

Experimental and Theoretical Studies of Diatomic Gold Halides

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The diatomic gold halides AuX are studied by means of Fourier-transform ion cyclotron resonance mass spectroscopy and ab initio theory at a quasi-relativistic CCSD(T) level of theory. A thermokinetic approach is used to determine the bond-dissociation energies of neutral AuCl, AuBr, and AuI as well as cationic AuI⁺, i.e., $D_0(\text{Au-Cl}) = 66 \pm 3$ kcal/mol, $D_0(\text{Au-Br}) = 50 \pm 5$ kcal/mol, as well as the brackets $52 \text{ kcal/mol} < D_0(\text{Au-I}) < 64$ kcal/mol and $54 \text{ kcal/mol} < D_0(\text{Au}^+\text{-I}) < 66$ kcal/mol at 0 K. These values allow an evaluation of previous experimental and theoretical data concerning diatomic gold halides. (J Am Soc Mass Spectrom 2002, 13, 485–492) © 2002 American Society for Mass Spectrometry

The properties of diatomic gold halides AuX (X = F – I) have been subject of numerous theoretical investigations because gold bears a local maximum of relativistic effects, thereby providing a benchmark to test relativistic techniques in quantum chemistry [1]. The experimental characterization of the gaseous gold halides is more difficult [2], however, and only recently decisive experimental measurements of some spectroscopic properties of AuF [3, 4], AuCl [5–7], AuBr [5], and AuI [8] have been published. As far as experimental determinations of the bond dissociation energies (BDEs) of AuX diatomics are concerned, only some extrapolations from spectroscopy [6, 8] and a few ion/molecule bracketing data are available [9, 10]. In marked contrast, numerous theoretical studies appeared on these species [11–17]. However, also the theoretical predictions show a considerable spread (Table 1).

In this study, Fourier-Transform mass spectrometry is used to perform experiments aimed at a determination of the BDEs of the neutral and cationic diatomic gold halides. These experimental studies are complemented by ab initio calculations employing the coupled cluster method as well as density functional theory (DFT).

Experimental Details

All experiments were performed using a Spectrospin CMS 47X Fourier Transform ion cyclotron (FTICR) spectrometer, described in more detail elsewhere [18]. In brief, Au⁺ cations were generated by laser desorption/ionization of a gold target and transferred by an array of electric focusing lenses to the FTICR cell situated in a 7 Tesla magnetic field. Then, Au⁺ was thermalized with pulsed-in argon gas, mass-selected, and reacted with the neutral reagents as indicated below at typical pressures between 10⁻⁹ and 10⁻⁸ mbar. Unless mentioned otherwise, all reactions described here followed pseudo-first order kinetics. In the determination of reaction rate constants (k_r), the respective ion-gauge sensitivities [19] as well as calibration factors [20] were considered. Gas-kinetic collision rates (k_c) were derived from the capture theory [21], and used to evaluate the associated reaction efficiencies defined as $\phi = k_r/k_c$. Explicit kinetic modeling of the Au⁺/CH₃Cl system was performed by an iterative processing of the underlying kinetic equations with the condition $k_r \leq k_c$ as the only restriction.

Computational Details

Ab initio calculations were performed using the Gaussian 98 program [22] at the CCSD(T) level. For gold, the basis set adjusted by Schwerdtfeger et al. [23] was contracted to give a (311111111/3111111/41111/111) set (starting from the functions with the highest exponent in each basis-type) and used with a Stuttgart pseudo-potential [24] which comprises a [Kr]4d¹⁰4f¹⁴

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Dedicated to our friend and cooperation partner Peter B. Armentrout.

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Table 1. Literature values of experimental and theoretical *BDEs* (in kcal/mol) of diatomic AuX species

	Experimental	Theory ^a
AuF	73 [10] ^b	67 [14], 71 [12], 76 [15], 77 [15]
AuF ⁺		18 [12]
AuCl	> 60 [9] ^b , 72 [6], ^c 78 [5] ^{cd}	58 [16]
AuBr	>36 [9] ^b , 68 [6] ^c	53 [16]
AuI	66 [8] ^c	48 [44], 49 [16]
AuI ⁺	> 56 [9] ^b	

^a“Best” levels chosen and converted to D_0 at 0 K.

