

To the 300th Anniversary of the founding of St. Petersburg University

Computational Study on the Route of Cooperative Organocatalysis Utilizing Thiourea and Halogen Bond Donor Mixture

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Abstract—A computational analysis of possible routes of cooperative catalysis involving hydrogen bond donating thiourea and halogen bond donating organocatalysts was carried out. For the model systems involving thiourea and 2-iodoimidazolium or iodonium salt derivatives, the previously suggested route including sequential electrophilic activation of a reaction electrophile via XB-activated HB donor was ruled out.

Keywords: organocatalysis, cooperative effects, thiourea, hypervalent compounds, iodine

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INTRODUCTION

Noncovalent organocatalysts providing formation of a hydrogen bonding (HB) [1–7] between a catalyst and reaction substrates, in particular, (thio)ureas [8–15] and squaramides [14–18], have attracted great attention over the last two decades since they typically have low sensitivity to moisture and negligible sensitivity to air under the reaction conditions while demonstrating a lower environmental footprint than metal-complex catalysts. Recently, the field of homogeneous organocatalysis has been significantly expanded due to the intake of catalytically active σ -hole carriers, among which halogen bond (XB) [19–21] donors featuring iodine-based σ -hole carriers exhibited a higher catalytic activity than that of well-proven (thio)urea-based organocatalysts (Fig. 1, **A**) [22]. Thus, cationic iodine(I)-containing species, in particular, iodoazoliums **B** [22–28], effectively catalyze many organic transformations, whereas cationic hypervalent iodine(III) derivatives **C** (i. e., diaryliodonium salts [29–36]) exhibit even greater activity than the iodine(I) species.

Recently Takagi et al. have reported an experimental observation of synergetic catalytic effect for the mixture of Schreiner's thiourea (**A**) and 2-iodoimidazolium salt

(**B**) in the reaction of cationic polymerization of isobutyl vinyl ether [22]. The authors [22] suggested that this effect might be realized via ligation of the thiourea to the XB donor via the S atom (**D**), which results in the increase of electrophilicity of the thiourea's H atoms, thus enhancing the total catalytic activity of the system.

Taking into consideration the fact that cooperative catalysis is an actual and growing trend in homogeneous catalysis [7, 37–39], which is almost unexplored for the XB donating species, and being inspired by the experimentally observed synergetic catalytic effect involving the XB donors, in this work we decided to carry out a computational study on the estimation of the catalytic potential of a mixture of well-proven HB and XB donating organocatalysts.

RESULTS AND DISCUSSION

Selection of the model reaction and catalysts. As a model reaction, hydrolysis of methyl chloride has been chosen, since this simple reaction includes the elimination of an anionic species and, thus, is similar to the reaction studied by Takagi and co-workers [22]. In addition, this reaction has been studied by us previously for many other noncovalent organocatalysts (Fig. 2)

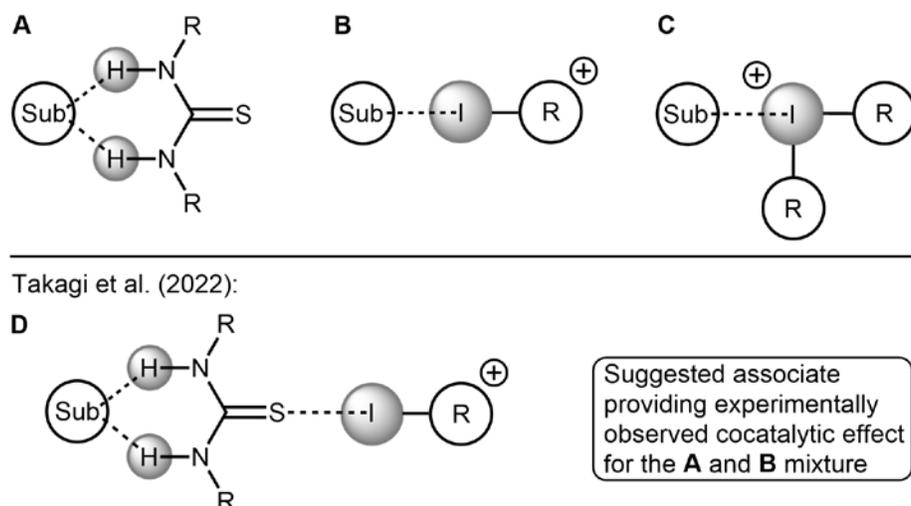


Fig. 1. Representative examples of HB and XB donating organocatalysts, their modes of association with reaction substrates, and the suggested [22] associate providing synergistic catalytic effect.

