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DFT B3LYP/6-311+G* calculation study of a new nonclassical mechanism of electrophilic functionalization of aromatic C–H bond *via* aryl cation formation

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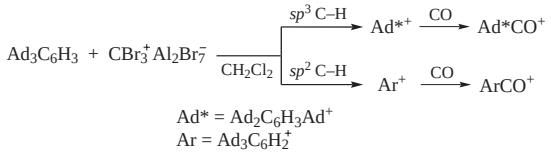
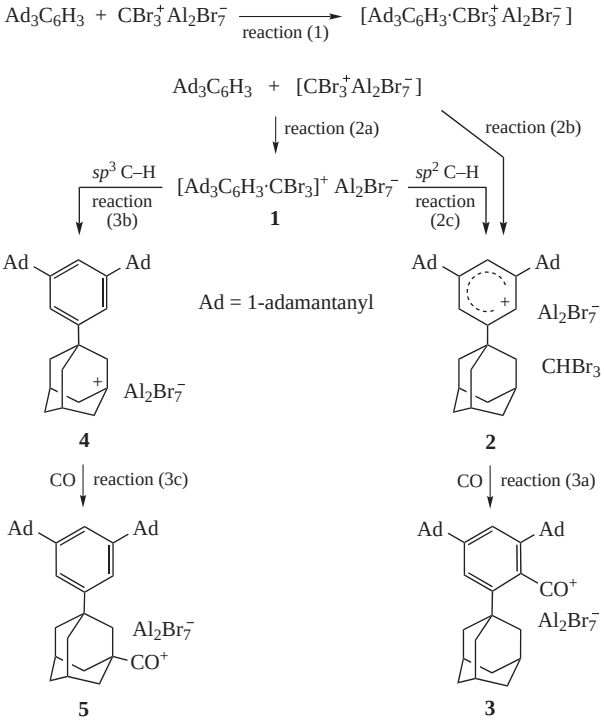
The DFT B3LYP-/6-311+G* calculations of the reactions beween 1,3,5-$Ad_3C_6H_3$ (Ad = 1-adamantyl) and $CBr_3^+Al_2Br_7^-$ with or without CO reveal that only sp^3 C–H route occurs.



The cleavage of sp^2 and sp^3 C–H bonds under the action of electrophiles plays the key role in the numerous organic reactions including large-scale processes of modern chemical industry.[1] Therefore, its mechanisms have been the subject of extensive research.[2–5] The action of electrophiles on the sp^2 C–H bond of arenes differs considerably from that on sp^3 C–H bond of alkanes. Classical scheme of electrophilic substitution at the aromatic C–H bond consists in the replacement of a proton by electrophile.[2–5] On the contrary, the key stage of reactions of alkanes with electrophiles is the hydride transfer from the C–H bond to electrophile to form a carbocation.[6,7] In contrast to alkane reactions, the elimination of arene hydride under the action of superelectrophiles is unknown, though the existence of phenyl cation has been firmly proved.[8]

The question arises whether the reactions involving hydride transfer from the aromatic C–H bond by electrophiles are possible. We assumed that *ortho*-C atoms in 1,3,5-$R_3C_6H_3$ (where R is a bulky group) could be hardly susceptible to the attack of a bulky electrophile due to steric hindrances. Hence, instead of the classical mechanism of C–H bond electrophilic substitution, a mechanism involving an attack of the electrophile on the H atom of C–H bond with hydride transfer to the electrophile seems to be possible.[9,10] The DFT B3LYP/6-31G* and DFT B3LYP/6-311+G* calculations of the reactions 1,3,5-$Ad_3C_6H_3/CBr_3^+$ (1),[9] 1,3,5-$Ad_3C_6H_3/CBr_3^+Al_2Br_7^-$ (2), and 1,3,5-$Ad_3C_6H_3/CBr_3^+Al_2Br_7^-$/CO (3)[10] have confirmed that the electrophile did not attack the aromatic C atom. Though the H atom of C_{aryl}–H bond was not completely exposed to the electrophile attack, the reaction on the H atom did occur, although having required a sufficiently high activation energy. Our calculations[9,10] have also shown that reactions (2), (3) require high temperature to overcome the energy barrier for arylium salt formation. However, taking into account that the carbonylation of arylium salt is a strongly exothermic process and that the conversion of the initial system to the acylium salt requires only a small amount of energy, it can be expected that, once initiated, the reaction would proceed easily. Our previous studies on reactions (1)–(3)[9,10] considered the reactions of aromatic ring only. In the present study, we carried out DFT B3LYP/6-311+G* calculations of the competing reactions (2) and (3) involving sp^3 C–H bond of adamantyl group (Scheme 1).

