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Elevated Reaction Order of 1,3,5-tri-*tert*-butylbenzene Bromination as Evidence of a Clustered Polybromide Transition State: a Combined Kinetic and Computational Stricty Online

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Abstract

Kinetics and mechanism of concurrent bromo-de-protonation and bromo-de-*tert*-butylation of 1,3,5-tri-*tert*-butylbenzene at different bromine concentrations were studied experimentally and theoretically. Both reactions have high order in bromine (experimental kinetic orders ~5 and ~7, respectively). According to quantum chemical DFT calculations, such high reaction orders are caused by participation of clustered polybromide anions Br_{2n-1} in transition states. Bromo-de-*tert*-butylation has a higher order due to its bigger reaction center demanding clusters of extended size. A significant primary deuterium kinetic isotope effect (KIE) for bromo-de-protonation is measured indicating proton removal is rate limiting, as confirmed by computed DFT models. The latter predict a larger value for the KIE than measured and possible explanations for this are discussed.

Introduction

The classical electrophilic halogenation of aromatics is still a popular subject of research in theoretical organic chemistry.¹ It has been shown in our previous paper² that the noncatalytic bromination of benzene requires high (5-14 M) concentrations of bromine to proceed at ambient temperature. An intriguing feature of the reaction is a very high (\sim 5) kinetic order in bromine. Such a high order³ was explained by the specific structure of transition states through which the bromination proceeds. According to DFT calculations, the reaction is concerted (S_EAr), with transition states resembling ionic pairs composed of arenium ions $C_6H_6Br^+$ and cluster polybromide anions⁴ Br_{2n-1}⁻. The calculated free energy barrier decreases sharply as the number of bromine molecules forming a transition state cluster increases: the predicted rate ratio is 1:10⁶:10¹⁴:10¹⁷ for one, two, three and four molecules, respectively. A big cluster simultaneously plays three different roles in the reaction pathway: as a Br⁺ donor, as a proton acceptor, and as a stabilizing arm forming weak dispersion interactions with the arenium ion (Figure 1). To assemble such a transition state for a reaction which incorporates a further increase in volume via e.g. a sterically hindered reaction center, a bromine cluster of even larger size may be required. Bromination of 1,3,5-tri-*tert*-butylbenzene (I, Scheme 1) provides a suitable model for verification of this hypothesis. The compound is known to undergo two reactions with bromine at comparable rates: electrophilic substitution of a hydrogen atom (bromo-de-protonation) or of a tert-butyl substituent (bromo-de-tert-butylation).^{5,6} The relevant reaction centers (H–C–Br and t-Bu–C–Br, respectively) are very different in volume. If the cluster hypothesis is correct, bromo-de-tertbutylation transition state must demand clusters of a larger size which will lead to increased order in bromine compared to that of bromo-de-protonation.



Results and Discussion

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As the kinetics were studied at a large excess of bromine, all involved bromination reactions can be considered as pseudo first order ones. It was explicitly verified that carrying out the reactions in the dark and in the presence of a bromine radical trap, *t*-BuONO, does not influence the reaction rates.⁸ In agreement with previous studies,^{5,6} the intermediate bromination products II and III also react with Br₂ forming the same final product, dibromide IV (Scheme 1). The observed concentration decay of the initial compound I is not mono-exponential (Figure 2) which clearly points to the reversibility of the first stage. An explicit experiment has shown that equimolar mixture of II and *t*-BuBr does not transform back into I, therefore by exclusion the reversible process must be I + Br₂ = III + HBr. Accounting for its reversibility allowed improved approximation accuracy for the whole kinetics scheme by more than an order of magnitude. Neither reaction of the second stage is reversible: after keeping the mixture for a long time, the NMR signals of all the compounds I, II, and III disappear. Thus, the kinetic system shown in Scheme 1 is inferred as complete.

Scheme 1. Bromination of 1,3,5-tri-tert-butylbenzene



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Accounting for HBr concentration changes in the numeric solution of the kinetics equations system was problematic, as it takes part in the reactions involved in the scheme in non-stoichiometric quantities. Additional HBr is formed due to the subsequent bromination of *tert*-butyl bromide (Scheme 2)⁹ in the process of bromo-de-*tert*-butylation of I and III. Moreover, up to 20% of HBr is evaporated from the solution and produces an excess pressure in the ~1.5 mL gas volume between the liquid phase and the sealed NMR tube cap. Knowing the exact HBr concentration is important for the evaluation of the bimolecular reaction III + HBr \rightarrow I + Br₂. HBr was therefore treated as an external agent, with the actual concentration directly determined from NMR spectra and used in the kinetics equations system as a predefined value.

