Supporting Information

for

Theoretical Study of the Mechanism of Cationic Polymerization of Isobutylene Catalyzed by $EtAlCl_2$/*t*-BuCl with Bis(2-chloroethyl) Ether in Hexanes

by

Xinrong Yan,[†] Meng Du,[†] Jiwei Li,[‡] Ying Xue,[†] Yibo Wu,[§] Hao Zhang, [‡] Xin Wang*,[†] and Dingguo Xu*,[†]

[†]MOE Key Laboratory of Green Chemistry and Technology, College of Chemistry, Sichuan University, Chengdu, Sichuan, 610064, PR China

[‡]Chengdu Migersi Medical Technology Co., Ltd, Chengdu, Sichuan, 610219, PR China

[§]The College of New Materials and Chemical Engineering, Beijing Key Lab of Special Elastomer Composite Materials, Beijing Institute of Petrochemical Technology, Beijing, 102617, PR China

* To whom correspondence should be addressed: wangxin@scu.edu.cn (X. W) dgxu@scu.edu.cn (D.X), Tel: 86-28-85406156.

Contents

Box sizes and CV settings

The first step is the chain initiation step as shown in Step **I** of Scheme 1. To obtain the free energy profiles, we conducted AIMD simulations on the *t*-BuCl and EADC·CEE complex in a periodic box with dimensions of 15.0 Å × 15.0 Å × 15.0 Å. The initial configuration, illustrated in Fig. 1a, exhibits a 3.305 Å distance between the Cl14 and the Al atom. The distance between *tert*-C atom of *t*-BuCl and metallic atoms (Al) of Lewis acid was set as CV1, and *tert*-C atom of *t*-BuCl and Cl atom of *t*-BuCl was used as CV2. A repulsive Gaussian potential hill with a height of 2.6 kJ/mol and a width of 0.2 was added.

The second step is the propagation step as shown in Step **II** of Scheme 1. It is not the aim to consider the role of the counterion. Therefore, we focused solely on the Gibbs free energy of the addition of carbocation to IB as shown in Scheme 2b. In the initial four chain propagations, CVs were established based on the distance between the end group C atom on the olefin moiety and *tert*-C atom on the carbon positive ion, as well as their CN.

Specifically, for $N = 1$, starting from an initial configuration placed in a periodic 12.0 Å × 12.0 Å × 12.0 Å box, two key CVs were utilized (Fig. 3a): the distance between C5 and C10 (CV3) and their CN (CV4). Chose 2.6 kJ/mol for the hill height and 0.2 for the hill width. For $N = 2$, the initial configuration was placed in a cubic periodic box of side 13.0 Å. The C7−C12 bond distance (CV5) and the CN (CV6) were selected as the CVs. The selected MTD parameters were a hill height of 0.3 kJ/mol and a hill width of 0.1. For $N = 3$, the periodic box size was set to 17.0 Å × 17.0 Å × 17.0 Å. The distance and CN of C29−C38 were selected as CV7 and CV8. The simulation utilized a Gaussian height of 0.3 kJ/mol and a hill width of 0.1. For $N = 4$, the initial configuration was placed in a cubic periodic box of side 17.0 Å. The selected MTD parameters were a hill height of 0.3 kJ/mol and a hill width of 0.1. The distance and CN were selected as CV9 and CV10.

The CVs for reaction of EADC·*i*-Pr_2O with *t*-BuCl are set to the distance of Al atom and *tert*-C atom of *t*-BuCl (CV11) and the distance of *tert*-C atom of *t*-BuCl and Cl atom of *t*-BuCl (CV12).

The CVs for reaction of EADC·CEEE with *t*-BuCl are set to the distance of Al atom and *tert*-C atom of *t*-BuCl (CV13) and the distance of *tert*-C atom of *t*-BuCl and Cl atom of *t*-BuCl (CV14).

