associates.

R-Br	X ⁻	$d_{\text{Br}\cdots\text{X}}^{\text{exp}}$, ^a Å	$d_{\text{Br}\cdots\text{X}}^{\text{calc}}$, ^b Å		Δq , ^c e	
			CH ₂ Cl ₂	Gas-phase	CH ₂ Cl ₂	Gas-phase
CBR ₃ H	Cl ⁻		3.210	2.899	0.034	0.128
CBR ₃ F	Cl ⁻		3.145	2.805	0.045	0.172
CBR ₄	Cl ⁻	3.090 ^d	3.133	2.723	0.050	0.226
CBR ₃ CN	Cl ⁻		3.059	2.652	0.065	0.275
CBR ₃ NO ₂	Cl ⁻	3.082	3.039	2.626	0.070	0.297
CBR ₃ H	I ⁻	3.571 ^e	3.595	3.326	0.048	0.124
CBR ₃ F	I ⁻	3.434	3.512	3.222	0.053	0.172
CBR ₄	I ⁻	3.422 ^d	3.455	3.126	0.066	0.238
CBR ₃ CN	I ⁻	3.404	3.406	3.026	0.082	0.305
CBR ₃ NO ₂	I ⁻		3.396	2.991	0.085	0.346

a) Mean value for short intermolecular R-Br...Br distances resulted from X-ray structural analysis of the (Pr₄N)X-R-Br co-crystals, see Table S2 in ESI for individual bond lengths. Sum of the van der Waals radii for the Br...Cl and Br...I contacts are 3.60 Å and 3.83 Å, respectively [27]. b) From M06-2X/6-311+G(d,p) computations, see Experimental section. c) From the NBO analysis. d) Ref. 20. e) Ref. 7a.

In our previous studies we found that experimental (structural, thermodynamic and spectral) characteristics of the halogen-bonded complexes between R-Br electrophile and bromide or pseudohalide anions could be accurately reproduced via DFT calculations with dispersion-corrected ωB97Dx and M06-2X functionals.[7c,10] As such, in the current work, we applied M06-2X/6-311+G(d,p) computations for the analysis of the halogen-bonded associates between R-Br electrophiles and chloride and iodide anions (see Experimental Section). To establish the amount of X⁻ → R-Br charge transfer, Δq , we carried out Natural Bond Orbital (NBO) analysis of the halogen-bonded [R-Br, X⁻] complexes.

The Br...X⁻ distances and C-Br...X⁻ angles resulted from the optimizations of the R-Br/X⁻ pairs in the gas phase and in dichloromethane are listed in Table 2 and Table S3 in ESI. The data in Table 2 show that while the calculated gas-phase R-Br...X⁻ separations are 0.3 – 0.4 Å shorter than the X-ray structural values, the R-Br...X⁻ distances and angles resulted from the M06-2X computations in dichloromethane are close to those measured in the solid-state associates. Similar tendency was observed earlier for the complexes of bromide or pseudohalide anions with various R-Br electrophiles.[7c,10] It suggests that, at least for the computational method used herein, the calculations in moderately-polar dichloromethane lead to a more realistic model of the experimental solid-state structures, in which halogen bonding is affected by inter-ionic forces. It should be also stressed that $d_{\text{Br}\cdots\text{X}}^{\text{calc}}$ values were calculated for the 1:1 associates, while $d_{\text{Br}\cdots\text{X}}^{\text{exp}}$ distances were measured in solid-state networks in which each halide anion was bonded with three R-Br molecules and vice versa. As such, the comparison of the calculated and experimental halogen-bond lengths should be made cautiously.[‡]

Consideration of the data in Tables 1 and 2 indicates that the values of ground-state $X^- \rightarrow R-Br$ charge transfer in the $[R-Br, X^-]$ associates in dichloromethane are correlated with the frontier orbital energies of the interacting species. In particular, for the series of complexes with the same halide, the Δq values are increasing roughly in parallel with the decrease of the LUMO energy of R-Br electrophile (i.e. from CBr_3H to CBr_3NO_2).[‡] For the series of complexes with the same bromocarbon, the amount of charge transfer is increasing with the rise of the HOMO energy of halide anion, i.e. from Cl^- to Br^- and to I^- (see Table S4 in ESI for the reported earlier data for the complexes with bromide anion). Comparison of the Δq values with the structural characteristics of the complexes revealed two clear trends.

First, the increase in the amount of the $X^- \rightarrow R-Br$ charge transfer, Δq , is accompanied by the lengthening of intramolecular C-Br bonds (Figure 5A, see Table S3 in ESI for details). Such a correlation is consistent with the fact that charge transfer in the $[R-Br, X^-]$ complexes results mostly in population of the antibonding $\sigma^*(C-Br)$ orbitals in the R-Br molecules. It confirms that the Δq values represent not just (more or less arbitrary) assignment of charges within complexes, but are also manifested in the experimentally measured characteristics.

