

**Electronic Supporting Information for
Electron-transfer reactions of halogenated electrophiles:
a different look into the nature of halogen bonding**

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Details of the experimental measurements and computations.

Spectral measurements. UV-Vis measurements were carried out under N₂ atmosphere using quartz (1-mm or 1-cm path length) spectroscopic cells equipped with a Teflon valve fitted with Viton O-rings. A Dewar equipped with quartz lens was used for measurements at +5 to -85 °C.

[R-Br, TMPD] and [R-Br, I⁻] complexes formation. The [R-Br, TMPD] formation constants and extinction coefficients were evaluated via UV-Vis titrations by an incremental addition of R-Br to the solutions of TMPD molecules in hexane, dichloromethane or acetonitrile. The [R-Br, I⁻] formation constants and extinction coefficients were evaluated via an incremental addition of the tetrabutyl- or tetrapropylammonium salt of iodide to the solutions of TMPD. Spectral measurements were followed by quantitative treatment of the data using Benesi-Hildebrand method,¹ and via regression analysis of the UV-Vis absorbance data, as described earlier.^{2,3} For example, the equilibrium constant for the [R-Br, TMPD] complex formation is expressed as:

$$K = x / (([R-Br] - x)([TMPD] - x))$$

where x is an equilibrium concentration of the complex and [R-Br] and [TMPD] are initial concentrations of the reactants in solution. When one of them is taken in large excess, i.e. [CBr₄] >> [TMPD], then [CBr₄] >> x, and [CBr₄] - x ≈ [CBr₄]. Therefore K = x / ([TMPD] - x)[CBr₄]) or 1/x = 1/[TMPD] + 1/(K [TMPD] [CBr₄]). Taking into account that: A = ε l x, where A is absorbance of the complex at a certain wavelength (obtained by subtraction of the absorption of components), and l is the length of the spectrophotometric cell, the latter can be rearranged as Benesi-Hildebrand equation:

$$[TMPD] / A = 1 / (\varepsilon l) + \{ 1 / (K \varepsilon l) \} \times 1 / [CBr_4].$$

A plot [TMPD] / A vs 1/[R-Br] is described by a linear trend line, which produces values of K and ε. It should be noted that the Benesi-Hildebrand procedure provided reliable results only if one reactant is present in large excess and the complexation of the other reactant (in deficit) is in the 20-80% range⁴ (which is difficult to obtain if the K values of ~ 1 or less). Thus, to verify the values of K and ε, we carried out regression analysis of the absorbance of complexes at various concentrations of the components, without the assumption made in the Benesi-Hildebrand method. In this case, the expression for the equilibrium constant, K = x / (([R-Br] - x)([TMPD] - x)), leads to the quadratic equation: x² - x([R-Br] + [TMPD] + 1/K) + [R-Br][TMPD] = 0. The physically meaningful solution of this equation is:

$$x = ([R-Br] + [TMPD] + 1/K)/2 - \{ ([R-Br] + [TMPD] + 1/K)² - 4[R-Br][TMPD] \}^{1/2}/2$$

Accordingly, the absorbance of the complex can be calculated as:

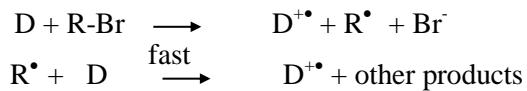
$$A_{\text{calc}} = \varepsilon l \{ ([R-Br] + [TMPD] + 1/K)/2 - \{ ([R-Br] + [TMPD] + 1/K)² - 4[R-Br][TMPD] \}^{1/2}/2 \}$$

Computer fitting of the series of experimental values of absorption Aⁱ_{exp} measured at different initial concentrations of R-Br and TMPD (by the variation of ε and K values to minimize the difference

between the experimental and calculated values of the absorption: $\Delta = \sum \{A_{\text{exp}}^i - A_{\text{calc}}^i\}^2$ and to maximize the correlation coefficient between A_{exp}^i and A_{calc}^i values) produced a unitary set of K and ϵ which describes the absorption of the complex over a wide range of concentrations of components.

3-4 series of experiments were performed for each R-Br/TMPD pair, and values of K were evaluated at two wavelengths. Values of K obtained from different series of measurements via different methods and different wavelengths were typically within ~30 %. It should be noted that the accurate measurements of the K and ϵ values in some systems were hindered by the strong absorption of the reactants or products of the redox reactions. The formation constants for such systems were extrapolated from the K values for the complexes of the same halogen-bond acceptor with the other R-Br electrophiles. This extrapolation was possible due to the fact that the previous works revealed that the variations of the formation constants in the series of the complexes of R-Br electrophiles with the same nucleophile were very similar. [2,6]

Kinetics of the redox reactions. Addition of R-Br electrophiles to the solutions of TMPD, I⁻, Fc* or Me₈Fc in dichloromethane or acetonitrile resulted in fast appearance of the characteristic absorption bands of products of their oxidation. P (P = I⁻, Fc*⁺, Me₈Fc⁺, or in case of iodide oxidation, I₃⁻ resulted from the fast follow-up processes, i.e. BrI[•] + I⁻ → I₂^{•-} + Br⁻ or BrI[•] dissociates into Br⁻ and I[•] with a large 1st order rate constant, leading ultimately to I₃⁻ anions).⁵⁻⁷ The rates of the products formation were measured at their absorption bands maxima, i.e. TMPD^{•+} at $\lambda = 612$ nm ($\epsilon = 12500$ M⁻¹ cm⁻¹), of the Fc*⁺ at 778 nm ($\epsilon = 580$ M⁻¹ cm⁻¹), Me₈Fc⁺ at 750 nm ($\epsilon = 475$ M⁻¹ cm⁻¹), and I₃⁻ at 365 nm ($\epsilon = 2.5 \times 10^4$ M⁻¹ cm⁻¹). It should be noted that under the conditions of experiments, 2 moles of TMPD^{•+}, Fc*⁺, Me₈Fc⁺ were formed per 1 mole of R-Br electrophile, since reductive cleavage of R-Br resulting in formation of R[•] and Br⁻ followed by the fast oxidation of the second molecule of D by R[•] (or a product of their recombination), i.e.



where $k' = \frac{1}{2} k^{\text{obs}}$.⁵ Some redox processes, e.g. between CBr₃ and TMPD,[5] could be described within the accuracy of measurements by this scheme from the beginning to practically 100% conversion of the limiting reagent. Yet, noticeable deviation from the 1st order reactions in each reactant were observed at later stages of reactions in some cases (e.g. reactions with participation of CBr₃CN and CBr₃COBr₃, acceleration of the redox processes took place at some reactants ratios). It suggests unaccounted participation of the product of these R-Br electrophiles reduction in the oxidation of the electron donors. To avoid complications from these processes, the rate constants in Table 1 were established from the studies of the initial rates of the reactions, which were proportional to the first order of concentrations of the reactants.