The CVs for reaction of $GaCl_3$·*i*-Pr_2O with *t*-BuCl are set to the distance of Ga atom and *tert*-C atom of *t*-BuCl (CV15) and the distance of *tert*-C atom of *t*-BuCl and Cl atom of *t*-BuCl (CV16).

The CVs for reaction of $Et_2AlCl{\cdot}i\text{-}Pr_2O$ with *t*-BuCl are set to the distance of Al atom and *tert*-C atom of *t*-BuCl (CV17) and the distance of *tert*-C atom of *t*-BuCl and Cl atom of *t*-BuCl (CV18).

The CVs for reaction of *t*-Bu^+ with CEE are set to the distance of O atom and *tert*-C atom of *t*-Bu^+ (CV19) and their CN (CV20).

The selection of CVs in solvent is the same as in vacuum.

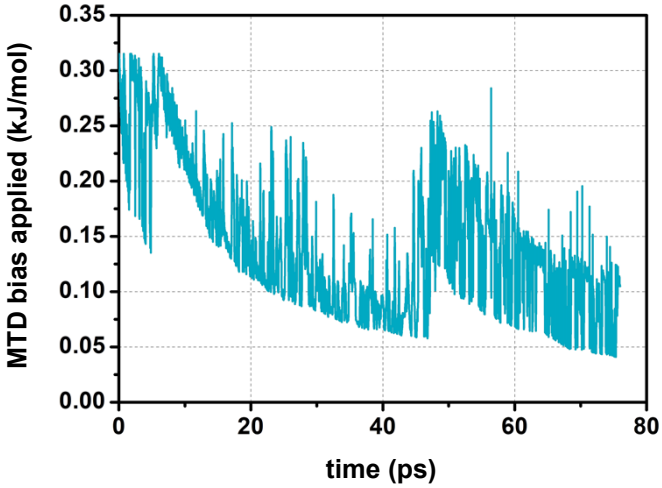

Fig. S1 Plot of the Gaussian height added to the system along the MTD simulation.

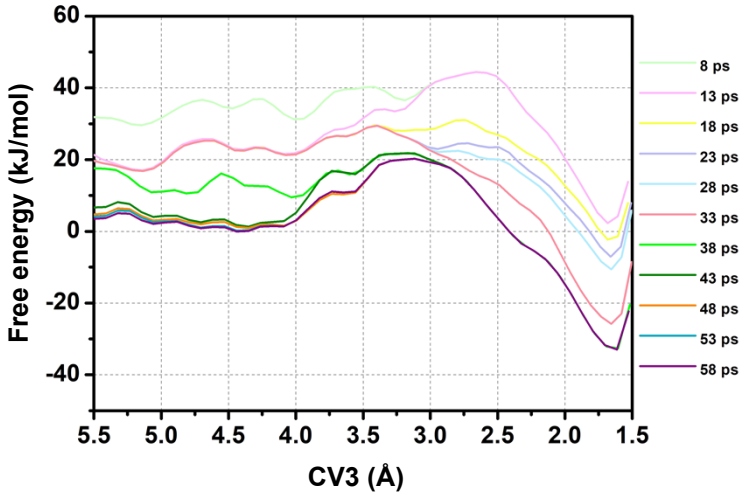

Fig. S2 Gradual build-up of the 1D free energy profiles for convergence testing in vacuum for $N = 1$.

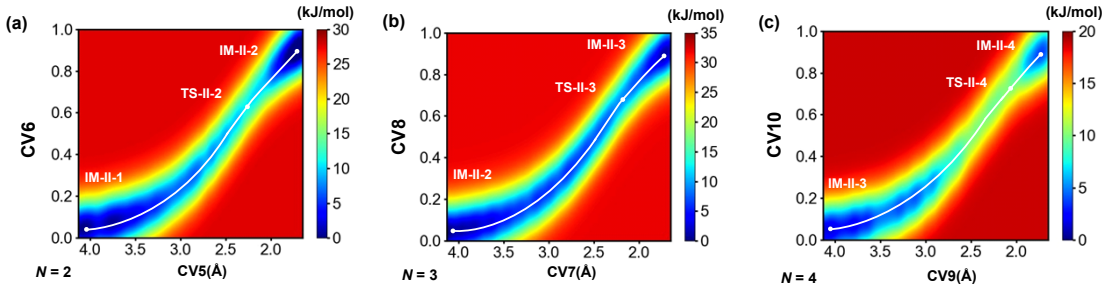

Fig. S3 2D FESs for chain propagation reactions in vacuum from $N = 2$ to 4. The white line represents the MEP. The simulated temperature is 273K.