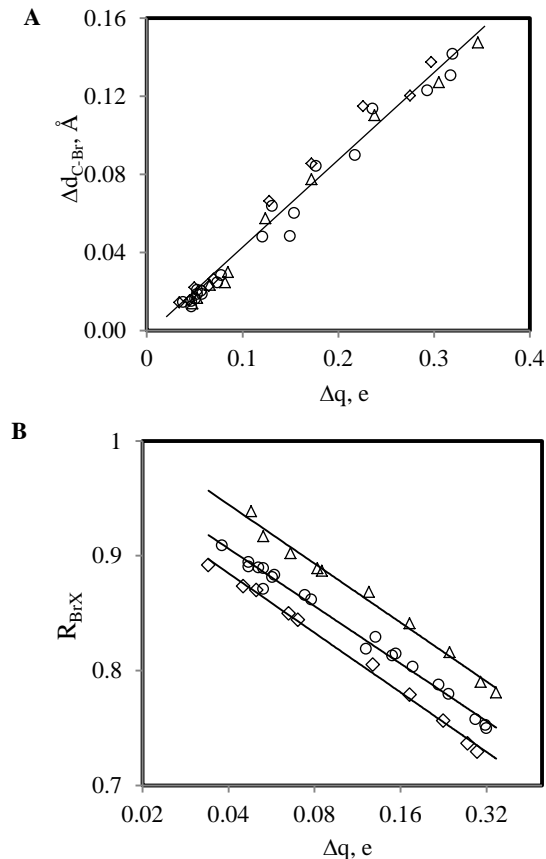


Figure 5. Correlations between the amounts of charge transfer, Δq , and lengthening of the C-Br bonds, Δd_{C-Br} (A) and shortening of the intermolecular separations R_{BrX} (B) in the $[R-Br, X^-]$ complexes (Br(\circ), Cl(\circ) and I(Δ)).

Second, the intermolecular separations in the $[R-Br, X^-]$ complexes are also correlated with the amount of the $X^- \rightarrow R-Br$ charge transfer (Figure 5B). The R_{BrX} values (i.e., ratios of the interatomic $B \dots X$ distances to the sum of the corresponding van der Waals radii) represents the structural manifestation of the strength of the inter-

molecular interactions.[28] As such, these correlations (as well as analogous trends observed with pseudohalide anions[7c]) imply, in agreement with the UV-Vis spectral data, that HOMO/LUMO interactions and charge transfer play a significant role in halogen bonding between R-Br bromocarbons and anions.

Thus, besides the lowering energy of the optical (vertical) charge transfer transition, the decrease of the HOMO/LUMO gap of the halogen-bonded species results in the increase of the ground-state $X^- \rightarrow R-Br$ charge-transfer, leading to the weakening of intramolecular C-Br and strengthening of the intermolecular $Br \dots X$ bonds. Most notably, UV-Vis studies revealed that the complex formation involving the strongest electron donor/acceptor pairs was followed by the irreversible redox reactions as follows.

Electron-transfer reactions in the R-Br/I⁻ systems. In contrast to the persistent absorption bands of the $[R-Br, X^-]$ complexes described above, the analogous bands which appeared upon mixing of iodide salts with CBr_3CN or CBr_3NO_2 bromocarbons were observed only at low temperature (Figure 6A and Figure S7 in ESI). Warming of the solutions resulted in disappearance of absorption of $[CBr_3CN, I^-]$ or $[CBr_3NO_2, I^-]$ complexes and formation of the bands at 293 nm and 365 nm of I_3^- anion[#] (Figure 6A and Figure S8 in ESI).[29,30]

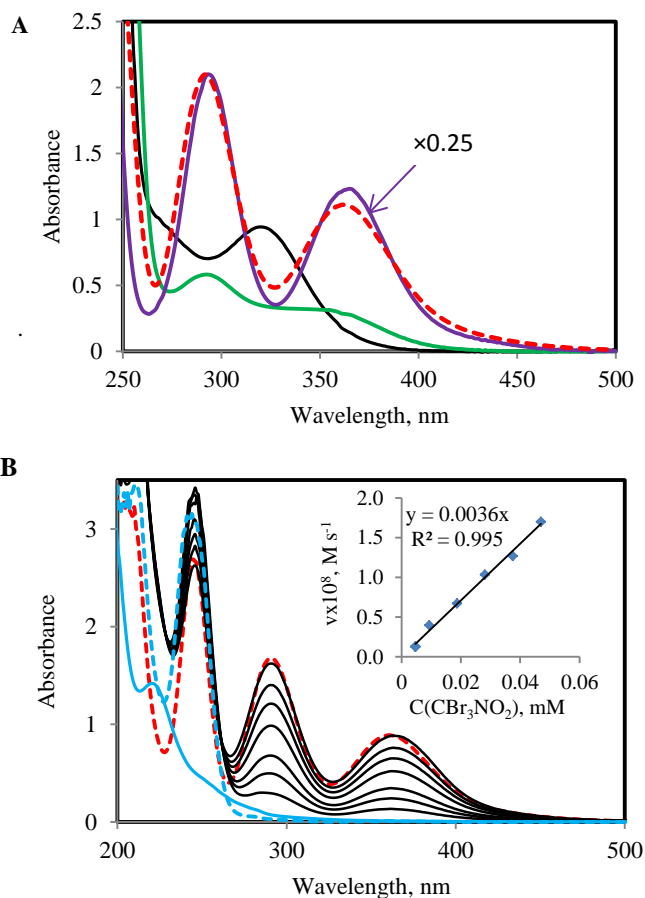
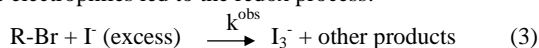