Scheme 2. Bromination of *tert*-butyl bromide



The experimental kinetic data were evaluated by numerical integration of the differential equations followed by a nonlinear least square fitting of the involved rate constants. The complete processing algorithm was implemented in the form of SciLab¹⁰ script. Representative kinetics are shown in Figure 3, while the fitted values of rate constants are given in Table 1. From the data of Table 1 it follows that *tert*-butyl groups exert a significant steric effect on the rates of reaction. Thus, substitution of a *tert*-butyl group with a bromine atom does not cause a strong deceleration of the bromo-de protonation reaction $(k_{13}/k_{24}\approx 2)$. Usually the deactivating effect of bromine is much greater (for example, $k_{PhH}/k_{PhBr}=11$).¹¹ Surprisingly, the rate of bromo-de-*tert*-butylation reaction III \rightarrow IV is higher than that of I \rightarrow II $(k_{12}/k_{34}\approx 0.1)$ in spite of the deactivating effect of bromine in compound III.

Figure 3. Representative kinetics of bromination of 1,3,5-tri-*tert*-butylbenzene (Table 1, run 2, experimental points are denoted by circles, fitted curves by solid lines). For other kinetics, see the supporting information. View Article Online DOI: 10.1039/C9OB00607A



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Table 1. Experimental conditions and fitted parameters (pseudo first order rate constants and equilibrium constants) for reactions of Scheme 1.

Run	$[I]_0$	$[Br_2]$	Т	k_{13} ,	<i>k</i> ₃₄ ,	$k_{12},$	$k_{24},$	K, ^a ΔG_0^a	
	mol/L	mol/L	Κ	$\times 10^{-5} \text{ s}^{-1}$	$\times 10^{-5} \text{ s}^{-1}$	$\times 10^{-5} \text{ s}^{-1}$	$\times 10^{-5} \ \mathrm{s}^{-1}$	$\times 10^{-3}$ kcal/mc	ol
1	0.16	3.9	296	5.16 ± 0.06	$4.34{\pm}0.09$	0.30 ± 0.01	2.1±0.3	2.4±0.3 3.55±0.0)8
2	0.17	5.8	298	27.2 ± 0.7	49±2	4.1 ± 0.2	15 ± 2	2.2±0.3 3.61±0.0)8
3	0.17	7.8	301	111 ± 6	380±30	36 ± 2	69 ± 4	2.7±0.4 3.53±0.1	10
4	0.065	11.6	298	_b	_b	650±110	500 ± 20	2.4 °	
5	0.17	5.8	273	9.2±0.4	28 ± 2	1.55 ± 0.06	6.2 ± 0.4	1.1±0.2 3.72±0.0)8

^a K (see considerations below) is the equilibrium constant for reaction I + Br₂ = III + HBr, ΔG_0 is corresponding free Gibbs energy. ^b Undefined, as the parameter deviation is too large (above 100%). ^c At fitting this value was fixed.

Deviations in the fitted values of rate constant were estimated by the two methods: bootstrap Monte Carlo¹² and parameter variation to constant chi-square¹³ (confidence limit 3σ). Both methods give similar results, while the parameter variation method seems to be more robust for large deviations. The error probability distribution analysis indicates considerable mutual correlation (Figure 4a) between the variable parameters k_{13} and k_{31} corresponding to the reversible reaction I+Br₂ = III+HBr. This would prevent accurate determination of the equilibrium constant K = k_{13}/k_{31} . Therefore, K and k_{13} were used as actual fitted parameters while k_{31} was derived from them. This simple change of variables allowed compensation for the correlation influence (Fig. 4b), reducing the deviation in K by a factor of almost two.

Figure 4. Correlation of the optimized parameters by bootstrap method (Table 1, run 2, 200 synthetic data sets).



In the case of high concentrations of bromine (Table 1, run 4), the initial compound I is exhausted too rapidly (96% in 5 min.) and hence hiding from NMR observation the most informative region of the reaction for least squares fitting. To obtain numerically stable results in this special case a fixed value of the equilibrium constant K was used, as this parameter was found to have very similar values in all other experiments. Nevertheless, the rate constants k_{13} and k_{34} could still be determined only with a huge uncertainty and their values are not included in Table 1 as deviations exceed 100%.