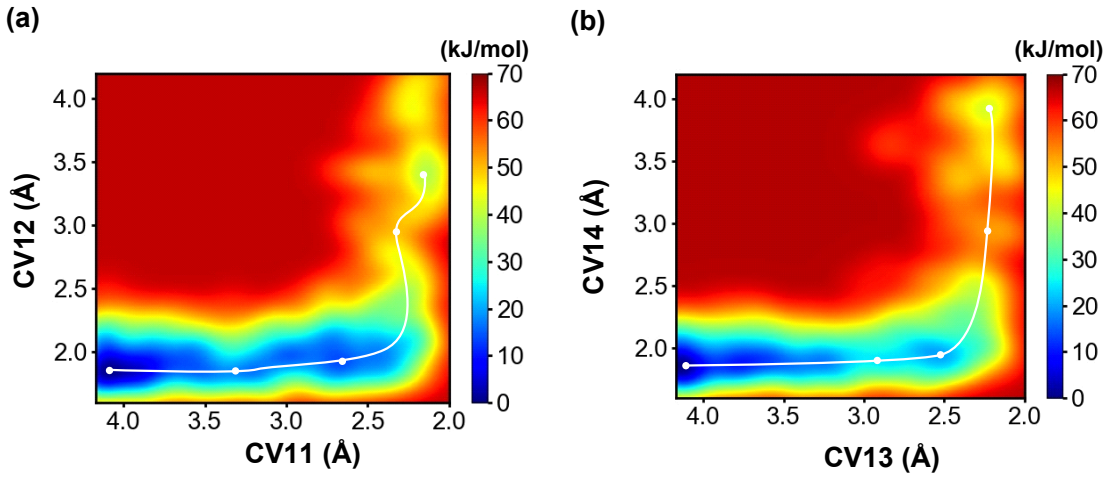

Fig. S4 2D FESs of initiation catalyzed by (a) EADC·*i*-Pr_2O and (b) EADC·CEEE, which were computed from MTD simulations in vacuum. The white line represents the MEP.