Figure 6. (A) UV-Vis spectra of the solution containing 0.4 mM CBr_3CN and 4.0 mM $(Bu_4N)I$ in CH_2Cl_2 showing formation of the $[CBr_3CN, I^-]$ complex after mixing of reactants at $-80^\circ C$ (black line), partial dissociation of the complex and formation of I_3^- after warming of the solution to $0^\circ C$ (green line) and formation of I_3^- after warming solution to room temperature (violet line). (B) Absorption spectra of the acetonitrile solution of 0.25 mM $(Bu_4N)I$ and 0.025 mM CBr_3NO_2 measured 13 s, 25 s, 56 s, 85 s, 112 s, 147 s and 205 s after mixing of reactants at $20^\circ C$ (solid black lines, from the bottom to the top). Solid and dashed blue lines represent absorption spectra of the separate solutions of CBr_3NO_2 and $(Bu_4N)I$, respectively. Inset: Dependence of the rate of I_3^- formation on concentration of CBr_3NO_2 at constant concentration of $(Bu_4N)I$ of 0.2 mM. Note: red dashed lines in A and B represent absorption spectra of I_3^- anions obtained by mixing of I_2 and $(Bu_4N)I$.

The solid-state (Pr₄N)I-CBr₃CN complexes (crystallized at -80°C) were also persistent only at very low temperatures and the warming of these crystals resulted in their fast decomposition. At room temperature, only fast formation of the absorption bands at 288 nm and 350 nm of I₃⁻ could be recorded in the CBr₃NO₂/I⁻ system with conventional spectrophotometric techniques (Figure 6B). Such spectral changes indicated that addition of iodide to a solution of these electrophiles led to the redox process:



Kinetic measurement revealed that initial rates of triiodide formation were linearly proportional to the concentration of each reactant (insert in Figure 6B and Figure S9 in ESI). For CBr₃NO₂/I⁻ pair in acetonitrile at 20°C, these measurements afforded 2nd-order rate constants of reaction in eq (3) of $k^{\text{obs}} = 18 \text{ M}^{-1}\text{s}^{-1}$.

To establish if the halogen-bonded complexes are intermediate (or merely dead-end bystanders) in the oxidation of iodide (eq 4),



we examined rate-determining step of this process, i.e. electron transfer from iodide to tribromonitromethane,[31-33][§] within two alternative frameworks, i.e. outer and inner-sphere ET pathways.

According to the outer-sphere Marcus theory, the rate constant of bimolecular ET reactions can be calculated as:[14]

$$k_{\text{ET}}^{\text{OS}} = Z \exp(-\Delta G_{\text{OS}}^*/RT) \quad (5)$$

where $Z = 10^{11} \text{ M}^{-1}\text{s}^{-1}$ is a collision factor.[34] Since reduction of tribromonitromethane represent dissociative electron transfer (DET) process,[18] the barrier for this reaction can be calculated according to Saveant's "sticky" DET mechanism as: [15]

$$\Delta G_{\text{OS}}^* = \lambda^{\text{OS}}/4 \{1 + (\Delta G^{\circ} - D_{\text{R}\bullet/\text{Br}^-})/\lambda\}^2 \quad (6)$$

where λ is a reorganization energy, ΔG° is a driving force of the ET reaction, and $D_{\text{R}\bullet/\text{Br}^-}$ is the interaction energy between ion-radical products of the reductive cleavage of the C-Br bond. The redox-potentials of reactants, $E_{\text{I}^-/\text{I}_3^-}^{\circ} = 1.06 \text{ V}$ [21] and $E_{\text{R}\bullet/\text{R}+\text{X}^-} = -0.39 \text{ V}$, [18] indicate that this electron transfer step is a highly endothermic reaction with $\Delta G^{\circ} = 33.4 \text{ kcal/mol}$. The reorganization energy, λ for the DET involving tribromonitromethane can be evaluated as:[15]

$$\lambda = \lambda_s + (D_{\text{RBr}}^{1/2} - D_{\text{R}\bullet/\text{Br}^-}^{1/2})^2 \quad (7)$$

where λ_s is a solvent reorganization energy and D_{RBr} is the C-Br bond dissociation energy.

For the $\text{I}^- \rightarrow \text{CBr}_3\text{NO}_2$ electron transfer in acetonitrile, the classical two-sphere model, which is commonly used for the calculation the solvent reorganization energy for the outer-sphere processes produced λ_s of 36.3 kcal/mol. Together with the earlier reported values of $D_{\text{RBr}} = 56.8 \text{ kcal/mol}$ and $D_{\text{R}\bullet/\text{Br}^-} = 1.6 \text{ kcal/mol}$, [18] it led (via eq 7) to $\lambda^{\text{OS}} = 75.4 \text{ kcal/mol}$ and (via eq 6) to $\Delta G_{\text{OS}}^* = 38.1 \text{ kcal/mol}$. Substituting the latter into the Marcus expression (eq 5) produced the negligibly small rate constant of $9 \times 10^{-18} \text{ M}^{-1}\text{s}^{-1}$ for the ET ($\text{I}^- \rightarrow \text{CBr}_3\text{NO}_2$) step.

The 18-orders of magnitude difference between the calculated value of the outer-sphere ET rate constant and the experimental rate constant of $18 \text{ M}^{-1}\text{s}^{-1}$ is much higher than any approximations and inaccuracies in the computations and/or experimental measurements. Such a difference is especially striking in view of the previously reported reasonable agreement (within an order of magnitude or so) between the experimental and calculated values of rate constants of oxidation of the outer-sphere reducing agent, Fc^{*}, by CBr₄ or CBr₃NO₂ acceptors.[18] This points out that the $\text{I}^- \rightarrow \text{CBr}_3\text{NO}_2$ electron transfer apparently occurs via alternative inner-sphere mechanism proceeding via strongly-bonded precursor complex.