Table 1 shows that intermediates, **1**–**3** and **TS1** involving reactions at sp^2 C–H bond of the arene[10] and intermediates **4**, **5** and **TS2** including reactions at sp^3 C–H bond of adamantyl group were found on the potential energy surface of the reaction $Ad_3C_6H_3/CBr_3^+Al_2Br_7^-/CO$. The transformation of intermediate **1** into adamantylium salt **4** is exothermic and occurs *via* a very low activation barrier [reaction (3b), see Table 1]. The exothermic CO addition to **4** leading to the acylium salt **5** occurs *via* a barrier-free process. The solvent has opposite effects on the enthalpies of compounds **4** and **5**. While for **4**, the enthalpy decreases by more than 16.8 kcal mol^{-1}, for **5**, it increases by more than 14.9 kcal mol^{-1}. This is probably due to the fact that the adamantylium salt **4** is strongly solvated, which makes its interaction with CO energetically less favorable [reaction (3c)].



Scheme 1

Table 1 DFT B3LYP/6-311+G* calculated energetic characteristics (in kcal mol^{-1}) for the reactions between $Ad_3C_6H_3$ and $CBr_3^+Al_2Br_7^-$ with or without CO.[a]

Reaction		$\Delta H^{\neq}$ ($\Delta H^{\neq}_{sol}$)	$\Delta G^{\neq}$ ($\Delta G^{\neq}_{sol}$)	ΔH (ΔH_{sol})	ΔG (ΔG_{sol})
(2a)	$Ad_3C_6H_3 + CBr_3^+Al_2Br_7^- \rightarrow Ad_3C_6H_3{\cdot}CBr_3^+Al_2Br_7^-$ (**1**)	0.00 (0.00)	0.00 (0.00)	–0.96 (4.00)	13.53 (18.49)
(2b)	$Ad_3C_6H_3 + CBr_3^+Al_2Br_7^- \rightarrow Ad_3C_6H_2^+Al_2Br_7^-$ (**2**) + $HCBr_3$	38.96 (40.54)	56.22 (57.80)	18.94 (12.31)	39.61 (32.97)
(2c)	$Ad_3C_6H_3{\cdot}CBr_3^+Al_2Br_7^-$ (**1**) → $Ad_3C_6H_2^+Al_2Br_7^-$ (**2**) + $HCBr_3$ **TS1**	39.92 (36.54)	42.69 (39.31)	19.90 (8.31)	26.09 (14.49)
(3a)	$Ad_3C_6H_2^+Al_2Br_7^-$ (**2**) + CO → $Ad_3C_6H_2CO^+Al_2Br_7^-$ (**3**)	0.00 (0.00)	0.00 (0.00)	–43.43 (–42.55)	–35.12 (–34.24)
(3b)	$Ad_3C_6H_3{\cdot}CBr_3^+Al_2Br_7^-$ (**1**) → $Ad_2(Ad^+)C_6H_3Al_2Br_7^-$ (**4**) + $HCBr_3$ **TS2**	5.70 (0.95)	6.99 (2.24)	–13.25 (–30.08)	–11.58 (–28.41)
(3c)	$Ad_2(Ad^+)C_6H_3Al_2Br_7^-$ (**4**) + CO → $Ad_2(AdCO^+)C_6H_3Al_2Br_7^-$ (**5**)	0.00 (0.00)	0.00 (0.00)	–22.24 (–7.31)	–15.45 (–0.52)

[a] $\Delta H^{\neq}$ is the activation energy of reaction; $\Delta G^{\neq}$ is the Gibbs free activation energy; ΔH is the enthalpy of reaction; ΔG is the Gibbs free energy of reaction; numbers in parentheses represent results of calculations with CH_2Cl_2 solvent effect.

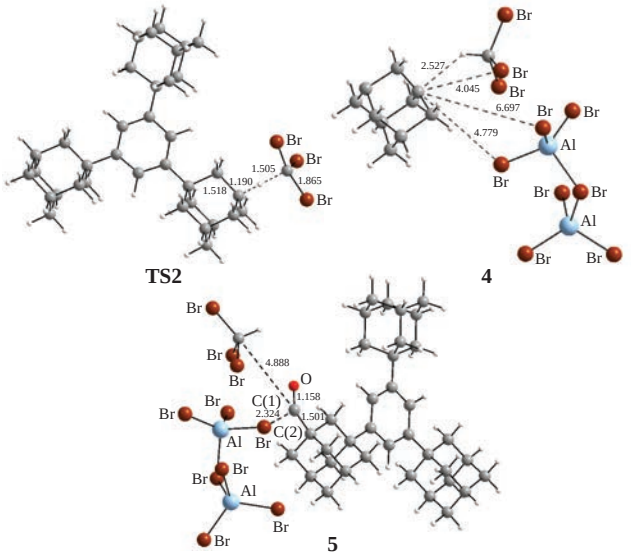


Figure 1 Structures of intermediates **TS2**, **4** and **5**.

Structures of intermediates **1**–**3** and **TS1** were considered in our earlier paper.[10] Structures of intermediates **4**, **5** and **TS2** are presented here (Figure 1).