^bValue obtained from bracketing experiments conducted at room temperature without acknowledging thermal effects, see text.

^cDerived from microwave spectroscopy.

^dDerived in ref. [6] from the data in ref. [5].

core and $5s^25p^65d^{10}6s^1$ valence space. For fluorine and chlorine, the augmented, correlation-consistent triple zeta basis sets of Dunning [25, 26] were used with the most diffuse f-functions removed. For bromine and iodine, the Stuttgart pseudopotential combinations were altered to give (211111/21111/11/1) and (211111/111111/11/1) sets for Br and I, respectively, with basis sets, pseudopotentials, and extra d- and f functions taken from refs. [16], [27], and [28]. In the course of these studies, also some calculations at the MP 2 level were performed including Mulliken population analysis.

Potential energy curves were calculated at r_e and $r_e = \pm 0.05, \pm 0.1, \pm 0.15, \pm 0.2, \pm 0.3, \pm 0.35, \pm 0.5$ and $+1.0$ and $+1.5$ Å. Rovibrational constants were derived using the numerical Numerov-Cooley procedure as implemented in Molcas3 [29]. Dissociation energies were calculated relative to the energies of the separated atoms. For AuX neutrals, spin-orbit corrections of the dissociation energies were derived from the atomic spin-orbit splittings of the Group 17 atoms [30].

In order to estimate thermal contributions to the experimental reaction energies, DFT calculations were performed initially using the SDD basis set for all atoms, as implemented in Gaussian 98. The calculations were then repeated using 6-311+G* basis sets on all atoms, except for Au, Br, and I (SDD-aug) where two extra d-functions were added to Br and I in order to mimic a 6-311+G* set. These calculations were performed with complete geometry optimizations and frequency analysis with the B3LYP functional as implemented in Gaussian 98.

Results

In this paper, we apply the thermokinetic method developed by Bouchoux and coworkers [31] to investigate the thermochemistry of the diatomic gold halides AuX and their cations. To this end, halide abstractions by the gold cation Au⁺ from various halides R—X are monitored by means of Fourier-Transform mass spectrometry. From an heuristic point of view, it is worth to note that the choice of the reactants used in the experiments was guided by the computational results which also assist the interpretation of the measurements.

Computed properties of neutral and cationic AuX diatoms

Table 2 displays some properties of neutral AuX and of the corresponding AuX⁺ cations for X = F – I as computed at the CCSD(T) level of theory. While we do not want to overrate the accuracy of the absolute *BDEs* computed at this level of theory, some qualitative conclusions can be drawn and particularly the relative trends appear reliable. Thus, the neutral gold(I) halides behave as expected for metal halides in that $D_0(\text{Au-X})$ decreases monotonically from X = F to X = I concomitant with increasing bond lengths and decreasing vibrational frequencies. As expected, the bonding of the neutral gold halides can be described as a mixture of ionic and covalent contributions, which is reflected by the trend of the positive charge on gold according to population analysis, i.e., $q_{\text{Au}} = 0.70$ in AuF, 0.48 in AuCl, 0.30 in AuBr, and 0.27 in AuI.