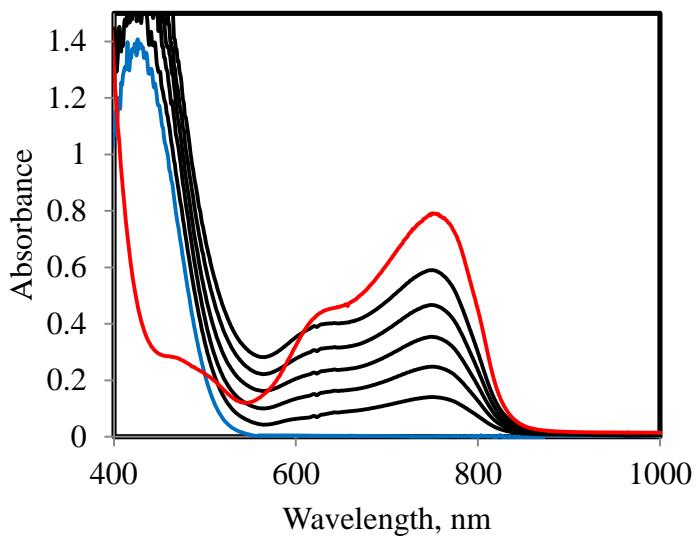


Figure S1. Spectral changes occurring upon addition of CBr_3CN to a solution of Me_8Fc in acetonitrile at 22°C (solid black lines, from the bottom to the top). Blue line represent a spectrum of the Me_8Fc and red line show spectrum of Me_8Fc^+ obtained by dissolving of their crystalline salt.

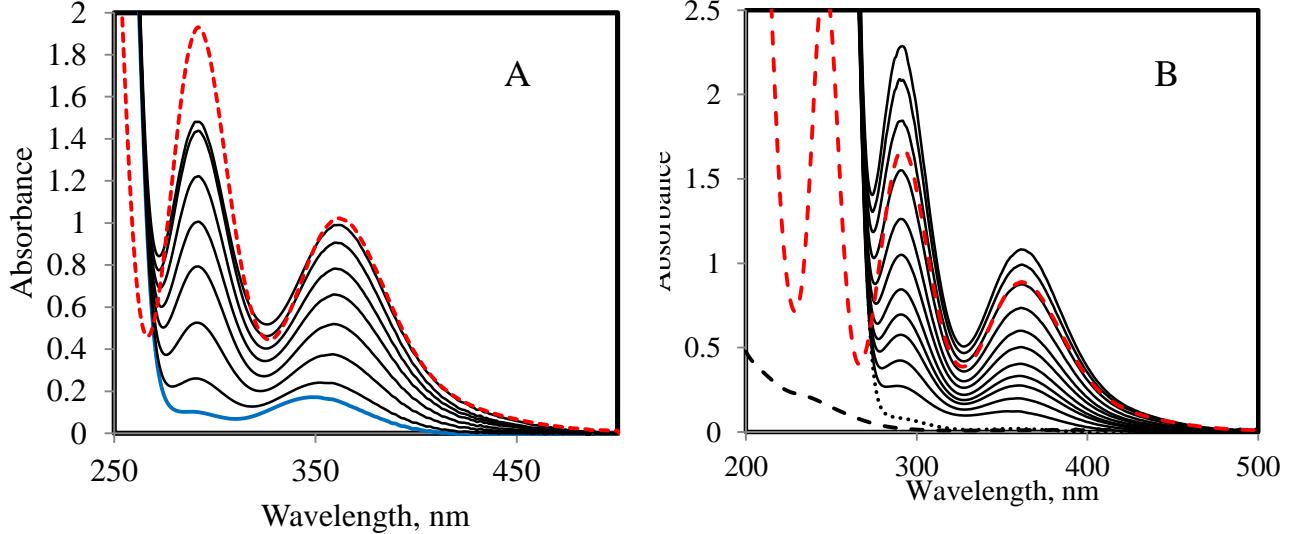


Figure S2. Absorption spectra of the solutions containing 10 mM of iodide and 2.5 mM of (A) and 0.025 mM of CBr_3CN and 4 mM iodide (B) in acetonitrile at 22°C showing rise of the absorption of the triiodide anion (solid lines, from the bottom to the top). Blue line in A shows spectrum of $[\text{CBr}_4, \text{I}]$ complex which is formed immediately after mixing. Black dot- and dashed-line in B correspond to the separate solutions of $(\text{Bu}_4\text{N})\text{I}$ and CHr_3CN , respectively. Red dashed-lines in A and B represent triiodide produced by addition of I_2 to solution of $(\text{Bu}_4\text{N})\text{I}$.

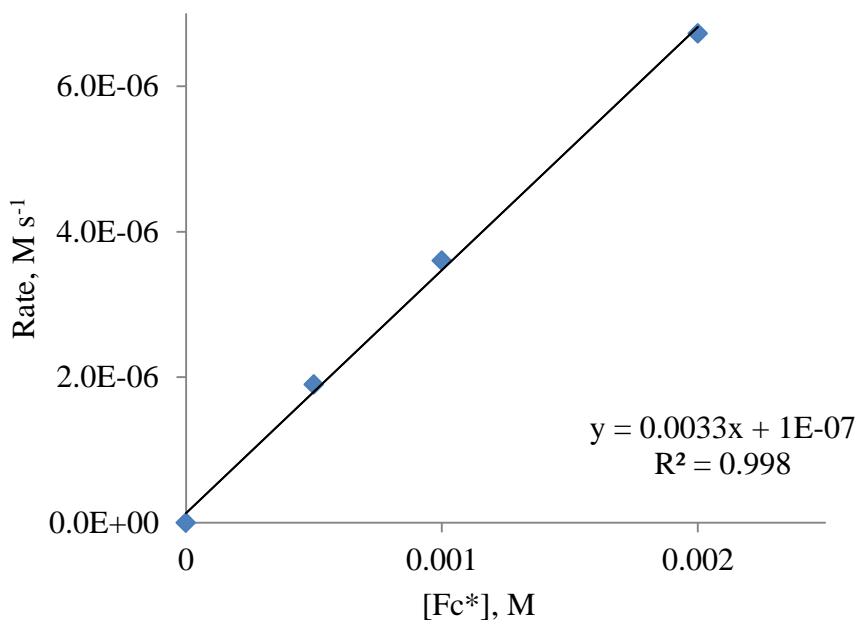
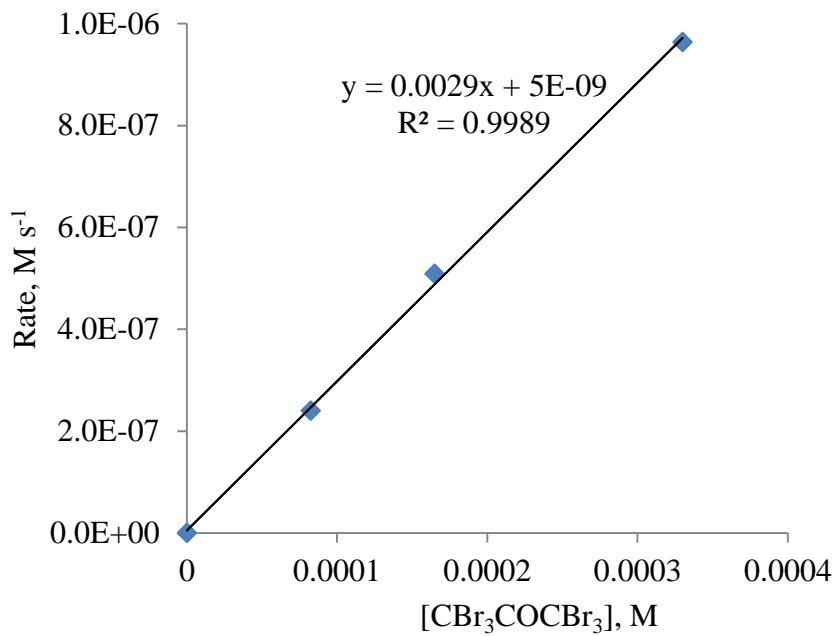