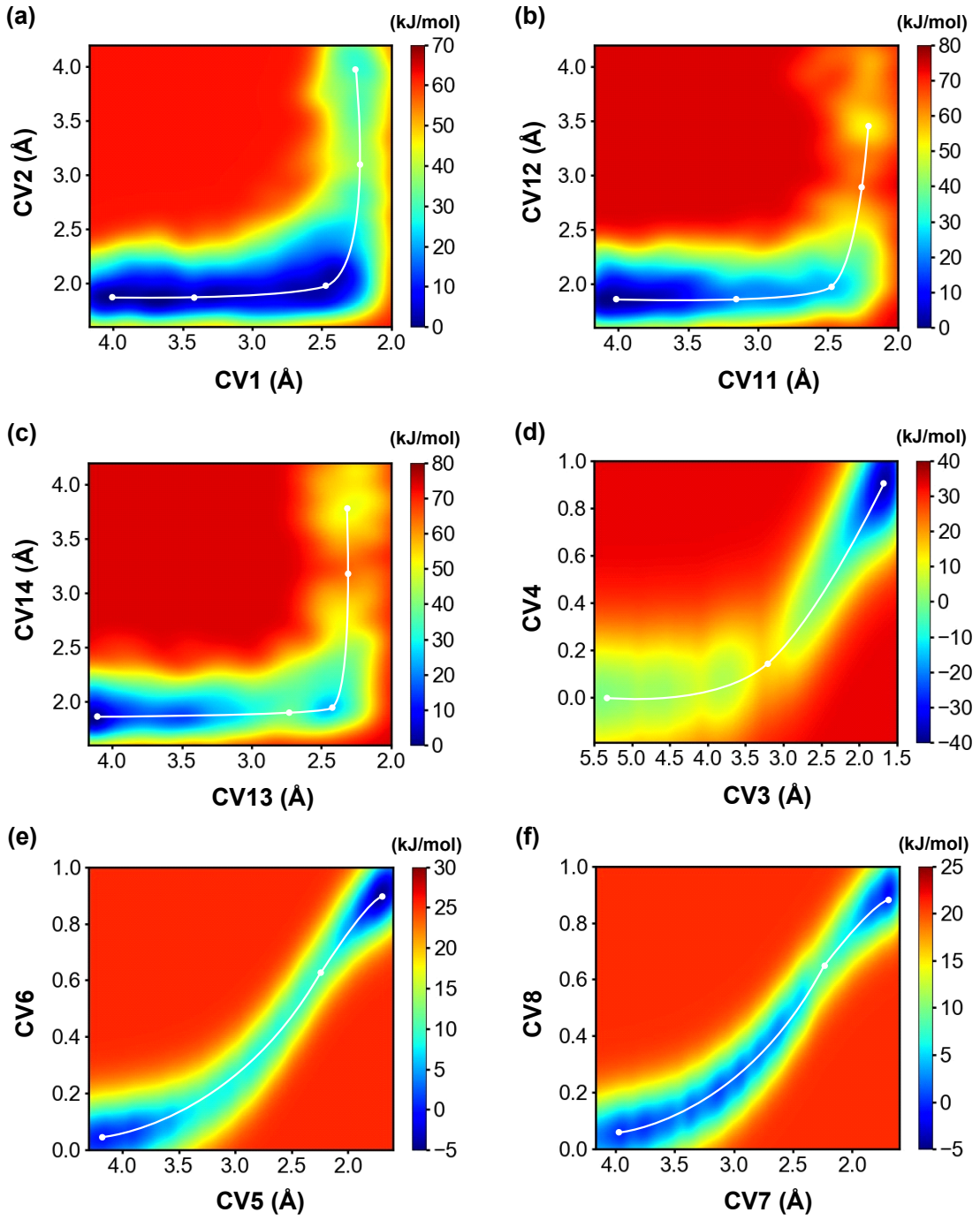

Fig. S5 2D FESs of the chain initiation and propagation steps in *n*-hexane. The initiations catalyzed by (a) EADC·CEE, (b) EADC·*i*-Pr_2O, (c) EADC·CEEE; propagations from N = (d) 1, (e) 2 and (f) 3. The white line represents the MEP.