The order of the reaction in bromine was determined by a differential method¹⁴ using the kinetic eqs. (1) and (2) relating a pseudo first order reaction to a formal reaction of order n+1. [Ar] stands for the concentration of any of compounds I, II, or III, and k stands for any of constants k_{12} , k_{13} , k_{24} , or k_{34} .

 $\begin{aligned} -d[Ar]/dt &= k [Ar] & (1) \\ -d[Ar]/dt &= k_{n+1} [Ar] [Br_2]^n & (2) \\ \log k &= n \log [Br_2] + \log k_{n+1} & (3) \end{aligned}$

After feeding the kinetic data into the eq. (3), the following orders in bromine have been derived (Figure 5); for reaction I \rightarrow III 4.4±0.3, for II \rightarrow IV 5.0±0.1, for I \rightarrow II 7.0±0.2 and for III \rightarrow IV 6.4±0.4.

Figure 5. Determination of the reaction orders in bromine.



Kinetic Isotope Effect

The presence of bulky *tert*-butyl groups in compound I may retard proton removal from the arenium intermediate, inducing a primary H/D kinetic isotope effect (KIE).¹⁵ To determine the KIE for the reaction I \rightarrow III, compounds I and I-d₃ were used.



Unfortunately, KIE determination by the common method of carrying out competitive reactions in a mixture of natural abundance and enriched reagents was not viable. The source of the problem is proton exchange with HBr, observed in broadening of NMR signals of aromatic protons of compound I as well as in the corresponding exchange cross peaks in 2D EXSY spectra. Comparison of ¹H NMR signal broadening of I in bromine and in mixtures of CF₃COOH and TfOH¹⁶ allowed estimating the rather high HBr acidity (Figure 6). The proton exchange rate increases sharply with increase in bromine concentration (the reaction order about 5, nearly the same as for bromo-de-protonation). This behavior can be explained by the Lewis acidity of bromine.¹⁷

Figure 6. ¹H NMR signal of compound I in the presence of acids. $[I] = [HBr] = [CF_3COOH+TfOH] = 0.1 mol/L, CD_2Cl_2: 0.1 mL. (Br_2 + CCl_4), mL: (0.1+0.28) (a), (0.15+0.23) (b), (0.2+0.18) (c), (0+0.38) (d,e); wt% TfOH in CF_3COOH: 35 (d), 21 (e).$



As proton exchange between I and HBr proceeds much faster than bromination, any H/D distribution (possibly distorted due to KIE) between I and I-d₃ in their mixture would be immediately averaged. Therefore, the reaction rates I \rightarrow III and I-d₃ \rightarrow III-d₂ were measured in separate experiments (SI, p. 2, runs 6, 7). The relevant concentrations were determined from integral intensities of ¹H NMR signals of *t*-butyl groups not involved in isotope exchange. As III participates in further processes (transformation back to I and bromo-de-*tert*-butylation), the rate constants k_{13} (H) and k_{13} (D) were determined at the very beginning of the reaction. The incomplete enrichment in I-d₃ sample ($\beta = 91.4\pm0.3\%$) makes some contribution to the value of the measured rate constant: k_{13} (D+H) = (1- β) k_{13} (H) + β k_{13} (D), assuming equality of proton substitution rates in compounds I and I-d₂ and to deuterium substitution rates in compounds I-d₃ and I-d₂. The measured values k_{13} (H) = (5.38\pm0.08)\times10^{-5} and k_{13} (D+H) = (1.665\pm0.007)×10^{-5} s⁻¹ for I and I-d₃, respectively, give KIE: k_{13} (H)/ k_{13} (D) = **4.1\pm0.2**. This value is close to that observed earlier for Br₂/Ag⁺ system.^{5,6}

Quantum Chemical Computations

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It follows from the experiments that the energy barriers for bromo-de-protonation and bromo-detert-butylation are drastically lowered with increasing bromine concentration, in particular for the latter reaction. To confirm the hypothesis of polybromide clusters participation it was necessary to find transition states I-Br⁺Br_{2n-1}⁻ for both reactions and compare their energies at different values of n, using a "pathfinder" DFT/PBE/A01 method with calculated thermochemical free energies and Grimme's D3+BJ¹⁸ dispersion corrections. The system under consideration has a variety of possible stationary points on the potential energy surface (scheme 1, first stage). Nevertheless, in all cases for $n \ge 3$, the most stable transition states (Figure 7, see SI for others) have "chelate" geometries where the reaction centers H–C–Br and *t*-Bu–C–Br are surrounded by the anionic fragment Br_{2n-1}⁻. For the reaction I→II (TS3, reaction center *t*-Bu–C–