Figure S3. Dependencies of the initial rates of the redox reactions on the concentration of reagents in the $\text{Fc}^*/\text{CBr}_3\text{COBr}_3$ system: $[\text{Fc}^*] = 0.38 \text{ mM}$, variation of concentration of $\text{CBr}_3\text{COBr}_3$ (top) and $[\text{CBr}_3\text{COBr}_3] = 0.5 \text{ mM}$, variation of concentration of Fc^* (bottom).

Table S1. Details of the calculations of outer-sphere ET rate constants (CH_3CN , 22 °C).

R-Br	$\Delta G^{\circ, \text{a}}$, kcal M ⁻¹	λ_s, b , kcal M ⁻¹	λ, c , kcal M ⁻¹	$\Delta G_{\text{OS}}^*, \text{d}$, kcal M ⁻¹	k^{OS}, e , M ⁻¹ s ⁻¹
Reactions of R-Br with Fc*					
CBr_3CN	2.1	18.9	57.7	14.30	6.0
$\text{CBr}_3\text{COBr}_3$	5.8	16.5	57.7	16.06	0.30
CBr_3NO_2	6.0	18.7	58.4	16.24	0.24
$\text{CBr}_3\text{CONH}_2$	6.0	18.2	60.3	16.98	5×10^{-2}
CBr_4	8.5	17.8	65.0	19.74	6×10^{-4}
CBr_3F	14.3	19.2	71.9	24.73	1×10^{-7}
CBr_3H	15.5	20.7	67.1	23.66	8×10^{-7}
Reactions of R-Br with Me ₈ Fc					
CBr_3CN	4.2	19.0	57.7	15.4	1.0
$\text{CBr}_3\text{COBr}_3$	7.8	16.7	57.7	17.2	0.04
CBr_3NO_2	8.1	18.8	58.4	17.4	0.03
$\text{CBr}_3\text{CONH}_2$	8.3	18.3	60.3	18.2	7×10^{-3}
CBr_4	10.6	17.9	65.0	20.9	8×10^{-5}
CBr_3F	16.4	19.3	71.9	26.0	1×10^{-8}
CBr_3H	17.5	20.8	67.1	24.9	9×10^{-8}
Reactions of R-Br with TMPD					
CBr_3CN	7.4	20.4	71.1	20.3	2×10^{-4}
$\text{CBr}_3\text{COBr}_3$	11.1	18.4	71.5	22.3	8×10^{-6}
CBr_3NO_2	11.3	20.2	71.9	22.3	7×10^{-6}
$\text{CBr}_3\text{CONH}_2$	11.3	19.8	73.8	23.1	1×10^{-6}
CBr_4	13.9	19.5	78.6	26.0	3×10^{-8}
CBr_3F	19.6	20.7	85.2	31.0	3×10^{-12}
CBr_3H	20.8	22.0	80.2	29.9	2×10^{-12}
Reactions of R-Br with I ⁻					
CBr_3CN	29.5	36.3	74.5	35.5	7×10^{-16}
$\text{CBr}_3\text{COBr}_3$	33.2	36.1	76.7	38.4	6×10^{-18}
CBr_3NO_2	33.4	36.3	75.4	38.1	9×10^{-18}
$\text{CBr}_3\text{CONH}_2$	33.4	36.2	77.7	38.9	2×10^{-18}
CBr_4	36.0	36.2	82.7	42.1	1×10^{-20}
CBr_3F	41.7	36.4	88.4	47.4	1×10^{-24}
CBr_3H	42.9	36.7	82.4	46.4	7×10^{-27}

a) $\Delta G^{\circ} = -F\Delta E$, where F is a Faraday constant. Redox-potentials are listed in Table S2.

b) The solvent reorganization energy calculated from the two-sphere Marcus expression as:⁸

$$\lambda_s = (1/\epsilon_{\infty} - 1/\epsilon_0) \times (\Delta q)^2 (1/2r_D + 1/2r_A - 1/r_{DA})$$

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, and r_{DA} is donor / acceptor separation. The effective radii of the donors and acceptors are listed in the Table S2 below.

c) Reorganization energy calculated for the “sticky” dissociative ET mechanism as:⁹

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

where λ_i is an intramolecular reorganization energy of the electron donors: $\lambda_i(\text{TMPD}) = 12.5$ kcal/mol, $\lambda_i(\text{Fc}^*) = 0.6$ kcal/mol, D_{RBr} is the C-Br bond dissociation energy of R-Br molecules calculated according to the literature²⁶ (Table S3; $D_{R\bullet/Br^-}$ is an interaction energy in the R^\bullet/Br^- radical/ion pair from M062X/6-311+G(d,p) computations (Table S2)).

d) Activation barrier for the “sticky” dissociative ET mechanism the latter is calculated as:⁹

$$\Delta G^* = \lambda/4 \{ 1 + (\Delta G^o + w_p - D_{R\bullet/Br^-})/\lambda \}^2$$

where w_p is the work of bringing products together calculated as an energy of electrostatic interaction between ionic products of the redox reactions in acetonitrile (i.e., $e^2/\epsilon r$) based on the effective molecular radii of cations and van der Waals radius of bromide of 1.85 Å: $w_p(\text{TMPD}^{+\bullet}/\text{Br}^-) = 1.43$ kcal/mol, and $w_p(\text{Fc}^{*+}/\text{Br}^-) = 1.19$ kcal/mol.

e) $k_{ET}^{OS} = 2 \times Z \exp(-\Delta G^*/RT)$, where $Z = 10^{11} \text{M}^{-1}\text{s}^{-1}$ is a collision factor^{8,10} and ΔG^* is an activation barrier, and factor 2 is included to take into account oxidation of the electron donors by the radicals resulting from the reductive cleavage of the R-Br electrophiles.