[28, 40, 41]. As model catalytic species, 2-iodoimidazolium **1** and dibenziodolium **2** were chosen as iodine(I) and iodine(III)-based XB donating representatives, whereas *N,N*-dimethyl thiourea **3** was selected as the HB donor.

The optimized by method 1 (see Computational details) structures of associates of **1–3** with the transition state (TS) exhibited nearly perpendicular arrangement of the organocatalytic species and TS (angle X–C–I = 87°–98°; where X is C–I or N–H atoms). The obtained results have indicated that dibenziodolium cation **2** exhibits higher stabilizing effect on the transition state than 2-iodoimidazolium **1** and thiourea **3** derivatives (145 vs 157 kJ/mol and 152 kJ/mol, respectively, Fig. 2). For the triple associates **1·3·TS** and **2·3·TS**, no synergistic catalytic effect was observed, since the Gibbs free energy of activation of such associates turned out to be higher by ca. 30 kJ/mol than that for the double associates **1·TS–3·TS** (174–185 vs 145–157 kJ/mol, respectively). Considering that increase in the energy of activation for **1·3·TS** and **2·3·TS** might be caused by negative entropy of association of the species **1** or **2** with **3·TS**, we further decided to estimate the possibility of electrophilic activation of thiourea moiety via its intramolecular ligation to the XB-donor's σ -hole, since such type of process is expected to have less entropy loss than intermolecular binding.

Study of bifunctional XB-HB donating species. To further study the possibility of realization of a synergistic effect during the catalysis, we decided to operate with thiourea-functionalized benziodolium salts **5–7** featuring

both the XB and HB donating functionalities in one species (Fig. 3). In this case, methylbenziodolium cation **4** was chosen as a referent XB donor. Although these complex species are yet unknown, the involvement of both types of catalytically active centers in one molecule should minimize the influence of entropy factor during the calculations, which is important for the study of “clear” electrophilic activation of the HB donating moiety by the ligation to the σ -hole. Open-chain species **5–7** featuring non-interacting XB and HB moieties, as well as their cyclic forms **5*–7*** including interacting XB and HB donating groups, can form two types of associates with TS, namely thiourea-bound and iodonium-bound species (**5HB–7HB** and **5HB*–7HB***, as well as **5XB–7XB** and **5XB*–7XB***, respectively, Fig. 3). The obtained results indicate that the cyclic form of cations (**5*–7***) stabilized by intramolecular XB between the I and S atoms is more stable than the corresponding open-chain form (**5–7**) by 4–12 kJ/mol in ΔG scale, which lays in expected energy interval [42].

The QTAIM analysis [43] of the catalyst···transition state associates demonstrated the presence of appropriate bond critical points (BCPs) for the optimized model structures (Table 1). The low magnitude of the electron density, positive values of the Laplacian of electron density, and near-zero energy density in these BCPs are typical for non-covalent interactions. The balance between the Lagrangian kinetic energy $G(r)$ and potential energy density $V(r)$ at the BCPs reveals the nature of these interactions; if the ratio $-G(r)/V(r) > 1$, the nature of the