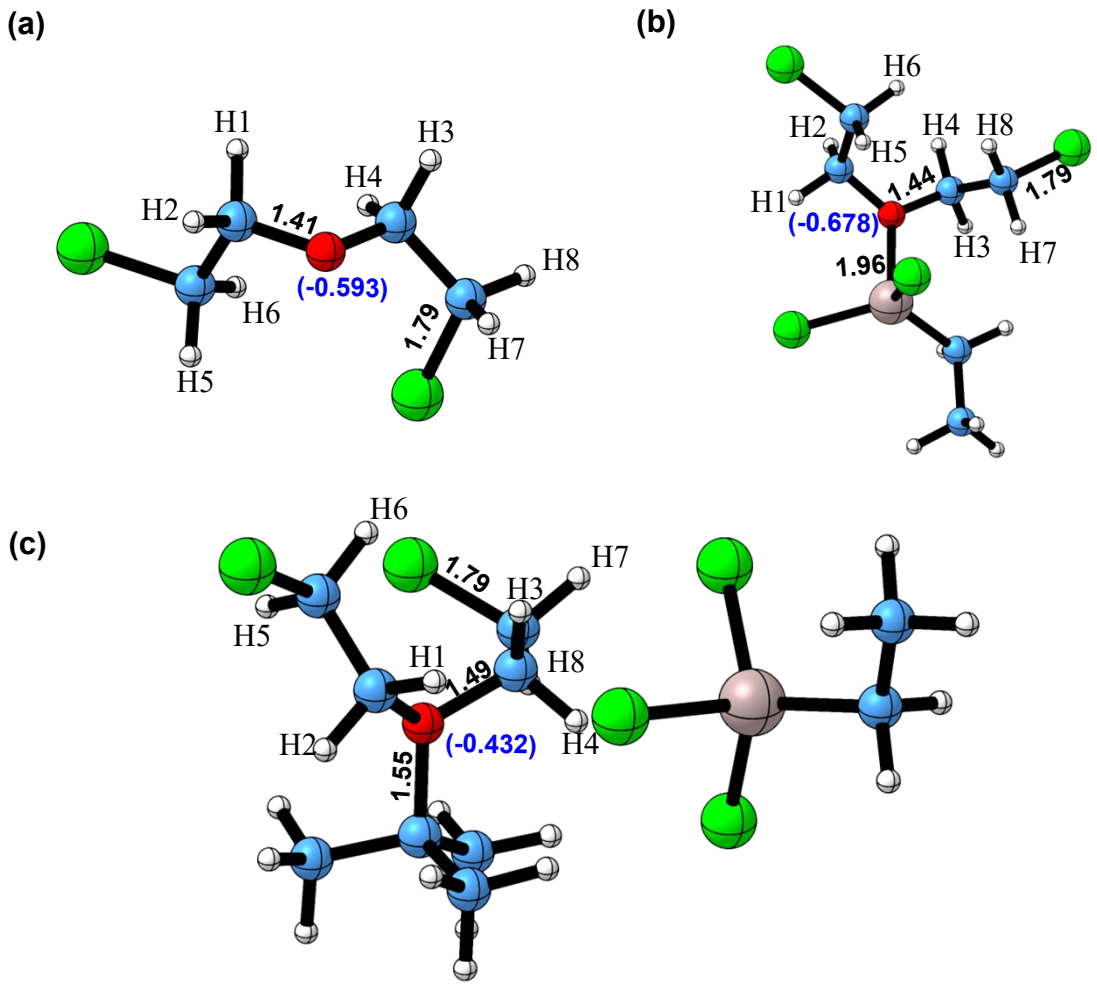

Fig. S6 Optimized structures of (a) CEE, (b) EADC·CEE and (c) *tert*-butyloxonium·$EtAlCl_3^-$. The units for bond distances are given in Å and the NPA charges are in parentheses.

We have tried to search the transition states (TSs) structures using the static method. As shown in the following Fig. S7, we used the TSs structures obtained from the CP2K MTD calculations as the initial structures to search possible TSs by Gaussian 09 at the M062X/6-31G(d) level. However, we failed to identify these TSs. We failed to obtain the **TS-I-2** and **TS-II-1**. The two optimized structures by Gaussian have no imaginary frequency. For **TS-II-2** and **TS-II-3**, the two structures have the only imaginary frequency of -93 cm-1 and -130 cm-1, respectively. However, the vibrational mode of the imaginary frequency of the two TSs corresponds to the rotation of the methyl group. The present calculations shown that the classical static DFT strategy failed to describe the titled polymerization reactions.

