

Reductive activation of C–I bond of CH₃I by Au cluster anions in the gas phase

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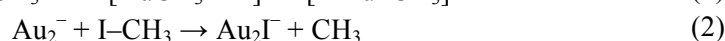
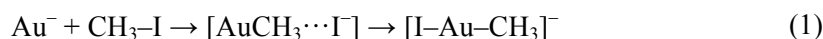
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Recently it has been demonstrated that Au nanoparticles and clusters catalyze various C–C bond formation such as Ullmann, Suzuki-Miyaura, and Sonogashira reactions, which require activation of C(sp²/sp³)–X (X: halogen) bond [1]. In contrast, catalytic activation of C(sp³)–X bond in haloalkanes is more challenging due to electron-rich nature of sp³ carbon [2]. In this work, we revealed by means of mass spectrometry, photoelectron spectroscopy, and DFT calculations that C(sp³)–I bond of methyl iodide (CH₃I) is reductively activated by Au atom and small Au cluster anions (Au_n[−] (*n* = 1–4)) in the gas-phase, where the activation mechanism largely depends on the cluster size, *n* [3,4].

Laser-ablated Au_n[−] (*n* = 1–4) were allowed to react with CH₃I molecules in a reaction cell. Pseudo-first-order kinetic analyses clarified the inverse correlation between the reactivity of Au_n[−] towards CH₃I and the electron affinity (EA) of Au_n as shown in Figure 1, indicating that the reaction proceeds via electron transfer from Au_n[−] to CH₃I (reductive activation).

With regard to products, Au[−] mainly afforded an oxidative addition product [I–Au–CH₃][−], while Au_n[−] (*n* = 2–4) yielded Au_nI[−] (+ CH₃). On the basis of DFT calculations for *n* = 1 and 2, we concluded that preferential site to attack on CH₃I is different between Au[−] and Au₂[−] (Figure 2): Au[−] attacks from the C side of CH₃I in an S_N2 manner followed by migration of leaving I[−] anion (eq. 1), while Au₂[−] attacks from the I side to directly abstract the I atom (eq. 2).



The drastic size dependence in the C–I bond activation by Au clusters demonstrated in this study raises a possibility that Au clusters can be used as catalysts that can control the products, or can enhance the selectivity, by precise tuning of the cluster size at the atomic level.

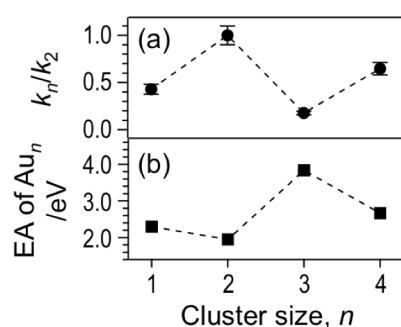


Figure 1. (a) Relative pseudo-first order rate constants of Au_n[−] toward CH₃I (k_n ; *n* = 1–4). (b) Electron affinity (EA) of Au_n

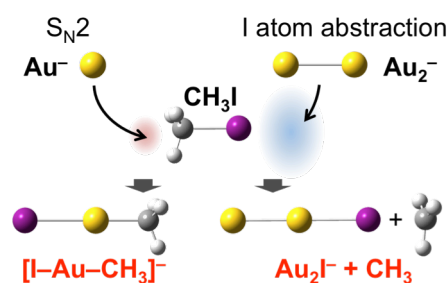


Figure 2. Preferential reaction site to attack on CH₃I by Au[−] and Au₂[−].