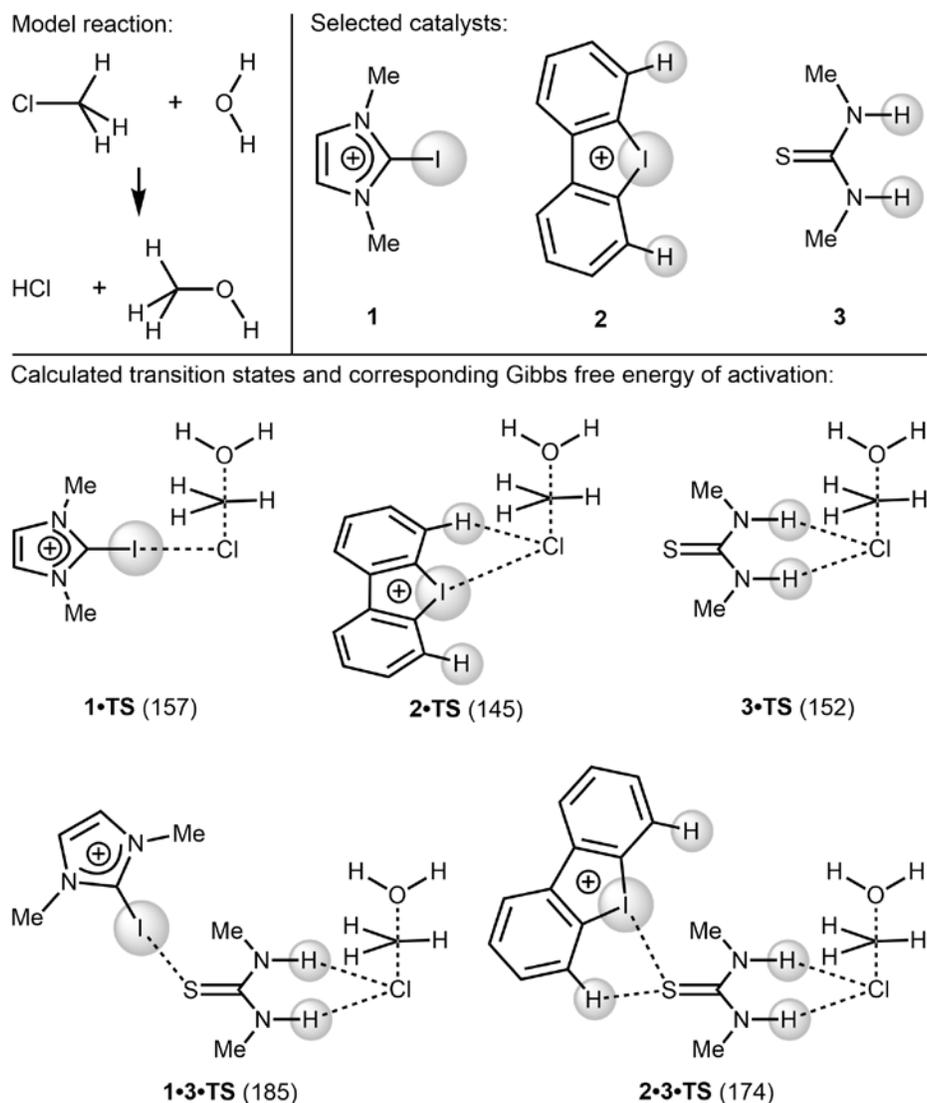


Fig. 2. Model reaction, selected catalysts 1–3, calculated transition state structures and the corresponding Gibbs free energy of activation in kJ/mol given in parentheses.

interaction is purely noncovalent, whereas $-G(r)/V(r) < 1$ indicates some covalent component [44]. Based on this criterion, we can conclude that the covalent contribution is almost absent in the studied interatomic interactions, although minor increase in covalent contribution to the bonding, as well as transition state-to-catalyst charge transfer values are observed for cyclic forms **5HB***–**7HB*** compared to their acyclic forms **5HB**–**7HB**, respectively.

Cyclic species **5***–**7*** include interacting XB and HB donating groups, which might be able to affect the catalytic activity of each other. Considering that ligation of the thiourea moiety to one of the iodine σ -hole should

provide electrophilic activation of the former, one may expect the increase of the catalytic activity of the HB donating functionality when it binds the **TS**. And vice versa, occupation of one of the σ -holes by the electron-donating species should result in the decrease of the catalytic activity of the iodonium moiety [28, 42]. For the iodine atom, this suggestion is coherent with our estimation of the values of maximum electrostatic potential [$V_s(\text{max})$]: 615–672 kJ/mol on the σ -holes of the I atom in **5**–**7** vs 525–549 kJ/mol on that of **5***–**7***, whereas $V_s(\text{max})$ values on the amide H atoms lay in similar intervals: 527–650 kJ/mol for **5**–**7** vs 568–622 kJ/mol for **5***–**7***. The comparison with the primary