Br), the chelate chain of most favorable transition states comprises 7 bromine atoms (n = 4), with a possible auxiliary side chain (for n > 4). A similar feature exists for the reaction I \rightarrow IIF (TS) \rightarrow 0000007 the more compact reaction center H–C–Br), but no transition states with a 7-membered chelating chain were found. 5-membered chains always appeared to be more energetically favorable, with the extra bromine atoms displaced into side chains. Notably, similar V-shaped, pyramidal and tetragonal Br_{2n-1}⁻ structures (n = 3, 4 and 5) were observed experimentally in the crystal phase^{4,19} in the forms of polybromide salts. For the reaction I \rightarrow II at n = 4,5 an additional energy minimum was found in the PES, corresponding to the II + *t*-Bu⁺Br_{2n-1}⁻ system.

Figure 7. Transition states of the bromination reactions (DFT/PBE/ Λ 01).



Figure 8. a) Dependence of the energy barriers of bromination reactions (DFT/PBE/A01 with thermochemical free energy + D3/BJ¹⁸ corrections) on the number of bromine molecules. Zero energy corresponds to separated area and bromine molecules. b) Dependence of free activation energy of bromination reactions on bromine concentration.^OAG[#] was derived from the pseudo monomolecular rate constants given in Table 1 according to the Eyring equation. The value of the rate constant for reaction I \rightarrow III at [Br₂]=11.6 mol/L was extrapolated according to equation (3).



Relative energies of the transition states identified using this method are shown in Fig. 7 and as a function of the number of bromine molecules in Figure 8a. The n = 1 case presents a model of low bromine concentration ([Br₂] ~ 1 mol/L) where cluster formation is unlikely. Non-catalytic bromination of benzene and other unactivated aromatics is known not to proceed under these conditions,²⁰ in line with very high calculated energy barriers (> 40 kcal/mol, see also refs.^{2,21}). As n increases, the energy barriers decrease and at n>2 can be overcome at ambient temperature. The bromo-de-tert-butylation barrier (I \rightarrow II) decreases more rapidly than that for bromo-deprotonation (I \rightarrow III,) which reflects qualitatively the experimental tendencies of the relative reaction rates (Fig. 8b). Thus, quantum chemical modeling supports the assumption of the formation of bromine clusters in the transition states.

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A previous quantum chemical study of benzene bromination concluded that this reaction proceeds *via* a concerted S_EAr mechanism with the transition state in the form of ion-pair of the cation $[C_6H_6Br]^+$ and polybromide anion⁴ $[Br_{2n-1}]^-$ (Fig. 1). The key difference for the bromination mechanism of the tert-butyl derivative I is a two-step mechanism with facile formation of a Wheland intermediate (WI-I, Scheme 3) as stabilized by the three electron donating substituents. It is also well known that Wheland intermediates (arenium ions) can easily undergo a further 1,2-shift of a hydrogen atom.²² In our case (Scheme 3) this latter process as followed by *tert*-butyl group elimination must lead to 1-bromo-2,4-di-*tert*-butylbenzene V. Indeed, the signals of product V are observed in NMR spectra of the reaction mixtures, although in very low concentrations (0.5%). Thus, the presence of product V serves as an additional argument for the participation of Wheland intermediates such as WI-III (scheme 3) in the bromination process of I.

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Scheme 3. Mechanistic scheme for bromination.

We then proceeded to a higher-level computational model which includes continuum solvation corrections (B3LYP+GD3BJ/Def2-TZVPP/SCRF=CCl₄) with the focus on two models for the bromine clusters selected from the ones shown in Figure 7, n=3 and n=5. Location of three transition states was attempted at this level. TS1 (Scheme 3) corresponds to the formation of a Wheland intermediate (WI-I) and corresponds to a very lower barrier process compared to TS2, the subsequent proton loss from WI-I. TS3 involves loss of one *tert*-butyl group from an isomeric Wheland intermediate WI-II. The latter is itself higher in energy than WI-I because the cationic Centre's are less stabilized by electron donation. WI-III is more stable than WI-II because of cationic stabilization by an adjacent bromine. The computational results are collected in Table 2.

