Journal of Molecular Structure: THEOCHEM 899 (2009) 18–24

Contents lists available at ScienceDirect

Journal of Molecular Structure: THEOCHEM

journal homepage: www.elsevier.com/locate/theochem

Dehydrohalogenation versus dehydrogenation in reaction of Au^+ with CH_3Cl: A theoretical study

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ARTICLE INFO

Article history:
Received 22 October 2008
Received in revised form 27 November 2008
Accepted 2 December 2008
Available online 13 December 2008

Keywords:
Dehydrohalogenation
Dehydrogenation
Gold cation
Methyl chloride

ABSTRACT

The reaction of Au^+ (^1S, ^3D) with CH_3Cl has been investigated at B3LYP and CCSD(T) levels of theory. The reaction pathways of both HCl- and H_2-elimination were identified on the singlet surface, whereas only H_2-elimination pathway was found on the triplet surface. The calculated results indicate that HCl-elimination is energetically much more favorable than H_2-elimination. Two reaction pathways were identified for HCl-elimination: (a) $Au^+ + CH_3Cl \rightarrow Cl–Au^+–CH_3 \rightarrow ClAuH^+–CH_2 \rightarrow (HCl)–Au^+–CH_2 \rightarrow HCl + AuCH_2^+$; (b) $Au^+ + CH_3Cl \rightarrow H–Au^+–CH_2Cl \rightarrow Au^+–CH_2(HCl) \rightarrow HCl + AuCH_2^+$. Pathway a has activation energy barrier of 25.2 kJ/mol at CCSD(T) level, while pathway b is barrierless. In addition, formation of other possible products ($AuCl^+$, AuCl, AuH^+ and AuH) has also been discussed. All the results of this study well rationalized the experimental observations.

1. Introduction

Halogenated methanes are the simplest substrates for studies on the competition between the C–H and C–X (X=F, Cl, Br and I) bond activation by metal ions. Many investigations of gas phase reactions of metal cations with methyl halides have provided insight into C–X bond activation processes [1–7]. In these studies, only halogen-atom transfer products were observed for the reactions of group 2–5 and lanthanide cations with methyl fluoride [1,5], whereas only HCl- and HBr-elimination channels were reported for the reactions of Au^+ with CH_3Cl [2] and CH_3Br [2,6]. Recently, by using inductively coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer, Bohme and co-workers surveyed the room-temperature reactions of CH_3F with 46 atomic transition metal and main-group cations [8]. The results of this study show that the F-transfer channel is the only product channel for early transition metal cations, whereas such product channel was not observed for late metal cations. Instead, H_2 and HF eliminations were observed for some late 5d transition metal cations, such as Os^+, Ir^+ and Pt^+. Again, for Au^+, only HF-elimination was observed. Very recently, Bohme et al. theoretically investigated the reactions of CH_3Cl and CH_3F with Pt^+ [9]. The results of their study show that such reactions are typical multi-channel and multi-step reactions. The calculated reaction mechanisms and potential energy surfaces indicate that H_2-elimination is energetically more favorable than HX-elimination. Based on their study, we speculate that the H_2-elimination channel should also be possible for Au^+ when it reacts with methyl halides, but this channel may have high kinetic activation energy barrier and cannot be observed at low-energy condition. To elucidate the reaction of Au^+ with CH_3X and to compare it with the case of Pt^+, herein, we explored the reaction of Au^+ with CH_3Cl. This reaction was first investigated by Wilkins et al., using Fourier transformation mass spectrometry in 1987 [2]. In their experiment, the dominant product channel was observed to be HCl-elimination (96%), while the $Au(CH_3Cl)^+$ association complex was a minor channel (4%). In 2002, Schwarz et al., re-examined this reaction by using Fourier transformation ion cyclotron (FTICR) spectrometer [10]. Similarly, HCl-elimination was also found as dominant channel (95%), but minor formation of AuH (5%) was also observed. In addition, some possible complexes formed in the reaction have been theoretically calculated, but the reaction mechanism and potential energy surfaces have not been investigated. Wilkins et al., proposed two possible mechanisms for the elimination of HCl [2]:

(1) $Au^+ + CH_3Cl \rightarrow Cl–Au^+–CH_3 \rightarrow ClAuH^+–CH_2 \rightarrow (HCl)–Au^+–CH_2 \rightarrow HCl + AuCH_2^+$
(2) $Au^+ + CH_3Cl \rightarrow H–Au^+–CH_2Cl \rightarrow ClAuH^+–CH_2 \rightarrow (HCl)–Au^+–CH_2 \rightarrow HCl + AuCH_2^+$

In the first mechanism, Au^+ inserts into the C–Cl bond, followed by the migration of an α-hydrogen onto the metal and subsequent

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doi:10.1016/j.theochem.2008.12.002

loss of HCl, giving $AuCH_2^+$ ions. In the second mechanism, Au^+ inserts into the C–H bond, followed by an α-Cl migration and loss of HCl. The two mechanisms have been theoretically confirmed by the study on the reactions of Pt^+ with CH_3F and CH_3Cl. In fact, mechanism (1) was also found in our recent study for the reactions of main group cations As^+ and Bi^+ with CH_3F [11]. Our present calculations also confirmed the mechanism (1) for the case of Au^+. However, mechanism (2) was not identified. Instead, we found another mechanism which is also initiated by C–H bond insertion, but followed by H-transfer back to Cl atom and subsequent loss of HCl from carbon atom, not from the metal center. In this study, our calculations provided an almost complete understanding of the entitled reaction.

2. Computational method

The hybrid density functional theory (DFT) method B3LYP [12,13] was employed to fully optimize the geometries of all the stationary points. The standard all-electron basis set 6-311+G** [14] was used for C, H and Cl atoms. The recently introduced correlated consistent basis set aug-cc-pvdz-pp of Peterson et al. [15] was used for Au^+. The aug-cc-pv*n*z-pp (*n*=D, T, Q, 5) basis sets employ a small-core relativistic pseudopotential where the 5s, 5p, 5d and 6s electrons of Au^+ are treated explicitly in the valence space. These basis sets have been shown to be of high quality when they were used on heavy atoms [16]. Harmonic vibration frequencies were calculated at the same level, both to characterize the stationary points and to estimate the contributions of zero-point vibration to relative energies. The intrinsic reaction coordinate (IRC) calculations were performed to track the reaction pathways. To obtain more reliable energetics, single point calculations were performed using CCSD(T) [17] method with the same basis and the relative energies obtained at this level were also corrected with the zero-point energies calculated at B3LYP level. It should be pointed out that the basis set superposition errors (BSSE) were not considered in the above calculations, since BSSE corrections are generally necessary for some systems in which weak interactions, such as hydrogen-bond or non-bonding molecular interactions, are concerned. For reaction systems, especially when large basis sets are used, the BSSE can be neglected. All calculations were carried out with Gaussian98 program package [18].

3. Results and discussions

Table 1 lists the bond dissociation energies (BDEs) [19,20] and the enthalpies of formation [9] of the relevant neutral molecules and ions. The thermochemistries of some product channels are deduced from these data and also list in Table 1 to compare with the calculated results. Apparently, compared with the results obtained at B3LYP level, the results obtained at CCSD(T) level agree better with the deduced data. One may note that the biggest difference between the deduced and our calculated results arises from the formation of $CH_3 + AuCl^+$. It should be pointed out that the bond energy for Au^+–Cl is not an experimental result, but a previously calculated value using CCSD(T) method with Stuttgart pseudo-potential basis set [10].

To fully understand the reaction of Au^+ with CH_3Cl, the reaction pathways were searched for both singlet ground state ($5d^{10}$,^1S) and triplet exited state ($5d^96s^1$, ^3D) of Au^+. On the singlet surface, two reaction pathways leading to HCl-elimination and one pathway leading to H_2-elimination were identified. They are demonstrated in Fig. 1 as a, b and c, respectively. On the triplet surface, only H_2-elimination pathway was found. The geometries of the stationary points on this surface are shown in Fig. 2. The potential energy profiles of the above pathways obtained at CCSD(T) level are given in Figs 3 and 4.