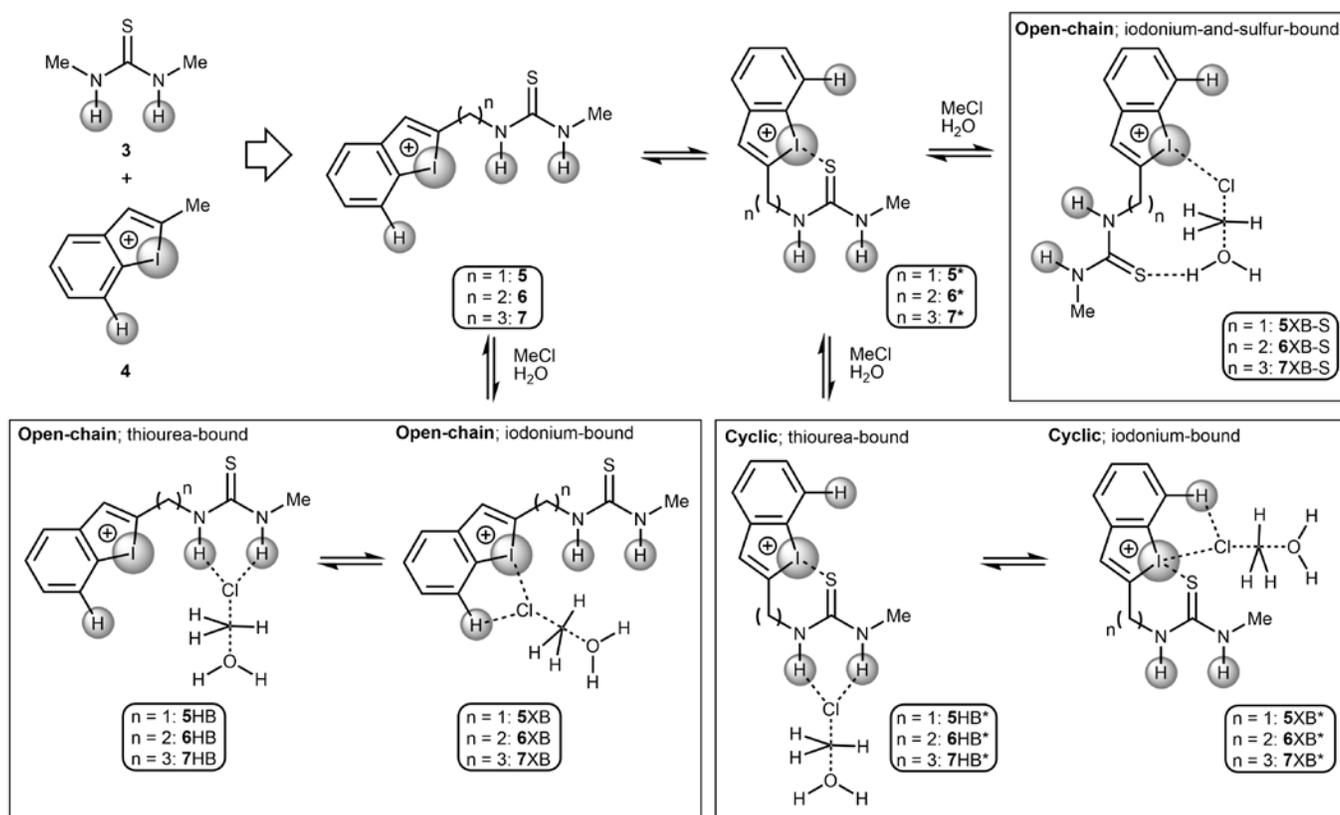


Fig. 3. The calculated structures of bifunctional catalyst-transition state associates.