To check if the high ET rates can be related to halogen bonding between tribromonitromethane and iodide in the precursor complex in eq 4, we turned to the general Marcus-Hush two-state model which explicitly takes into account electronic coupling between redox-sites and, thus, is applicable to the strongly-adiabatic systems.[35] In the framework of this model, the ground-state ET potential-energy surface is evaluated as:

$$E_{\text{GS}} = (H_{\text{aa}} + H_{\text{bb}})/2 - ((H_{\text{bb}} - H_{\text{aa}})^2 + 4H_{\text{ab}}^2)^{1/2}/2 \quad (8)$$

where $H_{\text{aa}} = \lambda X^2$ and $H_{\text{bb}} = \Delta G_{\text{ET}}^{\circ} + \lambda(X-1)^2$ are energies of the initial and final diabatic states at each point along the ET reaction coordinate, from $X = 0$ to $X = 1$, and H_{ab} is a coupling element.[35] Notably, as coupling element, H_{ab} , increases, the barrier for the electron transfer between redox centers decrease as compared to the outer-sphere processes, up to complete electron delocalization in the systems with $H_{\text{ab}} \geq \lambda/2$. Importantly, the values of H_{ab} can be established from the spectral and structural characteristics of these redox-systems via the Hush expression:[36]

$$H_{\text{ab}} = 0.0206(v_{\text{CT}} \Delta v_{1/2} \epsilon_{\text{CT}})^{1/2}/r_{\text{DA}} \quad (9)$$

where v_{CT} , $\Delta v_{1/2}$, and ϵ_{CT} are maximum, full-width at half maximum, and the extinction coefficient of the absorption band related to optical ET between the redox centers and r_{DA} is their separation. Earlier works demonstrated that this model produces barriers for the intra-molecular ET in the mixed-valence complexes which agree with the experimental ET kinetics measured in these systems.[37,38] Moreover, isolation and characterization of the transient precursor complexes allowed us to extend the same model to the intermolecular processes and to account for the high rate constants of the intermolecular ET reactions of organic π -donor and acceptors,[12] as well as oxidation of TMPD by CBr₃NO₂ or CBr₄ bromocarbons.[18]

Calculations of the electronic coupling element (via eq 9) based on the spectral and structural characteristics of the halogen-bonded [CBr₃NO₂...I⁻] complex afforded H_{ab} of 8.9 kcal/mol (see Experimental Section for the details). This value is much higher than the upper limit for the outer-sphere processes (200 cm⁻¹ or ~0.6 kcal/mol),[35] which confirms the inner-sphere character of the intra-complex $\text{I}^- \rightarrow \text{CBr}_3\text{NO}_2$ electron transfer. Since close contact of reactants in the precursor complex precludes the use of the simple two-sphere model, solvent reorganization energy for such electron transfer was calculated within the framework of the dielectric continuum model as a free energy of the inertial solvent response to a charge shift in the solute cavity containing the halogen-bonded CBr₃NO₂...I⁻ pair, as described earlier for the π -bonded pairs.[39] Such calculations afforded $\lambda_{\text{os}}^{\text{IS}} = 29.2 \text{ kcal/mol}$, which led (via eq 6) to the reorganization energy of inner-sphere ET, λ^{IS} , of 68.3 kcal/mol.

The free energy difference between precursor and successor complex for the inner-sphere ET also should be modified as compared to the outer-sphere process. Indeed, a precursor complex for the outer-sphere ET implies random arrangements of the iodide in the vicinity of the tribromonitromethane. Accordingly, electron transfer and C-Br bond breaking within such a pair results in the formation of a successor complex which is stabilized, in general, only by relatively minor CBr₂NO₂[•]/Br⁻ interaction (eq 5). In contrast, ET and intramolecular C-Br bond breaking in the halogen-bonded precursor complexes results in formation of partially-bonded bromide-iodine pairs and, upon thermal equilibration, BrI[•] anion-radicals. In essence, as illustrated in Chart 2, the inner-sphere ET results in the

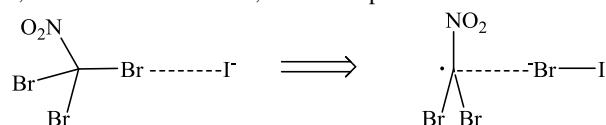


Chart 2. Electron and halogen transfer in halogen-bonded complex.

C-Br bond breaking and formation of the Br-I bond, i.e. in the bromine atom transfer. As such, the successor complex for inner-sphere ET, $[R^{\bullet}, BrI^{\bullet}]$, is significantly stabilized by the Br-I bond in BrI^{\bullet} anion-radical of 23.5 kcal/mol.[40](Note, that under condition of large excess of iodide, the fast anion exchange convert mixed anion-radical BrI^{\bullet} into $I_2^{\bullet-}$, i.e. $BrI^{\bullet} + I^{-} \rightarrow I_2^{\bullet-} + Br^{-}$ or BrI^{\bullet} dissociates into Br^{-} and I^{\bullet} with a large 1st order rate constant, leading ultimately to I_3^{-} anions.[32])

The values of coupling element, H_{ab} , free energy change, ΔG_{IS}° , and reorganization energy, λ^{IS} for the inner-sphere electron transfer allowed us to construct the potential energy diagram (see Figure S10 in ESI) and calculate the barrier for such process, $\Delta G_{IS}^{\ddagger} = 14.6$ kcal/mol (see Experimental section for details of computations). Notably, this barrier is nearly 24 kcal/mol lower than the corresponding value calculated for the outer-sphere process (Chart 3).