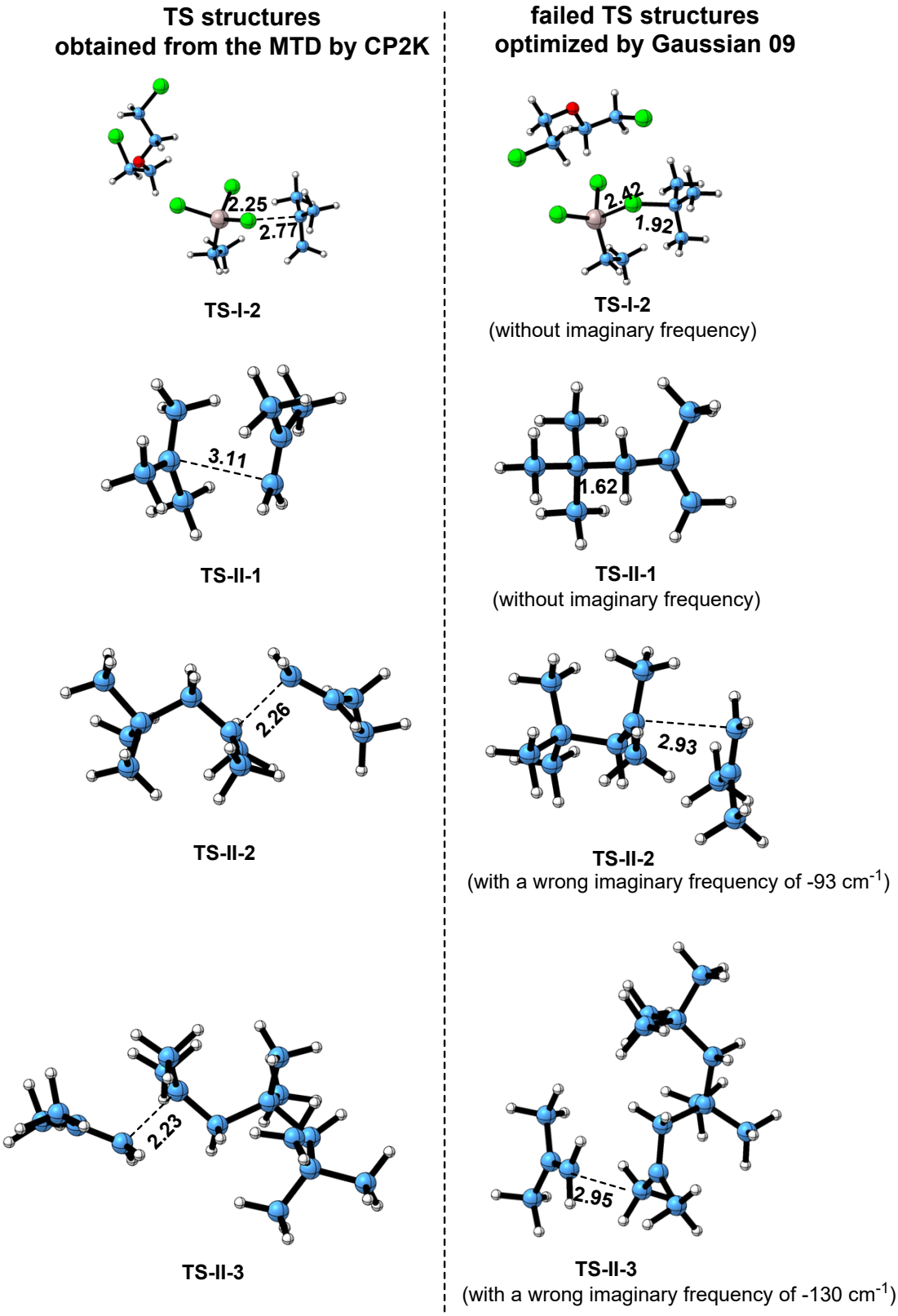

Fig. S7 Initial structures by CP2Kand failed TSs structures using the static method.

We chose the *t*-Bu^+, a reactant in present titled reaction, to test the different DFT methods. The calculated C–C bond length of the *t*-Bu^+ with different functionals were compared with the available experimental value from reference (*J. Am. Chem. Soc*. 1993, **115**, 7240-7245.). As shown the following **Table S1**, the most DFT methods overestimate the bond length. But the differences between experimental value and DFT calculated length are small and could be accepted. The M06-2X show good performance and then we chose the M06-2X the check the basis set effects on the bond distances. As shown in **Table S2**, the increments of basis sets have only a little effect on the results. The larger basis set is, the shorter bond distances. Considering the good performance and low computational cost, we think that the results at the M062X/6-31G(d) level are good enough for the present system. Therefore, all quantum mechanical calculations in present paper were calculated at the M062X/6-31G(d) level.