species 4 (619–633 kJ/mol on the iodine σ -holes) and 3 (332 kJ/mol on the amide H atoms) indicates a slight reduction of the $V_s(\text{max})$ value for the I atom for the cyclic forms 5*–7* and its significant increase on the amide H atoms irrespectively to configuration of the bifunctional species. Most likely, the latter observation should be explained in terms of overlap of electrostatic fields from the cationic iodonium species and the thiourea moiety. Thus, the 2-fold increase in the electrostatic potential on the amide H atoms is not provided by the potential located on these atoms but the long-ranging external field of the cationic iodonium species. Binding of the transition state by the HBs results in higher charge transfer values than ligation to the iodine σ -hole (61–101 vs 52–56 kJ/mol, respectively, Table 2), which may cause higher stabilization of the transition state by the ligation to thiourea moiety compared to binding to the iodine center. In addition, for associates involving cyclic form of the catalysts 5HB*–7HB* charge transfer values are higher than the corresponding values for the associates involving open-chain species (5HB–7HB), which also can indirectly

evidence that ligation of the thiourea group to the iodine σ -hole can increase electrophilicity of the former.

Study of the Gibbs free energies of activation.

The calculations carried out via default method 1 (see Experimental) indicate that although the Gibbs free energy of activation for the thiourea-bound associates 5HB*–7HB* is lower than that for 5HB–7HB (140–141 kJ/mol vs 143–147 kJ/mol, respectively, Fig. 3 and Table 2), the obtained values are similar within accuracy of the computational method. Moreover, for the iodonium-bound associates 5XB–7XB and 5XB*–7XB*, the activation energy turned out to lay in the same energy intervals irrespectively to the substrate configuration (143–147 and 142–154 kJ/mol, respectively) and these values are similar to that of primary iodonium salt 4 (141 kJ/mol). Pre-association of the substrates does not affect the activation barriers because it has the positive Gibbs free energy values (26–37 kJ/mol for 5–7 and 5*–7*) and thus does not lead the systems to the local energy minimum.

Table 1. Catalyst-transition state binding parameters^a

Model structure	Distance, Å	% of Bondi's vdW sum	-G(r)/V(r)	TS to catalyst charge transfer, kJ/mol
	N-H...Cl			
5HB	2.484	84	1.10	61
	2.395	81	1.00	
5HB*	2.326	79	0.93	99
	2.339	79	0.93	
6HB	2.367	80	1.00	97
	2.332	79	1.00	
6HB*	2.341	79	0.93	99
	2.341	79	0.93	
7HB	2.370	80	1.00	86
	2.374	80	1.00	
7HB*	2.363	80	1.00	101
	2.310	78	0.94	
		I...Cl		
5XB	3.179	85	1.08	52
5XB*	3.182	85	1.00	56
6XB	3.164	85	1.08	56
6XB*	3.172	85	1.08	55
7XB	3.172	85	1.08	56
7XB*	3.192	86	1.00	55
		I...S		
5HB*	3.199	85	1.09	
5XB*	3.246	86	1.10	
6HB*	3.270	87	1.11	
6XB*	3.341	88	1.11	
7HB*	2.280	60	1.00	
7XB*	3.340	88	1.13	

^aThe lengths of N-H...Cl, I...Cl, and I...S noncovalent contacts, ratio between the Lagrangian kinetic energy G(r) and potential energy density V(r) (a. u.) at the bond critical points (BCPs) from the QTAIM analysis of the N-H...Cl, I...Cl, and I...S noncovalent contacts in the model species, and calculated by natural bond orbitals (NBO) analysis charge transfer from transition state to catalyst.

To estimate the influence of the computational methods on the quantitative and qualitative features of the obtained results, we additionally carried out the calculations of the Gibbs free energy of activation via two other methods (see Computational details for description). Method 2 performed for the gas phase indicates that the cyclic form of cations (**5***-**7***) stabilized by intramolecular XB between the I and S atoms is more stable than the corresponding open-chain form (**5**-**7**) by 30-37 kJ/mol in ΔG scale, whereas method 3 considering the implicit form of the solvent leads to significantly lower energy gap (1-9 kJ/mol in ΔG scale), which is closer to that expected for more complex models involving ligated solvent molecules taken in explicit form [42]. Taking into account the inaccuracy in the relative energy between

two forms of the catalysts in real systems, further on they are discussed separately. The obtained results indicated that the binding of **5**-**7** and **5***-**7*** with methyl chloride is energetically unfavorable and lays in the range of 3-19 kJ/mol (method 2) or 27-46 kJ/mol (method 3) in ΔG scale. Considering these observations, similarly with method 1, pre-association of the substrates can be excluded from the consideration of an activation barrier because it does not lead the system to the local energy minimum affecting the total energy of activation of the reaction.