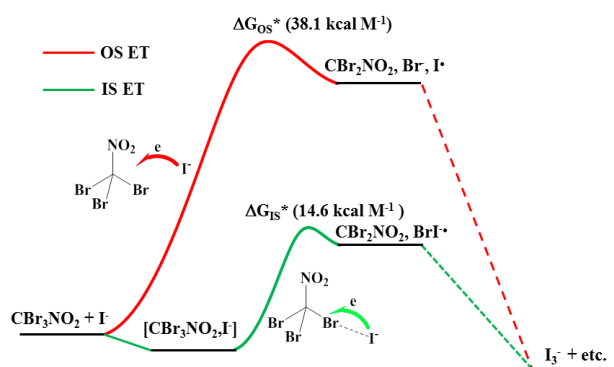


Chart 3. Energy diagrams for the inner- and outer-sphere pathways.

Such a difference between outer- and inner-sphere barriers is much larger than that established earlier for the electron transfer between CBr_3NO_2 and TMPD (about 6 kcal/mol).[18] More significant lowering of the barrier for of the barrier for inner-sphere process in the halogen-bonded complexes of bromocarbons with halide anions (which represents in essence the halogen transfer $R-Br \dots I^{-} \rightarrow R^{\bullet} \dots Br-I^{\bullet}$) as compared to the outer-sphere alternative results from the combination of the strong electronic coupling of reactants in precursor $[R-Br, X^{-}]$ complex, as well as lower solvent reorganization energy for the electron transfer between tightly-bound reactants and successor-complex stabilization by the new bond formed between ET products. Most notably, the inner-sphere barrier led to an intramolecular ET rate constant, k_{ET}^{IS} , within halogen-bonded $[CBr_3NO_2, I^{-}]$ complex of 17 s^{-1} . The product of the latter by the equilibrium constant of complex formation, $K \sim 8 \text{ M}^{-1}$, afforded the rate constant for the intermolecular electron transfer from iodide to tribromonitromethane, $k_{IS} = 1.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$. A reasonable agreement of this rate constant (which represent a rate-limiting step in the redox-process of leading to I_3^{-} anion) with the experimental value of $k^{obs} = 1.8 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$ supports the hypothesis that the halogen-bonded $[CBr_3NO_2, I^{-}]$ complex represent a critical precursor complex for the electron transfer in this system.®

Concluding Remarks

In accord with the Mulliken theory, the decrease of a gap between the HOMO of the halide and the LUMO of the bromocarbon reduces energy of the optical charge-transfer transition in the $[R-Br, X^{-}]$ complexes and increases the ground-state $X^{-} \rightarrow R-Br$ charge transfer taking place in these associates (leading to the weakening of the

intramolecular, C-Br, and strengthening of the intermolecular $Br \dots X^{-}$ bonds). Ultimately, for the strongest electron donor/acceptor pairs, e.g. I^{-}/CBr_3NO_2 , transient appearance of the $[R-Br, X^{-}]$ complexes is followed by the thermal redox-reaction leading to the formation of triiodide. Due to the involvement of the halogen-bonded complex, the barrier for this process is nearly 24 kcal/mol lower and its rate constant is more than 18-orders of magnitude higher than that calculated based on the classical outer-sphere ET theory. In fact, as shown in Chart 3, the barrier for the inner-sphere pathway involving halogen-bonded complex is even lower than the free energy change for the highly-endergonic outer-sphere ET step, ΔG° , calculated from the difference of the redox-potentials of reactants (which was used a lower limit for the activation energy for the processes involving ET step[41]).

A dramatic decrease of the electron and halogen transfer^Y barriers resulting from halogen bonding has important implications beyond the dissociative ET processes considered in the current work. It enables ET steps in chemical transformations involving halogenated species, e.g. electrophilic addition or substitution, in which they were previously discarded due to the prohibitively low rates calculated using the outer-sphere theory.[19,41] Likewise, it may contribute to carbon-heteroatom bond activation by halogen bonding.[42] A decrease in the ET barrier also suggests that similar to the π -bonding, which leads to electron delocalization and (super)conducting properties of the ion-radical and charge-transfer salts,[11, 43] halogen bonding may facilitate electron and halogen atom transfer along the chains of the halogen-bonded species in the solid state. In particular, while the successful applications of halogen bonding for crystal engineering of conducting materials involved, in most cases, common π -donors and acceptors, e.g. tetrathiafulvalene (so, the charge mobility in these systems was related primarily to the π - π interactions), the high conductivity and halogen-atom mobility which was reported recently in polyhalides salts, is probably related to the strong halogen bonding taking place in these systems.[44] On the whole, the halogen-bonding-induced considerable decrease of the ET barrier demonstrated in the current work extends the potential of this intermolecular interaction for chemical and material-science applications.

Experimental

Materials. Commercially available carbon tetrabromide, bromoform, and tribromofluoromethane were purified by sublimation or distillation, and Bu_4NX and Pr_4NX salts were purified by recrystallization. Tribromonitromethane was synthesized by bromination of nitromethane and tribromoacetone nitrile was synthesized by dehydration of tribromoacetamide.[45] Dichloromethane, hexane and acetonitrile (HPLC grade) were purified as described earlier[10] and stored under a dry nitrogen atmosphere.