Table S2. Parameters for the calculations of the outer-sphere ET rate constants (CH₃CN, 22 °C).

R-Br	$E^o_{R-Br/R^\bullet+X^-}$, V vs SCE ^c	r_A , Å ^a	BDE, kcal/mol ^b	$D_{R\bullet/Br^-}$, kcal/mol
CB ₃ CN	-0.22	4.01	52.7	1.16
CB ₃ COCB ₃	-0.38	4.84	57.2	1.42
CB ₃ NO ₂	-0.39	4.06	56.8	1.64
CB ₃ CONH ₂	-0.40	4.22	56.4	1.13
CB ₄	-0.50	4.34	58.7	0.70
CB ₃ F	-0.75	3.93	64.5	0.66
CB ₃ H	-0.80	3.58	64.9	1.67

a) Calculated from the molecular volume of the corresponding species obtained via B3LYP/6-311G* calculations, as described earlier.¹¹ Note that calculated radii of TMPD and Fc* used in calculations were 4.62 Å and 5.90 Å, respectively.⁵ b) From ref. 12. C) From ref. 12. Oxidation potentials of TMPD, Fc*, Me₈Fc and Γ^- are 0.10 V, -0.13 V, -0.02 and 1.06 V vs SCE, respectively [5,6,10,16].

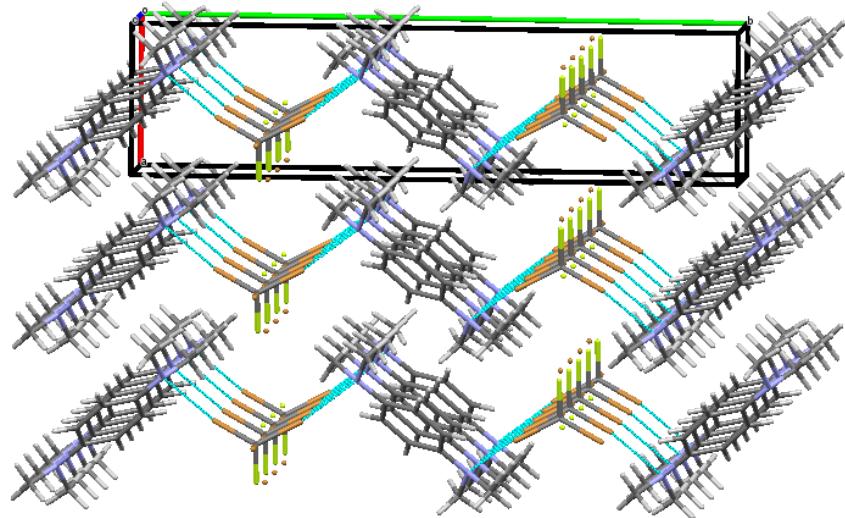


Figure S4. X-ray structure of $\text{CBr}_3\text{F}\bullet\text{TMPD}$ co-crystal (halogen bonds are shown as light blue lines).

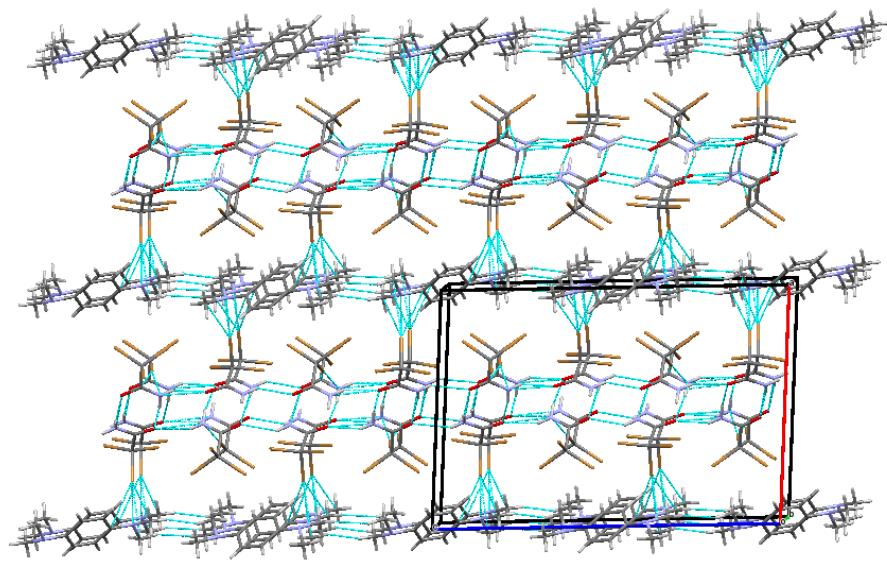


Figure S5. X-ray structure of $4\text{CBr}_3\text{CONH}_2 \bullet \text{TMPD}$ co-crystals comprising multiple halogen and hydrogen bonds (shown as light blue lines).

Table S3. Energies (hartree) of the R-Br molecules and R-Br·D complexes optimized with M062X functional in acetonitrile.^a

	E (R-Br)	E+ZPE (R-Br)	E (R-Br•TMPD)	E+ZPE(R-Br•TMPD)	E (R-Br•I)	E+ZPE (R-Br•I)
CBr ₃ CN	-7853.40900	-7853.39305	-16134.58313	-16134.30974	-14773.52468	-14773.50843
CBr ₃ COBr ₃	-15634.48435	-15634.45992	-8465.75637	-8465.48703	-22554.59924	-22554.57474
CBr ₃ NO ₂	-7965.65653	-7965.63662	-8353.50838	-8353.24297	-14885.77230	-14885.75224
CBr ₃ CONH ₂	-7929.88624	-7929.84179	-8429.98318	-8429.68968	-14850.00033	-14849.95554
CBr ₄	-10334.74447	-10334.73730	-8465.75637	-8465.48703	-17254.85920	-17254.85175
CBr ₃ F	-7860.42437	-7860.41492	-10834.84276	-10834.58643	-14780.53845	-14780.52875
CBr ₃ H	-7761.19376	-7761.17543	-8261.28900	-8261.02191	-14681.30671	-14681.28816

a) E (TMPD) = -500.0870046 , E+ZPE (TMPD) = -499.839679, E(I⁻) = -6920.108992.