(i) *Open-chain species 5-7.* The calculations performed via method 2 indicate that the Gibbs free energy of activation for the thiourea-bound associates **5HB** and **6HB** is very similar to that of **3-TS** (Table 2),

Table 2. Relative Gibbs free energies (kJ/mol) for all model associates obtained by different computational methods^a

Associate	Method 1	Method 2	Method 3
3·TS	152	158	144
5HB	146	152	73
6HB	143	159	73
7HB	143	173	69
5HB*	140	158	71
6HB*	141	166	72
7HB*	140	172	72
4·TS	141	144	149
5XB	147	158	76
6XB	143	151	76
7XB	144	157	78
5XB*	142	162	78
6XB*	154	172	83
7XB*	142	171	73
5XB-S	155	166	69
6XB-S	150	171	54
7XB-S	126	146	46

^a Method 1: M06-2X/SDD level of theory, SMD continuum solvation model for water solvent. Method 2: gas phase calculations at the M06-2X/MWB46 (iodine atoms) and 6-31G* (other atoms) level of theory. Method 3: M06-2X/CEP-121G level of theory, SMD continuum solvation model for water solvent.

whereas the energy of 7HB is remarkably higher (Table 2). For the iodonium-bound associates 5XB–7XB, the activation energy turned out to be slightly higher but comparable with that of 4·TS (Table 2). The obtained results gave expectable values of the activation energy, since non-interacting XB and HB donating functionalities in 5–7 provide similar stabilization of TS compared with that of separately taken XB and HB donating species 3 and 4, respectively. Method 3, on the one hand, give inadequately large energy gap between the activation energy for the reaction involving primary species 3 and 4 (144 kJ/mol for 3·TS and 149 kJ/mol for 4·TS) and that catalyzed by open-chain species 5–7 (76–78 kJ/mol for 5XB–7XB and 69–73 kJ/mol for 5HB–7HB). On the other hand, this method gives narrower ranges of the activation energy within series of the XB-bound and HB-bound associates and these results seems more reliable considering structural similarity of the organocatalytic species 5, 6, and 7. In addition, this method indicates that the activation energy for the thiourea-bound transition states should be lower than that of the iodonium-bound species, which correlates with the transition state-to-catalyst charge transfer values (Table 1).

(ii) *Cyclic species 5*–7**. The obtained via method 2 results clearly indicate a remarkably lower stabilization of TS then it is ligated to the I atom of cyclic 5*–7* species compared with non-functionalized benziodolium cation 4 (162–172 kJ/mol for 5XB*–7XB* vs 144 kJ/mol for 4·TS, respectively). But then TS is ligated to the amide H atoms of the thiourea moiety in cyclic 5*–7*, it unexpectedly does not provide a higher stabilization than that of *N,N'*-dimethylthiourea 3 (158–172 kJ/mol for 5HB*–7HB* vs 158 kJ/mol for 3·TS, respectively). Although method 3 does not allow credible comparison of the activation energy between 5HB*–7HB* with 3·TS and 5XB*–7XB* with 4·TS, similarly with open-chain species 5–7, it indicates that ligation of the transition state to the thiourea moiety is slightly more favorable than coordination to the iodine atom (71–72 kJ/mol for 5HB*–7HB* vs 74–83 kJ/mol for 5XB*–7XB*).