Table S1. Calculated *t*-Bu^+ C–C bond length in angstroms using different DFT methods with the 6-31G(d) basis set.

Exptl.[a]	M06-2X	WB97XD	B3LYP	BLYP	PBE0	PW91	PBE	TPSSH	X3LYP	TPSS
1.442	1.465	1.465	1.469	1.478	1.462	1.468	1.469	1.470	1.468	1.474

[a] experimental value from reference (*J. Am. Chem. Soc.* **1993**, *115*, 7240-7245.)

Table S2. Calculated *t*-Bu^+ C–C bond length in angstroms using M06-2X method with different basis sets.

Exptl.	6-31G(d)	6-31++G(d,p)	6-311G(d)	6-311++G(d,p)	cc-pVTZ	aug-cc-pVTZ	def2-SVP	def2-TZVP
1.442	1.465	1.464	1.462	1.462	1.459	1.459	1.462	1.459

To give deeper understanding solvent effect of the titled reaction, some more calculations were then carried out. Herein, due to CP2K suite of program lacks the capability to export the values of non-polar or polar interaction terms, we then simply calculated the solvent effects using the SMD solvation model of the Gaussian 09 program. The SMD model is new continuum solvation model based on the polarized continuous quantum mechanical charge density of the solute and the "D" in the name stands for "density" (see *J. Phys. Chem. B* 2009, **113**, 6378–6396). We made further analysis of the contributions of electrostatic and non-electrostatic portion in the solvation free energy only for two transition states (**TS-I-2** and **TS-II-1**). It should be emphasized that this treatment can only provide rough or qualitative analyses.

Table S3. Analyses of the free energies in solvent *n*-hexane for TSs.

	TS-I-2 in initiation step	**TS-II-1** in propagation step
Non-electrostatic energy (kJ/mol)	-30.6	-12.7
Electrostatic energy (kJ/mol)	-76.6	-126.8
Percentage of electrostatic portion in total free energy in solution (%)	71	91
Total free energy in solution (kJ/mol)	-107.2	-139.5

Cartesian coordinates in angstroms of the optimized structures of CEE, EADC·CEE, and EADC·CEE/t-BuCl.

CEE

O,0,-0.0016005801,1.2336910015,0.4384444626
C,0,-1.2899422786,1.0844315901,-0.1141455643
H,0,-1.2790913796,1.2106363498,-1.2054827888
H,0,-1.9150207618,1.8733548345,0.3119042386
C,0,1.0402142255,0.6813368903,-0.3302693728
H,0,0.6734890464,-0.1016768534,-1.0072854074
H,0,1.5136241651,1.4650698586,-0.9410380727
C,0,2.0804804392,0.1009585088,0.6025106354
H,0,2.9660546312,-0.2194865482,0.0520167823
H,0,2.3604916019,0.8337017006,1.3601169223
C,0,-1.8577507808,-0.2794096438,0.2565939451
H,0,-1.2508639986,-1.0950955406,-0.1403589555
H,0,-1.9209494995,-0.3840591842,1.3398486633
Cl,0,-3.5091400445,-0.4508804806,-0.4191271474
Cl,0,1.4354484642,-1.3322777934,1.4670342893