Atomic coordinates of R-Br·D complexes optimized with M062X functional in acetonitrile

R-Br·I⁻ complexes

R = CBr₃CN

C	0.69732900	-1.54538400	0.00000000
Br	0.09221100	-2.47340400	1.60038400
Br	0.09221100	0.31735900	0.00000000
Br	0.09221100	-2.47340400	-1.60038400
C	2.15072300	-1.55695000	0.00000000
N	3.29926400	-1.55683900	0.00000000
I	-0.94085400	3.61401100	0.00000000

R = CBr₃COBr₃

C	-1.84024900	-0.93755500	-0.14269700
Br	-3.57473100	-0.26411600	0.45578500
Br	-2.11944200	-2.36046300	-1.43472400
Br	-0.84592900	-1.67124800	1.34849300
C	-1.18826400	0.27972000	-0.88754800
O	-1.37464300	0.38656300	-2.05688300
C	-0.30940200	1.33729000	-0.15797200
Br	1.49881900	0.55834400	-0.13133500
Br	-0.28820300	2.95986600	-1.22630700
Br	-0.88474000	1.80787600	1.63276400
I	4.68910500	-0.81562800	0.01925800

R = CBr₃NO₂

C	-1.56775800	-0.00016300	0.130229001
Br	-2.31035700	-1.58032500	-0.666523001
Br	0.38373000	-0.00305400	0.063811001
Br	-2.30211600	1.58965200	-0.652201001
N	-1.89518600	-0.01016700	1.668370001
O	-2.00325400	1.05848000	2.205900001
O	-1.93997100	-1.08668300	2.200180001
I	3.81556000	0.00147600	-0.071446002

R = CBr₃CONH₂

C	-1.60921100	-0.01171300	0.17779500
Br	0.34624900	0.00997800	0.10460600
Br	-2.29994300	-1.38083800	-1.03671800
Br	-2.29098900	1.71607900	-0.35390500
C	-2.09312800	-0.38039100	1.61546100
O	-2.90152000	0.33256200	2.17658300
N	-1.57187100	-1.49210900	2.11029000
H	-0.87473100	-2.07861200	1.61034400
H	-1.87488600	-1.79478000	3.05983200
I	3.91967600	0.03637000	-0.04912800

R = CBr₄

C	-1.44610000	0.00023700	-0.00024000
Br	-2.09905200	-0.59372600	1.73413400
Br	-2.10857400	-1.20556100	-1.37743600
Br	0.50610500	0.00222700	-0.00535400
Br	-2.10668200	1.79760700	-0.35100600
I	3.99931600	-0.00038900	-0.00019700

CBr₃F

C	1.72022700	-0.00000200	0.44830400
Br	2.53183400	-1.59825600	-0.29565700
Br	2.53095700	1.59875700	-0.29549500
Br	-0.20644300	-0.00047400	0.19709500
F	1.96731200	-0.00004300	1.76604600
I	-3.73583700	-0.00001000	-0.09042000

R = CBr₃H

C	-0.71936200	1.76763900	0.00000000
H	0.00000000	2.57573500	0.00000000
Br	0.26604500	0.10047300	0.00000000
Br	-1.79131100	1.96762100	1.59997300
Br	-1.79131100	1.96762100	-1.59997300
I	2.27161900	-2.91378400	0.00000000

R-Br-TMPD complexes

R = CBr₃CN

Br	1.01205600	0.80747400	-0.26381800
Br	3.49573100	-0.07654400	1.58468700
C	2.66074400	-0.26995400	-0.16109400
N	-1.18434300	2.28227500	-0.37761400
C	-2.29177500	1.39603300	-0.21396100
C	-2.44146900	0.31983400	-1.09649200
H	-1.71463500	0.16929300	-1.88691900
C	-3.48426800	-0.58246200	-0.97357600
H	-3.54044000	-1.39632400	-1.68312100
C	-0.98511000	3.24806900	0.69521100
H	-0.90924500	2.73181800	1.65302800
H	-1.79592500	3.98758700	0.74661900

H	-0.04800400	3.77584200	0.51261800
C	-1.12307800	2.93413800	-1.68914300
H	-1.20566300	2.19846600	-2.48677700
H	-0.16066800	3.43961000	-1.78720000
H	-1.92760100	3.67306500	-1.80246800
N	-5.51744600	-1.33641600	0.15288100
C	-4.44275400	-0.45834000	0.05351300
C	-4.26556200	0.59964900	0.95845400
H	-4.94779100	0.73589200	1.78591700
C	-3.22028300	1.51042800	0.81998000
H	-3.14714600	2.31118200	1.54472200
C	-5.41917200	-2.60645600	-0.54901600
H	-6.31686100	-3.18773600	-0.34726900
H	-5.36399800	-2.45080100	-1.62766600
H	-4.54319100	-3.19197200	-0.23684300
C	-6.25886500	-1.35469400	1.40320400
H	-7.05343000	-2.09467400	1.32833100
H	-5.62391300	-1.60484900	2.26486000
H	-6.72679600	-0.38636200	1.58858700
Br	2.28604300	-2.14070300	-0.54290700
C	3.59299700	0.21598300	-1.16318300
N	4.31791100	0.61394700	-1.96076300

R = CBr₃COCBr₃

Br	-0.21274500	0.95444900	0.73296200
Br	0.75649400	2.65277500	-1.75042100
C	1.33179100	1.41181700	-0.36613800
Br	2.73966400	2.26415800	0.69501100
N	-2.26744800	0.11131500	2.29272400
C	-3.38946600	-0.06619900	1.43320500
C	-3.88619900	1.02924300	0.71628900
H	-3.41161000	1.99874400	0.82211000
C	-4.95727500	0.90571500	-0.15240700
H	-5.28702200	1.78850600	-0.68242300
C	-1.67384600	-1.10809300	2.82156200
H	-1.41492100	-1.78243500	2.00304100
H	-2.33825800	-1.63128200	3.52398600
H	-0.75535600	-0.84311900	3.34799900
C	-2.45406600	1.11155200	3.34513400
H	-2.82575300	2.04515600	2.92712100
H	-1.49063100	1.30820900	3.81933500
H	-3.16079200	0.75965100	4.10967900
N	-6.70113200	-0.45256200	-1.19817400
C	-5.59563300	-0.33505800	-0.35783100
C	-5.06985000	-1.43698000	0.33353300
H	-5.49238400	-2.42338200	0.20072000
C	-3.99962200	-1.30132200	1.21599300
H	-3.64842900	-2.18783900	1.72835000
C	-6.91466400	0.60134700	-2.17806400
H	-7.79113100	0.35289300	-2.77369300
H	-7.11181800	1.55506700	-1.68632600

H	-6.05547100	0.72809400	-2.85173800
C	-7.08025100	-1.79154300	-1.61885600
H	-7.94203400	-1.72167400	-2.27999300
H	-6.26936900	-2.31004700	-2.15002900
H	-7.37262400	-2.39745000	-0.75974000
C	2.03874500	0.20496400	-1.05064700
O	2.45478000	0.31313000	-2.15900600
C	2.20608800	-1.18164000	-0.33194500
Br	2.40665500	-1.15843800	1.59439300
Br	3.76922400	-2.06495200	-1.08067800
Br	0.60284800	-2.17994200	-0.83547100