In marked contrast, the *BDEs* of the cationic species strongly rise from only 20.7 kcal/mol for AuF⁺ to 50.6 kcal/mol in the case of AuI⁺. To a first approximation, this unusual behavior can be ascribed to the valence configuration of the Au⁺ cation which bears a quasi-closed $6s^25d^{10}$ shell. Thus, covalent binding to the halide radical would require excitation to the 6p-manifold which is very unfavorable energetically. Consequently, the bonding situation in AuX⁺ is best described as the interaction of a Au⁺ cation with a halide radical (Au⁺···X). Such a type of bonding is governed by ion/induced-dipole and charge-transfer interactions (both Au²⁺···X⁻ and Au⁺···X⁺) leading to the strongest

Table 2. Properties of neutral and cationic gold halides calculated at the CCSD(T) level of theory

	AuF	AuCl	AuBr	AuI
r_e (Å)	1.930	2.226	2.339	2.506
D_0 (kcal/mol)	62.0	58.9	51.0	43.4
ω_e (cm ⁻¹)	550.8	372.7	260.6	208.7
	AuF ⁺	AuCl ⁺	AuBr ⁺	AuI ⁺
r_e (Å)	1.867	2.226	2.351	2.521
D_0 (kcal/mol)	20.7	31.2	40.7	50.7
ω_e (cm ⁻¹)	645.1	307.6	248.7	184.7

bond for the largest, least electronegative halogen iodine. Nevertheless, it is interesting to note that despite of the weaker bonding, the fundamental frequency of AuF^+ exceeds that of the neutral counterpart, pointing to notable covalent contributions to the bonding of the AuX^+ cations. Notwithstanding, the electrostatic description as $\text{Au}^+\text{X}^{\cdots}$ is chemically insightful and can directly explain the unusual trend of the bond strengths in the AuX^+ cations for $\text{X} = \text{F} - \text{I}$. This bonding mnemonic is further supported by population analysis which reveals that the spin density in AuX^+ is mostly located on the halogens, i.e., $\rho_{\text{X}} = 0.88$ in AuF^+ , 0.93 in AuCl^+ , 0.92 in AuBr^+ , and 1.02 in AuI^+ , respectively.

In addition, the ionization energies of diatomic AuX species are calculated as $IE(\text{AuF}) = 11.05$ eV, $IE(\text{AuCl}) = 10.39$ eV, $IE(\text{AuBr}) = 9.82$ eV, and $IE(\text{AuI}) = 9.18$ eV, respectively, at this level of theory. Note, however, that the computed $IE(\text{Au}) = 8.95$ eV is underestimated at this level in comparison to the experimental value of $IE(\text{Au}) = 9.2255$ eV [32].

With regard to the experimental studies, the computational results imply that except of AuI^+ (see below), AuX^+ cations are unlikely to be formed via X-abstraction from any substrate R-X by Au^+ under thermal conditions. For example, even $D(\text{Br-Br}) = 51$ kcal/mol is too large to allow for the formation of AuBr^+ ; hence, this reaction was not examined for obvious reasons. Further, the formation of AuX^+ is unfavorable because the IE of the remaining radical R^{\cdot} is likely to be lower than the computed $IE(\text{AuX})$. Accordingly, the formation of neutral AuX concomitant with R^+ is expected and indeed observed experimentally (see below). Of course, AuX^+ cations with $\text{X} = \text{F} - \text{Br}$ can be formed under more energetic conditions, such as electron ionization of gaseous gold halides [9, 33–35].

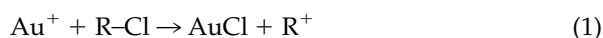
Experimental Results

In 1994, bracketing methods predicted $BDE(\text{Au-F}) \approx 73$ kcal/mol [10] which is in excellent agreement with computational predictions ($D_0 = 70.7$ kcal/mol [12]). While we originally intended to measure all four gold halides, a lack of suitable new substrates prevented any further work on AuF , beyond that done already. We note in passing, however, that the speculation of Saenger and Sun [36] that AuF^+ might contribute to their reported AuF spectrum can be ruled out, because the computed fundamental vibrations differ largely (Table 2).

Therefore, we concentrate on the higher gold halides with $\text{X} = \text{Cl}, \text{Br},$ and I . Qualitative information on these species is available from the early studies of Chowdhury and Wilkins [9] who examined the reactions of Au^+ with some haloalkanes (see Table 1). Here, we intend to refine and extend these studies by appropriate choice of the substrates in conjunction with application of thermokinetic criteria.