UV-Vis measurements. Absorption spectra were recorded under dry nitrogen atmosphere using a quartz spectroscopic cells equipped with a Teflon valve fitted with Viton O-rings. A Dewar equipped with quartz lens was used for the measurements at +10 to -95 °C. The temperature was adjusted with an ethanol-liquid nitrogen bath ($\pm 0.5 \text{ K}$). Formation constants, K , of $[R-Br, X^{-}]$ complexes and extinction coefficients of their absorption bands were evaluated via UV-Vis titrations followed by quantitative treatment of the data as described earlier.[10] The bands at 325 nm and 360 nm which appeared upon addition of iodide to CBr_3CN and CBr_3NO_2 , respectively, at -90°C were assigned to $[CBr_3CN, I^{-}]$ and $[CBr_3NO_2, I^{-}]$ complexes based on their energies (which follow Mulliken dependence established for the complexes with the other R-Br and X⁻ species) and reversible changes of their intensity with temperature (if such variations were carried at low temperatures). Warming of these solutions resulted in irreversible formation of I_3^{-} anions (with

possible admixture of BrI_2^-). The rate constants k^{obs} were obtained *via* measurements of the initial rates of the increase of the intensity of absorption at $\lambda = 365$ nm (corresponding to the maximum of the I_3^- absorption band with $\epsilon = 2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ [30]) of the solutions obtained by mixing of the R-Br and excess of Bu_4NI in acetonitrile or dichloromethane at 22°C .

X-ray Crystallography. Single crystals of halogen-bonded associates suitable for X-ray measurements were obtained by diffusion of hexane into solutions containing a 1:1 mixture of the R-Br molecule and a tetrapropylammonium halide salt in CH_2Cl_2 at -80°C . (Note, that solutions of Pr_4NI and CBr_3CN were mixed at -80°C to prevent follow-up reactions). Crystals were selected and mounted in inert oil and transferred to the cold gas stream of a Kappa Apex 2 diffractometer. The crystals were kept at 100.04 K during data collection. The structures were solved with the XM structure solution program using Dual Space and refined with the ShelXL refinement package using Least Squares minimization.[46][†]

Computations. Quantum-mechanical calculations were carried out using the Gaussian 09 suite of programs.[47] The geometries of [R-Br, X⁻] complexes were optimized in the gas phase and in dichloromethane *via* DFT calculations with MO6-2X functionals.[48] Recent theoretical study demonstrated that this method provide the best (among DFT and MP2 ab initio methods) characteristics of the halogen-bonded complexes with anionic halogen-bond acceptors (e.g. Cl^- and Br^-).[49] 6-311+G(d,p) basis set was used for all atoms except iodine, for which 6-311G* basis set was downloaded from EMSL Basis Set Exchange Library.[50] Geometry optimizations in dichloromethane were carried out using polarizable continuum model (PCM).[51] Energies and atomic coordinates of halogen-bonded R-Br-Br⁻ associates are listed in ESI.(Table S4) Atomic charges were calculated *via* Natural Population Analysis phase of NBO analysis.[52] Following earlier work,[25] the HOMO/LUMO energies of halide anions and R-Br electrophiles were obtained from MP2/6-311+G(d,p) calculations with SCI PCM solvation.[53] The HOMO/LUMO energies resulted from the computations with the different solvation model or from the DFT calculations with MO6-2X or ωB97XD functionals follow generally the same trends and the Mulliken correlations based on the frontier orbital energies resulted from such computations are characterized by comparable correlation coefficients (see Table S5 and Figure S11 in ESI).

The driving force for the outer-sphere electron transfer was calculated from the difference of the redox potentials of CBr_3NO_2 and I^- as $\Delta G^\circ = -F\Delta E$, where F is a Faraday constant. The standard redox potentials for the halogen/halide redox pairs, $E^\circ_{\text{X}^-/\text{X}}$, were determined in the recent work of Isse, Lin, Coote and Gennaro.[21] They examined recent thermodynamic data and reported values of $E^\circ_{\text{X}^-/\text{X}}$ in acetonitrile as 2.03, 1.60 and 1.06 V vs SCE for Cl^-/Cl , Br^-/Br and I^-/I redox-couples, respectively (these redox-potentials are consistent with the spectral and electrochemical properties of halide anions,[54] and their halogen-bonded complexes and π -bonded associates[7]). The reduction potential of CBr_3NO_2 in acetonitrile was calculated earlier.[18]

The solvent reorganization energy for the outer-sphere ET was calculated as:[14]

$$\lambda_o^{\text{OS}} = (1/\epsilon_\infty - 1/\epsilon_0) \times (\Delta q)^2 \times (1/2r_D + 1/2r_A - 1/r_{\text{DA}}) \quad (10)$$

where ϵ_∞ and ϵ_0 are optical and static dielectric constants of acetonitrile, Δq is the transferred charge, r_D and r_A are effective molecular radii of the donor and acceptor (4.06 Å and 2.0 Å for CBr_3NO_2 and I^- , respectively, evaluated from the molecular volume of the corresponding species[18]), and r_{DA} is their separation.