R = CBrNO₂

Br	-0.85468100	0.75128800	0.15147000
Br	-3.56509300	0.11208400	-1.45825800
C	-2.47381600	-0.36134000	0.04756300
N	1.28933200	2.26289500	0.29826800
C	2.42301100	1.40235300	0.17456800
C	2.57473600	0.33816500	1.07114400
H	1.83171600	0.17677800	1.84420800
C	3.64181500	-0.53960100	0.98426200
H	3.69860100	-1.34566000	1.70259000
C	1.09967700	3.21633500	-0.78800600
H	1.06567100	2.69129100	-1.74340200
H	1.89423500	3.97411600	-0.82016600
H	0.14508800	3.72246400	-0.63796900
C	1.17509700	2.92300300	1.60258400
H	1.24244900	2.19396400	2.40773800
H	0.20270600	3.41473100	1.66520900
H	1.96450500	3.67439800	1.73595600
N	5.72204400	-1.25249300	-0.07995600
C	4.62488800	-0.40041500	-0.01751700
C	4.44726300	0.64607900	-0.93610600
H	5.14914400	0.79299400	-1.74513800
C	3.37668400	1.53161600	-0.83441000
H	3.30398200	2.32446200	-1.56781300
C	5.63832700	-2.51732300	0.63309300
H	6.55614600	-3.07649900	0.46211900
H	5.54984900	-2.35218800	1.70818600
H	4.78663600	-3.12889800	0.30425900
C	6.50147900	-1.25992000	-1.30701500
H	7.30721600	-1.98438300	-1.20568600
H	5.89795400	-1.52501500	-2.18647100
H	6.95590900	-0.28308700	-1.48182100
Br	-2.04405500	-2.23294500	0.03221900
N	-3.25055600	-0.02477100	1.36520100
O	-3.98026300	0.93052500	1.33151400
O	-2.99705300	-0.69397000	2.33130600

R = CBr₃CONH₂

Br	0.89258300	0.72469600	-0.16870300
Br	3.32026300	-0.16601500	1.71723300
C	2.54566400	-0.33265200	-0.06549100
N	-1.38697700	2.28634100	-0.32541800
C	-2.50479500	1.41480600	-0.19832900
C	-2.65943000	0.35674500	-1.10323300
H	-1.92535600	0.21085800	-1.88770400
C	-3.71493100	-0.53458500	-1.00949700
H	-3.77282900	-1.33338500	-1.73597600
C	-1.19014600	3.23035600	0.76366500
H	-1.14125900	2.69896200	1.71528200
H	-1.98636400	3.98710200	0.81621900
H	-0.23933500	3.74237000	0.60763700
C	-1.26788600	2.94538800	-1.62645000
H	-1.34623200	2.22028500	-2.43412500
H	-0.28864000	3.42351100	-1.69212200
H	-2.04579500	3.71015200	-1.76112700
N	-5.77143500	-1.28779700	0.07803000
C	-4.68320400	-0.42005100	0.00898800
C	-4.50318600	0.61745800	0.93606000
H	-5.19310800	0.74641600	1.75847600
C	-3.44588100	1.51891600	0.82640800
H	-3.37189500	2.30478400	1.56730600
C	-5.67234600	-2.54857700	-0.64055100
H	-6.57846600	-3.12460000	-0.46233000
H	-5.59817100	-2.37811200	-1.71578100
H	-4.80655900	-3.14663800	-0.32310900
C	-6.51746700	-1.32779400	1.32505100
H	-7.31721700	-2.06009800	1.23135100
H	-5.88770600	-1.60143500	2.18358400
H	-6.97888900	-0.36032800	1.53019600
Br	2.16200200	-2.19755300	-0.41667000
C	3.49060800	0.22546900	-1.17383300
O	3.52161700	-0.30287500	-2.26287000
N	4.16761200	1.33530900	-0.84824400
H	4.72133100	1.78039900	-1.56493600
H	4.13745800	1.75339900	0.06772800

R = CBr₄

Br	0.69058300	0.70972500	-0.06792600
Br	3.09645700	-0.14436100	1.84814900
Br	1.99362400	-2.19856100	-0.30985900
C	2.35361500	-0.32119100	0.05782700
Br	3.63862000	0.35420100	-1.23825300
N	-1.54326000	2.23186900	-0.24301800
C	-2.68201200	1.37837400	-0.16654100
C	-2.82756400	0.33823500	-1.09288200
H	-2.07128500	0.18938700	-1.85565900
C	-3.90424800	-0.53161700	-1.04805900
H	-3.95494100	-1.31826800	-1.78815100

C	-1.36824800	3.15447300	0.86973600
H	-1.35983200	2.60540500	1.81233500
H	-2.15467000	3.92164700	0.90765800
H	-0.40518700	3.65385700	0.75403500
C	-1.38329400	2.91768300	-1.52688900
H	-1.43554700	2.20821600	-2.35046200
H	-0.40287100	3.39701200	-1.55080100
H	-2.15749900	3.68426900	-1.66879400
N	-6.01197600	-1.25326500	-0.04179300
C	-4.90422700	-0.41023000	-0.06116600
C	-4.73366400	0.60974700	0.88771600
H	-5.44881900	0.74245000	1.68771000
C	-3.65434400	1.48872200	0.82742700
H	-3.58835900	2.26199800	1.58201900
C	-5.92582900	-2.49881400	-0.78781700
H	-6.85285600	-3.05252900	-0.65200500
H	-5.81341100	-2.30475400	-1.85576800
H	-5.08727800	-3.12870400	-0.45920800
C	-6.80141900	-1.29534600	1.17813000
H	-7.60843500	-2.01396000	1.04884400
H	-6.20556200	-1.58871100	2.05396300
H	-7.25433900	-0.32286700	1.37919800

R = CBr₃F

Br	1.10495600	0.84174900	-0.29655700
Br	3.68033300	-0.02214300	1.42042000
C	2.74048800	-0.20905800	-0.27009000
N	-1.20718500	2.34252100	-0.45046200
C	-2.27219000	1.42083900	-0.24701400
C	-2.39317000	0.31146200	-1.09396000
H	-1.67582600	0.16573300	-1.89357100
C	-3.39276800	-0.63127900	-0.92262800
H	-3.42513800	-1.46855800	-1.60602000
C	-1.03848900	3.35752400	0.57830600
H	-0.93313200	2.88571200	1.55631300
H	-1.87703500	4.06807400	0.61109500
H	-0.12491000	3.91441100	0.36492900
C	-1.15160100	2.93006300	-1.78975700
H	-1.20287800	2.15597300	-2.55293700
H	-0.20328200	3.45827300	-1.90411900
H	-1.97521100	3.63982600	-1.95065700
N	-5.36875600	-1.44387500	0.26743600
C	-4.33552500	-0.51950900	0.11964300
C	-4.18865000	0.57246200	0.98759600
H	-4.86001800	0.70438800	1.82465200
C	-3.18783200	1.52472100	0.80045700
H	-3.13806300	2.35006000	1.49903700
C	-5.20645400	-2.73836600	-0.37641200
H	-6.07102200	-3.35653300	-0.14158300
H	-5.16527700	-2.63021900	-1.46127800
H	-4.29877400	-3.26143600	-0.04366200