3.1. Elimination of HCl

3.1.1. Reaction pathway a on singlet surface

The initiation of this pathway is the association of Au^+ with the chlorine atom of CH_3Cl to form the complex ^{1}IM1 which lies below the reactants by 196.1 kJ/mol. As shown Table 1, this complex is the most stable intermediate on all the surfaces and this is consistent with the calculation of Schwarz et al. [10]. ^{1}IM1 has C_s symmetry and the C–Cl bond stretches from 1.806 Å in free CH_3Cl to 1.859 Å. The Mulliken charges on Au and Cl are 0.45 and 0.44, respectively. This implies significant electron-transfer from chlorine to Au atom. NBO analysis for this complex shows a strong donor–accepter interaction between the empty 6s orbital of Au and the lone-paired p_x orbital of Cl. Therefore, besides the electrostatical interaction, the donor–accept interaction should also largely accounts for the remarkable stability of such complex.

The next step of this pathway is the insertion of Au^+ into the C–Cl bond to form the insertion intermediate ^{1}IM2 which has relative energy of −103.8 kJ/mol, with respect to the entrance reactants. This step undergoes through the insertion transition state ^{1}TS1. As ^{1}TS1 locates below the reactants by 50.7 kJ/mol, the C–Cl bond insertion is kinetically barrierless process. NBO analysis for ^{1}TS1 indicates that the breakage of C–Cl bond can be attributed to the strong back-donation of 5d lone-paired electrons of Au^+ to the anti-bonding orbital of C–Cl bond and such interaction can be denoted as $5d_{xy}(Lp) \rightarrow \sigma*(C–Cl)$.

Flowing ^{1}IM2, an α-hydrogen can migrate from the carbon atom to Au atom, via ^{1}TS2, to form the structure ^{1}IM3 in which both the chlorine and hydrogen atom locate on the metal center. As shown in Fig. 1, ^{1}TS2 lies above the reactants by 17.3 kJ/mol. The higher energy of this transition state than ^{1}TS1 is not surprising, because it involves formation of multiple bonds. The geometry of ^{1}IM3 is so close to that of ^{1}TS2 that the CCSD(T) calculation placed ^{1}IM3 very slightly above ^{1}TS1 in energy, although B3LYP optimization defined it as a local minimum.

Via ^{1}TS3, ^{1}IM3 can convert to ^{1}IM4 with a small barrier of 7.1 kJ/mol. Since ^{1}TS3 has the higher energy than both ^{1}TS1 and ^{1}TS2, this step is the rate-determining step and the activation barrier of this step is 25.2 kJ/mol, relative to the entrance reactants. In ^{1}IM4, Au atom bonds to CH_2 by a π bond and a σ bond and both of them are doubly occupied. Although the Au–Cl distance is long as 2.445 Å,

Table 1
The available bond dissociation energies (BDEs, kJ/mol), enthalpies of formation (Δ_fH^0, kJ/mol) at 298 K, the deduced and calculated reaction enthalpies (Δ_rH, kJ/mol).

Bonds	BDE	Species	Δ_fH^{0a}	Products	Δ_rH	Δ_rH_{B3LYP}	$\Delta_rH_{CCSD(T)}$
H–CH_2Cl	420.8[a]	CH_3Cl	−84.0	$^1AuCH_2^+$ + HCl	−13.6	1.8	−7.6
Cl–CH_3	351.5[a]	CH_2	387.9	$^2AuCl^+$+CH_3	220.5	171.5	168.8
Au^+–CH_2	392.9[a]	HCl	−92.6	$^2AuCl^+$+CH_2Cl	210.6	202.0	212.5
Au^+–Cl	131.0[b]	CHCl	334.4	–	–	–	–
Au^+–H	210.2[c]	–	–	–	–		–

[a] Taken from Ref. [9].
[b] Taken from Ref. [10].
[c] Taken from Ref. [20].