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-1	Λ
1	υ

	bromine ^a	View Article Onlin DOI: 10.1039/C9OB00607/
Species ^b	3Br ₂	5Br ₂
Ι	0.0° [4.4] ^d	0.0 [5.4]
TS1	_e	3.1 [15.3]
WI-I	3.9 [12.9]	-2.7 [16.2]
TS2	18.0 [12.6]	14.2 [12.5]
III	6.1 [4.7]	4.3 [4.8]
WI-II	15.1 [14.6]	9.2 [18.1]
WI-III	12.4 [12.3]	6.2 [13.8]
TS3	23.8 [23.4]	12.8 [20.0]
II (ion pair)	-1.7 [14.4]	-10.8 [10.1]
II	-9.8 [7.1]	-12.4 [6.7]

As follows from Table 1, the bromination reaction $I + Br_2 = III + HBr$ is thermodynamically unfavorable, with experimental free energy of the reaction being 3.5÷3.7 kcal/mol. The calculated value for the reaction I + 5Br₂ = III + HBr + 4Br₂ of ΔG_{298} is +4.3 kcal/mol (Table 2) in good agreement with experiment. This can be compared with the similar bromination reaction of benzene $C_6H_6 + 4Br_2 = C_6H_5Br + HBr + 3Br_2$ which is thermodynamically favorable, $\Delta G_{298} = -$ 11.0 kcal/mol.² The reason for the equilibrium shift is the reduced stability of the product III due to a bulky bromine atom situated in a close vicinity of two *tert*-butyl groups. The synthetically suitable preparation of III from I seems to be practically possible only in the presence of reagents sequestering HBr (Ag+²³, trimethyl phosphate²⁴). The stability of the Wheland intermediate WI-I depends on the bromine cluster size, with ΔG_{298} for its formation being favourable only with the 5Br₂ cluster, for which a discrete transition state TS1 indicates a very lower barrier to its formation. No equivalent transition state could be found for the 3Br₂ cluster, in probability because of a more sensitive requirement to rearrange the bromine cluster during the reaction path. The ring-bound Br in WI-I occupies a hyperconjugated pseudo-axial position, with the adjacent proton being pseudoequatorial (Figure 9). This intermediate, which is the kinetic resting state, then reacts by proton abstraction via TS2 to give product III, TS2 rather than TS1 being rate limiting. As previously noted, (Figure 7), $\Delta G^{\#}$ for TS3 (loss of the tert-butyl group) becomes lower than TS2 for the larger $5Br_2$ cluster compared to the smaller $3Br_2$ one, again confirmed by experiment. The overall reaction profile is shown in Figure 10.

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Figure 9. Calculated structure for the Wheland intermediate for the reaction 2,6-di-tertbutylbenzene +5Br₂ at the B3LYP+GD3BJ/Def2-TZVPP/SCRF=CCl₄ level. Interactive models of all structures can be obtained from DOI: 10.14469/hpc/4948



Figure 10. Overall energy profile for (a) 3Br₂ reagent and (b) 5Br₂ reagent. Dashed lines correspond to fast intermolecular rearrangements for which a true transition state could not be located.

The computed hydrogen KIE derived from the vibrational wavenumbers computed for TS2 (Scheme 3) is 7.2 at 298K. This is larger than the measured value for the process I \rightarrow III (4.1±0.2), which itself had confirmed that TS2 is rate limiting. The discrepancy between the measured and

calculated values might originate in the geometry of WI-I. If the pseudo-axial C-Br bond in WI-I

were to be transposed with the C-H bond, the latter will become significantly weakened by hyperconjugation, thus reducing the expected isotope effect. Attempts to locate such an alternative conformation for WI-I showed that for a 5Br₂ cluster it is at best merely a higher energy inflexion point in the potential surface. Nonetheless an approximate normal coordinate analysis at this geometry suggests a lower value for the KIE of 4.9 at 298K. It remains possible that for significantly larger bromine clusters (beyond the scope of the currently methodology employed here), the C-H axial conformation of WI-I might be preferred. It might be also that the complexity of the required kinetic analysis and the necessary approximations for its solution means that the measured KIE might be subject to a larger than normal experimental error. A variety of cluster bromide anions Br_{2n-1}⁻ discovered by X-ray of their crystal salts were actively studied over the past decade. According to our data, similar clusters can be formed in the transition states of chemical reactions. In case of electrophilic bromination of aromatics, bromine clusters coordinate with the reaction center, drastically speeding up the reaction. Participation of several bromine molecules in the transition state is manifested by unusually high reaction order in bromine. For the example reported here, a threefold increase in bromine concentration accelerates the substitution of a hydrogen atom and *tert*-butyl group in 1,3,5-tri-*tert*-butylbenzene by bromine by 150 and 2000 times respectively, via a stepwise reaction involving rapid initial formation of a Wheland intermediate. Apparently, enlarged clusters of bromine are needed to cover the bulky Br-C-t-Bu fragments. The highest bromine concentration achieved with liquid bromine as a solvent promotes the fast bromination of non-activated aromatics without the need for any catalyst. Bromine, the simplest brominating agent, is thus far from being simple. Its tendency for the formation of cluster structures should not be ignored when studying its chemical reactions.