C	-6.07431500	-1.45837800	1.53849800
H	-6.83887900	-2.23248500	1.50644500
H	-5.40542300	-1.65739700	2.38813100
H	-6.57726000	-0.50561300	1.71120600
F	3.55310300	0.24900100	-1.23511300
Br	2.38125000	-2.08031100	-0.65125200

R = CBr₃H

Br	1.08872800	0.29569900	-0.04045900
Br	3.50646900	-1.08793000	1.54277800
C	2.66667700	-0.82226800	-0.18153000
Br	3.92512100	-0.12119600	-1.47531800
N	-1.15528300	2.00750800	0.24067600
C	-2.33667500	1.22687200	0.12563800
C	-2.57513500	0.49944600	-1.04796800
H	-1.85339800	0.53598400	-1.85623700
C	-3.69971500	-0.29442200	-1.19894400
H	-3.81954300	-0.83435200	-2.12799700
C	-0.89692300	2.58040600	1.55178100
H	-0.89734400	1.79594300	2.31032700
H	-1.63331900	3.34845600	1.83199700
H	0.09164800	3.04204400	1.53756600
C	-0.96573500	2.99755700	-0.81879600
H	-1.06973300	2.53891400	-1.80025600
H	0.04247800	3.40892000	-0.74116500
H	-1.69078800	3.81996800	-0.73480300
N	-5.81604300	-1.17479400	-0.33840600
C	-4.65840800	-0.41322200	-0.17171700
C	-4.39637900	0.28494400	1.01617800
H	-5.07441700	0.21676000	1.85548000
C	-3.27042500	1.09463400	1.15451500
H	-3.13592400	1.61789000	2.09227200
C	-5.80953600	-2.17890200	-1.39087500
H	-6.76535400	-2.69966500	-1.38442200
H	-5.69740000	-1.71314100	-2.37090800
H	-5.00565400	-2.91766300	-1.26226400
C	-6.55384400	-1.53242600	0.86236500
H	-7.41551100	-2.13464300	0.57983900
H	-5.94270500	-2.10340600	1.57624000
H	-6.92783600	-0.63942800	1.36559600
H	2.35956200	-1.79733300	-0.53609200

Table S4. Intermolecular C-Br...N and C-Br....I distances in the halogen-bonded complexes of R-Br electrophiles with TMPD or iodide in various media.

R-Br	M062X			ω B97XD			Exp ^a
	CH ₃ CN	CH ₂ Cl ₂	Gas-phase	CH ₃ CN	CH ₂ Cl ₂	Gas-phase	
[R-Br,TMPD]							
CBr ₃ NO ₂	2.627	2.637	2.704	2.702	2.705	2.749	2.744
CBr ₃ CN	2.648	2.654	2.708	2.709	2.713	2.753	-
CBr ₃ COCBr ₃	2.714	2.720	2.827	2.800	2.765	2.801	-
CBr ₄	2.709	2.714	2.752	2.755	2.760	2.795	2.776
CBr ₃ CONH ₂	2.768	2.772	2.802	2.807	2.812	2.856	2.722
CBr ₃ F	2.761	2.764	2.794	2.805	2.809	2.848	2.803
CBr ₃ H	2.836	2.836	2.842	2.902	2.896	2.902	-
[R-Br,I ⁻]							
CBr ₃ NO ₂	3.435	3.396	2.991	3.504	3.460	3.093	-
CBr ₃ CN	3.455	3.406	3.026	3.514	3.473	3.114	3.404
CBr ₃ COCBr ₃	3.477	3.532	3.111	3.581	3.492	3.110	-
CBr ₄	3.493	3.455	3.126	3.618	3.583	3.211	3.422
CBr ₃ CONH ₂	3.557	3.515	3.268	3.688	3.672	3.324	-
CBr ₃ F	3.541	3.512	3.222	3.654	3.618	3.280	3.434
CBr ₃ H	3.620	3.595	3.326	3.795	3.772	3.363	3.571

a) From X-ray crystallographic measurements.

Table S5. Absorption spectrum maxima and extinction coefficient resulted from TD-DFT computations of the [R-Br, D] complexes

R-Br	[R-Br, I]		[R-Br, TMPD]	
	λ , nm	ϵ , $10^3 M^{-1} cm^{-1}$	λ , nm	ϵ , $10^3 M^{-1} cm^{-1}$
CBr ₃ CN	284	13	320	8.5
CBr ₃ NO ₂	307	3.5	320	9
CBr ₃ COCBr ₃	309	3.2	341	1.9
CBr ₄	302	11.5	356	6.5
CBr ₃ CONH ₂	264	11	297	11
CBr ₃ F	275	13.5	320	6.5
CBr ₃ H	260	11	292	8

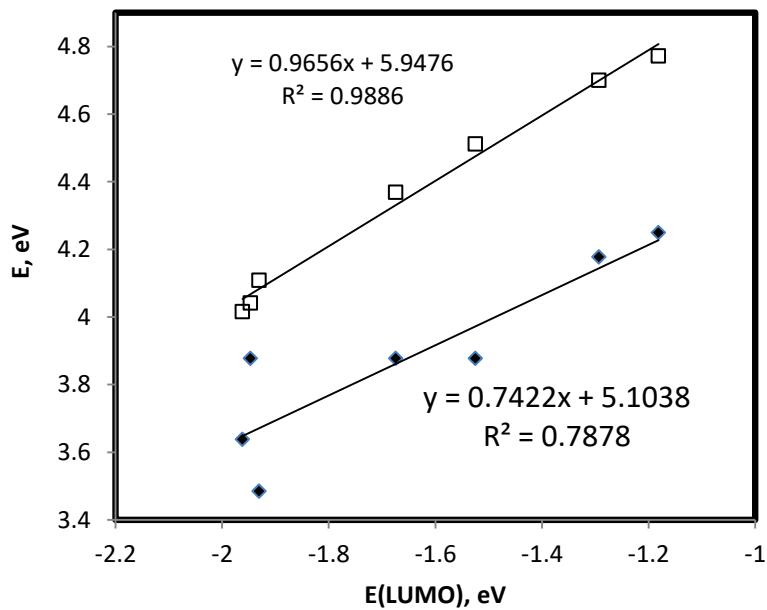


Figure S6. Mulliken correlation between calculated energies of the absorption bands maxima for [R-Br, D] complexes and energy of the LUMO of R-Br electrophiles (squares – complexes with TMPD, rhombics – complexes with iodide).