EADC·CEE

Al,0,1.6680527208,-0.0268022062,0.0229431687
O,0,-0.0877727242,-0.4286387013,-0.7376442217
C,0,-0.6059833342,-1.7751533448,-0.8397353102
H,0,-1.1002862459,-1.8715607166,-1.8106159973
H,0,0.2664211883,-2.429851609,-0.8163794391
C,0,-1.01613717,0.6490030333,-0.9850942571
H,0,-1.8743245697,0.2386886785,-1.5247993106
H,0,-0.5023637907,1.3697244291,-1.6247587281
C,0,-1.4504950969,1.3043344275,0.3179177635
H,0,-0.6105585722,1.7776194377,0.8272714829
H,0,-1.9189489624,0.5949216339,1.0007429708
C,0,-1.5545782982,-2.0903995208,0.3044491396
H,0,-1.0499947953,-1.9904460678,1.267164468
H,0,-2.4469832061,-1.4616851985,0.2827608101
Cl,0,-2.6435485955,2.5714122167,-0.0814420744
Cl,0,-2.0981269255,-3.7798575234,0.1138376491
C,0,2.0763503793,1.7894447001,-0.556827912
H,0,2.0783346798,1.8263214763,-1.6554178762
H,0,1.3232413529,2.5189130151,-0.2285107939
C,0,3.458336367,2.2249487095,-0.03348853
H,0,3.7270472201,3.2300378721,-0.3753030522
H,0,3.4839983808,2.2335254714,1.0615071005
H,0,4.2452241006,1.543007082,-0.373413572

Cl,0,2.837036143,-1.6018074141,-0.814567771
Cl,0,1.218948874,-0.3343174406,2.0998782625

tert-butyloxonium·$EtAlCl_3^-$

Al,0,1.0084148413,-1.0214493673,-2.6268178092
Cl,0,1.908547077,0.7745133253,-1.7449963371
Cl,0,-0.9972141614,-0.3673567514,-3.2863428324
Cl,0,0.5847130745,-2.3267111458,-0.891232021
C,0,2.0912944986,-1.8924408773,-3.99019601
H,0,1.5355971054,-2.7511292328,-4.3894185976
H,0,2.2273346696,-1.2032338379,-4.8337807821
C,0,3.4587743179,-2.352175139,-3.4619164988
H,0,3.3460879109,-3.0582738266,-2.631828774
H,0,4.0565257283,-2.8487514402,-4.2353590494
H,0,4.0451319091,-1.50518654,-3.0889495421
C,0,-3.1102300306,-0.3904741886,0.3754365338
C,0,-2.9178261887,-1.7156658399,-0.3336918949
H,0,-2.602923533,-2.5128012151,0.3445648565
H,0,-3.8837470173,-2.0028395554,-0.7609946443
H,0,-2.1948462411,-1.6375140353,-1.1506194909
C,0,-4.0760129798,-0.4364039717,1.5513694335
H,0,-3.9337832929,-1.302459269,2.2009381997
H,0,-4.0056117446,0.481734296,2.1419843949
H,0,-5.0895630461,-0.5044148291,1.1471567232
C,0,-3.5139670581,0.7159795478,-0.5830179513
H,0,-3.6144026463,1.6740568969,-0.0655760102
H,0,-2.8424803563,0.7982360951,-1.4415932948
H,0,-4.4973579265,0.4444748059,-0.9766688994
O,0,-1.7511612571,0.0261574797,1.0016862311
C,0,-1.1652132358,-0.9455583192,1.9475334256
H,0,-0.4284861149,-1.5378513695,1.3987390424
H,0,-1.9788424438,-1.5847205288,2.2775077632
C,0,-0.7212874285,0.640010305,0.1222387245
H,0,0.2360975847,0.2956643663,0.5105193586
H,0,-0.8571110087,0.2305857859,-0.8786197025
C,0,-0.797471344,2.148981483,0.1027831651
H,0,0.1266664462,2.4956786255,-0.3644806213
H,0,-1.6432971805,2.5293769727,-0.4642175452
C,0,-0.5825895268,-0.1950761969,3.1297814164
H,0,0.298580501,0.3895845888,2.8657099491
H,0,-1.3262638681,0.4591260789,3.5854766967
Cl,0,-0.0885892417,-1.4217031412,4.3286882552
Cl,0,-0.8992451421,2.8498058252,1.7466120594