Experimental

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Conclusion

General methods and materials: NMR spectra were obtained at the Multi-Access Chemical Service Centre of Siberian Branch of the Russian Academy of Sciences on Bruker AV-600, AV-400 and DRX-500 spectrometers, using the residual proton and carbon signals of deuterated methylene chloride as internal references (CHDCl₂, $\delta_{\rm H}$ 5.33 ppm; CD₂Cl₂, $\delta_{\rm C}$ 53.6 ppm). For NMR signal assignment 2D correlation spectra ¹H-¹H (NOESY) and ¹³C-¹H (HETCOR) were used.

Bromine was boiled and distilled over KBr and then over P_2O_5 . CCl₄ was distilled over P_2O_5 . CD₂Cl₂ was drained by molecular sieves 4Å. A sample of 1,3,5-tri-*tert*-butylbenzene (I) prepared according to²⁵ was purified by crystallization from methanol followed by sublimation in vacuum. By analogy, compound I-d₃ (91 atom % D) was prepared from benzene-d₆. 1-Bromo-3,5-di-*tert*butylbenzene (II) was kindly provided by Dr. T. F. Mikhailovskaya.

Preparation of samples: To bromine introduced into the NMR tube were added CCl₄, 0.1 mL of CD_2Cl_2 and 5-20 mg of solid aromatics (or solution of the aromatics in 0.1 mL CD_2Cl_2) as the three distinct layers. Total reaction mixture volume was 0.5 mL. The volumes of Br₂ and CCl₄ were chosen so as to ensure the desired bromine concentration (SI, p. S2). The tube was sealed by PTFE cup and heat shrink tubing. The reaction was launched by stirring the layered content immediately before recording NMR spectra. Representative ¹H NMR spectrum is shown in SI (p. S3).

Kinetics: The composition of the reaction mixtures was determined by integration of ¹H NMR spectra. For kinetic data processing a dedicated SciLab script was developed.²⁶ The following built-in SciLab functions were used: ode (automatically selecting between nonstiff predictorcorrector Adams method and stiff Backward Differentiation Formula method) - for the solution

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of the kinetic equations, lsqrsolve (Levenberg-Marquardt nonlinear least squares fitting) – for numeric determination of the rate constants by fitting kinetics to the experimental curves^{le} and lsq_splin (least squares cubic spline fitting) – for interpolation of HBr concentrations. The input data and output results for all the kinetics experiments are given in SI, p. S5-S11; an example of graphical output is shown on p. S4.

Computational details: Pathfinder calculations involving optimization of geometries of nonrigid systems I-Br_{2n} with a many possible stationary points on the PES used a fast DFT code implemented in the PRIRODA program²⁷ and employing a PBE functional²⁸ with full-electron basis $\Lambda 01^{29}$ similar to the cc-pVDZ basis, as a gas-phase model. Since the considered transition states are in fact ion-pairs with a possible high solvation contribution, more realistic computations with solvation model support were then undertaken. Our chosen computational model used the B3LYP density functional as implemented in the Gaussian 16 program (Rev A.03 and B.01),³⁰ which is a thoroughly explored method for a wide variety of reactions, combined with the Def2-TZVPP basis set, an improvement on the earlier study of a similar system.^{2,21} We have also added Grimme's D3 dispersion correction¹⁸ with BJ weighting, together with the Karplus and York smoothed-cavity SCRF continuum solvation model with CCl₄ specified as the solvent.³¹ We retained this continuum solvation model for higher mole fractions of Br₂ noting that the dielectric constants of liquid bromine (3.1) and CCl₄ (2.2) are similar. Computational data for this method are available *via* a FAIR data repository.³²

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