TableS6. Details of the computations of the rate constants for the inner-sphere ET reactions between R-Br electrophiles and TMPD (the data for the CBr_3NO_2 and CBr_4 electrophiles are reported in ref. 5).

R-Br	$\lambda_s(\text{IS})$, ^a kcal M ⁻¹	λ_{IS} , ^b kcal M ⁻¹	v, 10 ³ cm ⁻¹	Δv , 10 ³ cm ⁻¹	ϵ , 10 ³ M ⁻¹ cm ⁻¹	r _{DA} , Å	H _{ab} , ^c kcal M ⁻¹	ΔG^*_{IS} , ^d kcal M ⁻¹	k _{ET} , ^e s ⁻¹	K, ^f M ⁻¹	k ^{IS} , ^g M ⁻¹ s ⁻¹
CBr_3CN	19.3	70.0	27.7	5.9	3.0	7.109	6.80	15.3	5.9	1.0	11
$\text{CBr}_3\text{COBr}_3$	15.1	68.2	25.0	7.0	3.0	7.140	6.99	16.8	0.43	2.0	1.7
$\text{CBr}_3\text{CONH}_2$	18.6	72.7	31.9	4.0	2.5	7.230	5.39	19.3	6.0×10^{-3}	0.5	6.0×10^{-3}
CBr_3F	18.3	82.9	27.6	5.4	2.6	7.093	6.03	26.2	4.9×10^{-8}	0.3	2.9×10^{-8}
CBr_3H	19.7	77.9	31.3	5.5	3.0	7.336	6.73	25.3	2.4×10^{-7}	0.2	1×10^{-7}

a) Due to the close contact of the donor and acceptor in the precursor complex, Marcus (two-sphere) model is not suitable for the calculation of the solvation reorganization energy. As such, the solvation component of the reorganization energy was calculated 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:¹³

$$\lambda_s = G_s(\epsilon_{\infty 1}, \epsilon_{\infty 2}, \dots, \epsilon_{\infty N}, \Delta q) - G_s(\epsilon_{01}, \epsilon_{02}, \dots, \epsilon_{0N}, \Delta q)$$

where Δq is the point-charge representation of the full shift in the charge density of the donor/acceptor dyad upon electron transfer. Thus the limiting Marcus two-sphere model (TSM) for the reorganization energy λ_o in bimolecular ET (vide supra) is replaced by the general approach in which the more realistic dielectric continuum framework is based on the full solution of the Poisson equation for the solute cavity of a given size, shape, and charge distribution immersed in a solvent environment. 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). In other words, this equation represents the outer-shell reorganization energy λ_s as the free energy of the inertial solvent response to a solute with charge density Δq . This solvent inertial response involves solvent nuclear polarization modes and is calculated as the difference between the optical response and the full response given as the first and the second term, respectively. [Such a difference is also implicit in the classical Marcus two-sphere model in which the solvation energies, G_s and λ_o are quadratic functions of Δq_i when the solute is linearly coupled to the solvent medium.] The reorganization energies λ_s for [R-Br, TMPD] complexes were calculated using the Delphi Poisson solver. The Δq_i values were evaluated as the difference between corresponding ESP atomic charges calculated for the isolated neutral donor and acceptor molecules and their ion-radicals. These ESP charges (as fitted to reproduce the electrostatic potential due to the solute in its immediate environment), were obtained with the aid of the ChelpG option in B3LYP/6-311G(d) calculations. The geometries of the complexes were based on their X-ray crystal structures.

b) Calculated as described above for outer-sphere ET in Table S1, with λ_s replaced with $\lambda_s(\text{IS})$.

c) $H_{ab} = 0.0206(v_{CT} \Delta v_{1/2} \epsilon_{CT})^{1/2}/r_{DA}$.¹⁴ Note, that the absorption band of the [$\text{CBr}_3\text{COBr}_3$, TMPD] complex were overshadowed by the absorption of the separate reactants and products of the redox process. Therefore, they were obtained by extrapolation of the spectral properties of the other complexes.

d) ΔG^*_{IS} was evaluated via accurate expression derived by Sutin and Brunschwig for the unsymmetric adiabatic systems with non-negligible H_{ab} :

$$\Delta G^* = \lambda/4 + \Delta G^o/2 + (\Delta G^o)^2/(4/(\lambda - 2H_{ab})) - H_{ab} + H_{ab}^2/(\lambda + \Delta G^o) - H_{ab}^4 \Delta G^o / (\lambda + \Delta G_T)^2$$

e) Intra-molecular rate constant calculated, as described earlier for the π -bonded complexes, as $k_{ET} = \kappa_{el} v_n \exp(-\Delta G^*/RT)$, where $\kappa_{el} v_n \sim 10^{12} \text{ s}^{-1}$.¹⁵

f) Formation constant of the [R-Br, TMPD] complex .

g) 2nd-order rate constant calculated as $k^{\text{IS}} = 2Kk_{ET}$ (which is valid for the reactions that are significantly slower than the diffusion rates) and term 2 is related to the fast oxidation of the second TMPD molecule by radical R[•], resulting from the reductive cleavage of the C-Br bond in the R-Br electrophile.

TableS7. Details of the computations of the H_{ab} values for complexes of R-Br electrophiles with I^- anions.

R-Br	$\nu, 10^3$ cm^{-1}	$\Delta\nu, 10^3$ cm^{-1}	$\varepsilon, 10^3$ $\text{M}^{-1}\text{cm}^{-1}$	$r_{DA}, \text{\AA}$	$H_{ab}, ^c$ kcal M^{-1}
CBr_3CN	30.8	3.6	10	5.413	11.4
$\text{CBr}_3\text{NO}_2^a$	27.8	8.0	3.0	5.400	8.9
$\text{CBr}_3\text{COCB}_{3}^b$	27.8	7.0	4.0	5.445	9.5
$\text{CBr}_3\text{CONH}_2$	33.7	5.6	5.0	5.511	10.4
CBr_3F	32.1	4.5	12	5.483	14.1
CBr_3H	34.2	4.5	11	5.555	13.8

a) From ref 25; b) Note, that the absorption band of the $[\text{CBr}_3\text{COCB}_{3}, \text{I}^-]$ complex were overshadowed by the absorption of the separate reactants and products of the redox process. Therefore, the spectral properties were estimated based on the calculated spectra taking into account the correction due to the difference between the experimental and calculated spectral properties of the other complexes.

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