Due to the close contact of I^- and CBr_3NO_2 in their halogen-bonded complex, two-sphere model is not suitable for the calculation of the solvation reorganization energy for the inner-sphere $\text{I}^- \rightarrow$

CBr_3NO_2 electron transfer. As such, the latter was calculated using the Delphi Poisson solver [55] within the framework of the dielectric continuum model (DCM) as the free energy of the inertial solvent response to a charge shift in the solute cavity as described earlier:[39]

$$\lambda_o^{\text{IS}} = G_S((\epsilon_{\infty 1}, \epsilon_{\infty 2}, \dots, \epsilon_{\infty N}, \Delta q) - G_S((\epsilon_{01}, \epsilon_{02}, \dots, \epsilon_{0N}, \Delta q)) \quad (11)$$

where Δq is the point-charge representation of the full shift in the charge density of the donor/acceptor dyad upon electron transfer. For the cavity containing the precursor complex, the change in charge density is represented by the variation of the point charge (Δq_i) at each atomic site (i). The Δq_i values were evaluated as the difference between corresponding ESP atomic charges calculated with the aid of the ChelpG option, and the geometry of the complex was taken from the M062X/6-311+G(dp) computations in dichloromethane.

Since our study and the recent report[9] showed minor variations of the properties of the halogen-bonded complexes on solvent, coupling element for the inner-sphere ET was evaluated (eq 9) based on spectral characteristics of the [CBr_3NO_2 , I^-] complex and its calculated structure in CH_2Cl_2 ($\nu = 27.8 \times 10^3 \text{ cm}^{-1}$, $\epsilon = 3000 \text{ M}^{-1} \text{ cm}^{-1}$, $\Delta\nu = 8.0 \times 10^3 \text{ cm}^{-1}$, $r_{\text{DA}} = 5.4$ Å). ΔG^*_{IS} was calculated using expression derived by Sutin and Brunschwig for the ET barrier in the asymmetric strongly-adiabatic systems:[35] $\Delta G^* = \lambda/4 + \Delta G^\circ/2 + (\Delta G^\circ)^2 / (4/(\lambda - 2H_{\text{ab}})) - H_{\text{ab}} + H_{\text{ab}}^2 / (\lambda + \Delta G^\circ) - H_{\text{ab}}^4 \Delta G^\circ / (\lambda + \Delta G^\circ)^4$ (The value obtained using this expression agrees with that evaluated graphically from the ET energy diagram in Figure S9 in ESI). The intramolecular rate constant was calculated as $k_{\text{ET}} = \kappa_{\text{el}} \nu_n \exp(-\Delta G^*/RT)$, where $\kappa_{\text{el}} \nu_n \sim 10^{12} \text{ s}^{-1}$ as described earlier.[11] The 2nd-order rate constant was calculated as $k_{\text{ET}}^{\text{IS}} = K k_{\text{ET}}$ (which is valid for the reactions that are significantly slower than the diffusion rates), in which value of $K = 8 \text{ M}^{-1}$ was extrapolated from the characteristics of complexes of tribromonitromethane with chloride and iodide based on the similarity of formation constants of complexes of the same R-Br with different anions (Tables 1 and S1).

Acknowledgements

We thank Rory Stewart for the initial UV-Vis measurements of the [CBr_3F , Cl^-] and [CBr_3F , I^-] complexes and Alan Swartz for the initial UV-Vis measurements of the [CBr_3CN , Cl^-] and [CBr_3NO_2 , Cl^-] complexes, and Charlotte L. Stern for the X-ray structural analysis of the $\text{Pr}_4\text{NCl} \cdot \text{CBr}_3\text{NO}_2$, $\text{Pr}_4\text{NI} \cdot \text{CFBr}_3$ and $\text{Pr}_4\text{NI} \cdot \text{CBr}_3\text{CN}$ co-crystals. We also thank National Science Foundation (grant CHE-1112126) for financial support of this work.

Notes and references

[†] For example, the energy minima for 3(CBr_3F)- I^- and 3(CBr_3NO_2)- Cl^- clusters resulted from the gas-phase MO6-2X/6-311+G(d,p) computations are characterized by the average C-Br...X angles of 170.8 deg and 171.7 deg and average interatomic $d^{\text{calc}}_{\text{Br}\dots\text{X}}$ distances of 3.399 Å and 2.957 Å, respectively (Figure S12 in ESI). These $d^{\text{calc}}_{\text{Br}\dots\text{X}}$ values are somewhat higher than those calculated (in the gas phase) for the corresponding 1:1 associates and, thus, they are much closer to the corresponding $d^{\text{exp}}_{\text{Br}\dots\text{X}}$ values measured in the $\text{Pr}_4\text{NCl} \cdot \text{CBr}_3\text{NO}_2$ and $\text{Pr}_4\text{NI} \cdot \text{CFBr}_3$ co-crystals (Table 2). NBO analysis of these clusters revealed charge-transfer from halide anions to R-Br electrophiles, with remaining charges of -0.746 on chlorine in 3(CBr_3NO_2)- Cl^- and of -0.765 on iodine in 3(CBr_3F)- I^- . The $\text{X}^- \rightarrow \text{R-Br}$ charge-transfer was accompanied by the elongation of C-Br bond length in the R-Br molecules as compared to the separate molecules. Furthermore, the relationship between amount of charge transfer (per one halogen bond) and intermolecular and intramolecular bond length are, on the whole, consistent with those which were found in 1:1 associates (Figure 5). We should stress, however, that while a comparison of the solid-state associates and calculated 1:1 complexes and clusters formed by several species deserves a separate thorough study, the current article is focused primarily on the charge-transfer and electron-transfer processes occurring in the solution. Since experimental measurements established formation of 1:1 complexes in solutions, the theoretical analysis is focused on the calculated 1:1 complexes as well.