Adamantylium salts were generated in strong superacid media[11(*a*)] and studied by quantum-chemical methods.[11(*b*)] The geometrical data that we calculated for **4** and 1-Ad^+ are close to those of 1,3,5-$Me_3Ad_1^+Sb_2F_{11}$ (Ad_1 = $C_{10}H_{12}$) proved by X-ray method[12] (see Online Supplementary Materials). In both cases, the dihedral angles are close to 151°, indicating non-planar structure of adamantyl cation. A different situation is observed for acylium salt **5**. Its structure differs considerably from those of acylium salts whose ionic structure was proved by X-ray method.[13–19] In cation **5**, the CCO angle is 138.94° instead of *ca*. 180° for the acylium salts and the contact between C and Br atoms is 2.324 Å, that is, shorter than the sum of van der Waals radii by 0.73 Å. Since the structure **5** differed from the known ionic acylium salts and no quantum-chemical calculations of $AdCO^+$ and its salts were published, we have carried out the calculations of $AdCO^+$ and salts $AdCO^+Y^-$ (Y = $AlCl_4$, Al_2Br_7) using different basis sets. The geometrical characteristics of $AdCO^+$ turned out to be very close to those for the studied crystal acylium salts.[13–19] By contrast, salt **5** and the acylium salts $AdCO^+Y^-$ (Y = $AlCl_4$, Al_2Br_7) have different geometrical parameters as compared to both the studied acylium salts and $AdCO^+$. For instance, the angles CCO are *ca*. 136–143° instead of 180°, both C–C and C=O distances are considerably larger, while the distances between non-bonded atoms C and Hal are considerably shorter than those in ionic acylium salts. However, the calculations performed with CH_2Cl_2 solvent show that all the calculated acylium salts including **5** have the structures similar to those of $AdCO^+$ and crystal ionic acylium salts (the angles CCO are 164–174°, the distances C=O are 1.126–1.134 Å, and R–CO are 1.426–1.432 Å, see Online Supplementary Materials). Thus, our calculations involving CH_2Cl_2 solvent effect reveal that in the considered reactions, the cleavage and carbonylation of sp^3 C–H bond lead to ionic adamantylium (**4**) and acylium (**5**) salts, which are similar to ionic salts with other organic groups.

The comparison between two competitive reactions (see Table 1) shows that elimination of hydride from sp^3 C–H bond in $Ad_3C_6H_3$ [reaction (3b)] is energetically more favorable (by ~35 kcal mol^{-1}) than its elimination from the sp^2 C–H bond [reaction (2c)]. However, the addition of CO to the highly unstable arylium salt **2** occurs with the release of greater energy than its addition to the adamantyl cation **4** (by about 21 and 35 kcal mol^{-1}, for gas and liquid phases, respectively). Figure 2 depicts energy level diagrams for reaction (3) in the gas and liquid phases.

Using the Erying equation[20] we have calculated the half-conversion time $t_{1/2}$ for the reaction $Ad_3C_6H_3/CBr_3^+Al_2Br_7^-/CO$ involving aryl cation (see Online Supplementary Materials). These calculations predict that the reaction *via* aryl cation should proceed in the acceptable rate at 290–320 °C. However, the low barrier competing reaction *via* adamantyl cation would occur with the high rate even at room temperature. Therefore, our calculations neglecting the reverse transformations demonstrate that the direct reactions $Ad_3C_6H_3/CBr_3^+Al_2Br_7^-/CO$ occur exclusively with the participation of sp^3 C–H bond. However, Figure 2 shows that the reverse transformations of **5** to the starting system would occur much more easier than the corresponding transformations of **3**. We believe that the calculation of those two reverse reactions at high temperature will allow us to ascertain whether the sp^2 channel is possible in the above system.

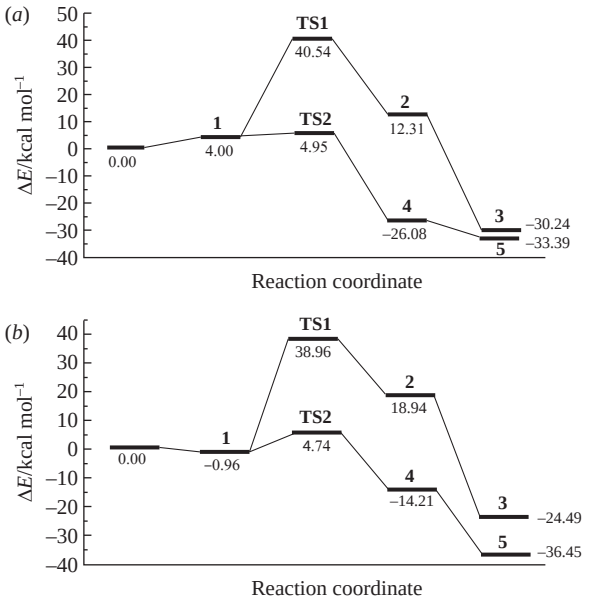


Figure 2 Energy level diagrams relative to the starting system for the reactions of $Ad_3C_6H_3$ with $CBr_3^+Al_2Br_7^-$ and CO in (*a*) liquid and (*b*) gas phases. The upper diagrams refer to the reaction (sp^2) with formation of the aryl cation. The lower diagrams refer to the reaction (sp^3) involving the adamantyl cation.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.05.035.

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