The absence of the increase of catalytic activity might also arise from different binding modes of TS to the thiourea moiety in 3 and 5*–7*, namely parallel arrangement between 3 and TS with two Cl···H and one H···S bonds and linear arrangement between 5*–7* and TS without the H···S bond. The obtained via method 2 values indicated a higher stabilization of TS by 7XB-S compared to 3·TS and 5HB*–7HB* (146 vs 158–172 kJ/mol, respectively) but even in this case the catalytic activity was not higher than that of the primary iodolium cation 4 (146 vs 144 kJ/mol). Thus, method 2 indicated that the H···S bonding does not have a crucial role in the stabilization of TS, which somehow contradicts with general principles of physical organic chemistry according to which donation of electronic density on the nucleophile should increase its nucleophilicity. From this point of view, the results obtained by method 3 seem more plausible, since they indicate gradual increase in the stabilization energy of the transition state from with 5XB-S to 7XB-S (from 69 to 46 kJ/mol) relatively to 5XB–7XB (73–83 kJ/mol).

(iii) *Effect of ligation of thiourea to the iodine σ -hole.*

Although all the applied computational methods gave quantitatively different results, they agree with each other at qualitative level. Considering that the key factor determining the possibility of the synergistic catalytic effect between the XB and HB donors via the suggested electrophilic activation of the latter is reduction of the Gibbs free energy of activation after coordination of the thiourea to the iodine σ -hole, analysis of the data obtained by any of methods 1–3 does not confirm the feasibility

of such cooperative catalytic effect. Taking into account that no synergetic catalytic effect has been determined for the intramolecular binding of the catalytic centers in **5–7**, realization of this effect via intermolecular cooperation of two catalytically active species seems even less possible due to the entropy penalty, which has been confirmed by the results represented on Fig. 2. Nevertheless, the obtained results indicate that the catalytic activity of iodonium salts can be increased by involving of their structure auxiliary groups able to bind a transition state jointly with halogen bonding (7XB-S, Fig. 3).

In summary, in this note we have presented the computational study which indicates that cooperative catalysis by XB and HB donors is unlikely proceed via a sequential activation of the electrophile by the XB-donor-activated HB donor. Several indirect routes leading to the increased catalytic activity are discussible for these systems. On the one hand, the thiourea can stabilize the catalytically active XB donor (potentially unstable under the reaction conditions), thus prolonging its action during the reaction. This route has been briefly mentioned in reference [22], recently observed by us [45] for the case of silver(I) triflate–iodolium triflate mixture, and suggested [46] for iodopyridinium-based XB-donating catalysts. On the other hand, the HB donor can bind the counter-ion of the XB donating species leading to a higher concentration of the dissociated (and catalytically active) form of the latter.

We sincerely hope that this work will stimulate further development of the field of cooperative organocatalysis involving σ -hole carriers, which certainly deserves a deeper study.

EXPERIMENTAL

Computational details. The preliminary conformational search was carried out in Avogadro program (<https://avogadro.cc/>) at the UFF level of theory, we manually checked various possible conformations and chosen the most energetically profitable ones for future DFT calculations. Also, we have applied CREST automated algorithm (release 2.12) [47] at the GFN-FF level of theory [48] for conformational search and found that generated structures are very close to the optimized geometries of model systems obtained by DFT calculations. The full geometry optimization of all model structures was carried out using DFT calculations by three approaches: M06-2X/SDD level of theory, SMD continuum solvation model [49] for water solvent

(method 1, default approach unless otherwise stated), gas phase calculations at the M06-2X/MWB46 (iodine atoms [50]) and 6-31G* (other atoms) level of theory (method 2), M06-2X/CEP-121G [51–53] level of theory, SMD continuum solvation model for water solvent (method 3) with the help of the Gaussian-09 Revision C.01 program package [54, 55]. The selection of this moderate level of theory for computational studies is due to limited computational resources at our disposal. We have chosen this level of theory also according to our previous experience and its successful performance in a number of halogen and chalcogen bond studies in various similar supramolecular systems and organocatalysis processes [40, 42]. No symmetry restrictions were applied during the geometry optimization procedure. We used default integration grid and SCF convergence criteria. The Hessian matrices were calculated analytically for all optimized model structures to prove the location of the correct minimum or saddle point (transition state) on the potential energy surface (no imaginary frequencies or only one imaginary frequency corresponding to transition state, respectively). The calculation of molecular surface electrostatic potentials was performed using the Multiwfn program (version 3.7) [56].

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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