≠ While the energy of the charge-transfer transition in a series of the [R-Br, X⁻] complexes with the same anion X⁻ decrease in the order CBr₃H > CBr₃F > CBr₃CN > CBr₄ > CBr₃NO₂, the ground-state charge transfer increase in the order CBr₃H < CBr₃F < CBr₄ < CBr₃CN < CBr₃NO₂. The switch of the CBr₄ and CBr₃CN positions is apparently related to the fact that the variations of energies of the optical (vertical) transition are related primarily to the LUMO energies, which is lower in CBr₄ as compared to CBr₃CN (Table 1). In contrast, ground-state charge-transfer (and electron-transfer) is determined by the redox-potentials of reactants, and preliminary computations revealed that reduction potential of CBr₃CN is more positive than that of CBr₄, i.e. in the thermal redox reactions in solutions, CBr₃CN is a stronger oxidant than CBr₄.

In CH₂Cl₂ or CH₃CVN, I₃⁻ anion is characterized by strong absorption bands at 363 nm ($\epsilon = 2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 293 ($4.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). [29,30]

§ The focus on the CBr₃NO₂/I⁻ pair as a model for the halogen-bond assisted ET reaction is related to the fact that characteristics which are required for the theoretical estimation of the dissociative ET rate constants with participation of these reactants were either reported previously or could be evaluated following literature methods. [18,21]

¶ Earlier studies of oxidation of iodide anions revealed that rate-determining steps in these processes usually involve (thermal or photoinitiated) electron transfer from the I⁻ donor to the electron acceptor resulting in formation of iodine radical followed by fast radical processes, e.g. I⁻ + I⁻ → I₂^{•-}, 2I₂^{•-} → I₃⁻ + I⁻, 2I⁻ → I₂, I₂ + I⁻ → I₃⁻. [31-33] This points to the I⁻ → CBr₃NO₂ electron transfer as a rate-determining step of the redox process in eq 3.

⊖ Besides rate-determining ET from I⁻ to CBr₃NO₂, there are several factors which affect concentration of the triiodide, and thus the observed rate constant k^{obs}. They include: (i) oxidation of additional iodide by the radical product of the tribromomethane reduction, CBr₂NO₂^{•-}, which is a stronger oxidant than CBr₃NO₂, [10] (ii) triiodide formation requires oxidation of two I⁻ anions, (iii) equilibrium between I₂ + I⁻ and I₃⁻, etc. While some of these factors, e.g. i) and ii), compensate each other, only approximate agreement between k^{obs} and the calculated value of k_{ET}^{IS} (which represents the rate-determining step) can be expected.

⊕ As such, halogen transfer is facilitated by halogen bonding similarly to that as the proton transfer is facilitated by hydrogen bonding. We thank Prof. P. Metrangolo for pointing out this analogy.

⊞ *Pr₂NCl·CBr₃NO₂*. C₁₃H₂₈N₂O₂ClBr₃ (*M* = 519.55): monoclinic, space group P2₁/n (no. 14), *a* = 16.0589(13) Å, *b* = 13.6380(9) Å, *c* = 18.3496(13) Å, β = 95.258(4)°, *V* = 4001.9(5) Å³, *Z* = 8, *T* = 100.1 K, $\mu(\text{MoK}\alpha)$ = 6.187 mm⁻¹, *D*_{calc} = 1.725 g/mm³, 52204 reflections measured (3.534 ≤ 2 θ ≤ 60.072), 11363 unique (*R*_{int} = 0.1003, *R*_{sigma} = 0.0941) which were used in all calculations. The final *R*₁ was 0.0674 (*I* > 2 σ (*I*)) and *wR*₂ was 0.1750 (all data). CCDC 1026790.

Pr₂Nl·CFBr₃. C₁₃H₂₈Br₃FIN (*M* = 583.99): orthorhombic, space group Pna2₁ (no. 33), *a* = 33.76(3) Å, *b* = 8.427(6) Å, *c* = 14.421(11) Å, *V* = 4102(5) Å³, *Z* = 8, *T* = 99.92 K, $\mu(\text{MoK}\alpha)$ = 7.405 mm⁻¹, *D*_{calc} = 1.891 g/mm³, 121246 reflections measured (4.826 ≤ 2 θ ≤ 60.132), 11920 unique (*R*_{int} = 0.0866, *R*_{sigma} = 0.0458) which were used in all calculations. The final *R*₁ was 0.0283 (*I* > 2 σ (*I*)) and *wR*₂ was 0.0596 (all data). CCDC 1026791.

Pr₂Nl·CBr₃CN. C₁₄H₂₈N₂Br₃I (*M* = 591.01): monoclinic, space group P2₁/n (no. 14), *a* = 8.5118(3) Å, *b* = 18.3083(7) Å, *c* = 13.3813(5) Å, β = 97.315(2)°, *V* = 2068.32(13) Å³, *Z* = 4, *T* = 100.04 K, $\mu(\text{CuK}\alpha)$ = 18.899 mm⁻¹, *D*_{calc} = 1.898 g/mm³, 12105 reflections measured (8.228 ≤ 2 θ ≤ 130.13), 3484 unique (*R*_{int} = 0.0286, *R*_{sigma} = 0.0279) which were used in all calculations. The final *R*₁ was 0.0239 (*I* > 2 σ (*I*)) and *wR*₂ was 0.0621 (all data). CCDC 1026792.

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