AuCl. Mass-selected, thermalized Au^+ was reacted with various chlorine-containing substrates (Table 3). Formation of the corresponding carbocations concomitant with neutral AuCl prevails in most cases. For chlorobenzene, electron transfer is observed to predominate which is trivial, however, because $IE(\text{C}_6\text{H}_5\text{Cl}) = 9.07$ eV [38] is significantly smaller than $IE(\text{Au}) = 9.2255$ eV [37]. Formation of cationic gold compounds is only observed for CH_3Cl and CH_2Cl_2 which afford the corresponding gold-carbene cations AuCH_2^+ [9, 38] and AuCHCl^+ , respectively, concomitant with losses of neutral HCl .

In order to apply the thermokinetic method of Bouchoux and coworkers [31], the chloride abstraction reaction (eq 1) is considered in more detail.



Under thermal conditions, the energetics of the left-hand side of eq 1 are given by the sum of the heats of formation $\Delta_f H(\text{Au}^+)$ and $\Delta_f H(\text{R-Cl})$, while the right-hand side is given by the sum of $\Delta_f H(\text{AuCl})$ and $\Delta_f H(\text{R}^+)$, where all values except $\Delta_f H(\text{AuCl})$ are available in ref. [37]. In the thermokinetic method, it is assumed that a very exothermic reactions occurs at collision rate while a very endothermic process is unmeasurably slow. In the intermediate range close to thermoneutrality, a sigmoid function of the type $\phi_{rel} = a/[1 + \exp(b \cdot (\Delta E - c))]$ can be used to describe the energy dependence of ϕ , where ϕ_{rel} is the normalized reaction efficiency, ΔE includes thermochemical quantities of the species involved, and $a - c$ are variable parameters of which a is a scaling factor, b describes the slope of the sigmoid curve, and c shifts the position of the onset [31]. In the present case, ΔE is chosen such that c corresponds to $BDE(\text{Au-Cl})$. Applying this scheme to the reactions shown in Table 3 for $\text{X} = \text{Cl}$, a graph is obtained (Figure 1) from which $BDE(\text{Au-Cl}) = 69 \pm 2$ kcal/mol can be derived (parameters: $a = 0.95$, $b = 0.53$ mol/kcal, $c = BDE = 69.3$ kcal/mol).

So far, we deliberately used the somewhat vague term BDE instead of D_0 , D_{298} etc. This is done because processes such as eq 1 which involve an atomic species on only one side of the equation bear non-negligible thermal contributions $\Delta E_{thermal}$ which favor the right-hand side of eq 1 provided that also R is polyatomic. With respect to the specific set of reactions considered here, these thermal corrections were calculated using the B3LYP approach. These contributions, defined as $\Delta E_{thermal} = E_{0K} - G_{298K}$, are also included in Table 2. On average, $\Delta E_{thermal}$ amounts to 3 ± 1 kcal/mol [39], and accordingly, we arrive at $D_0(\text{Au-Cl}) = 66 \pm 3$ kcal/mol at 0 K.

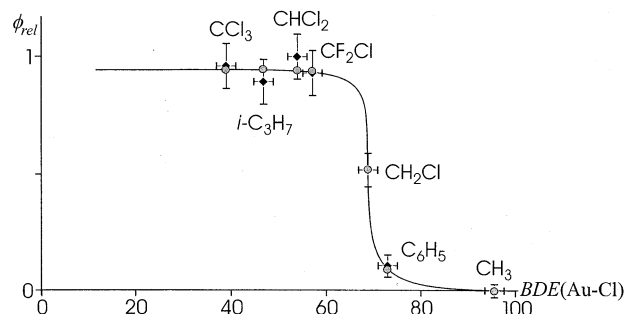
AuBr. Application of the same strategy for various bromine compounds (Table 3) is somewhat less straightforward, because we have not found suitable substrates which show intermediate reactivity. Either,

Table 3. Efficiencies (ϕ in %) ^a and products^b in the reactions of several chlorine- and bromine-containing molecules R-X (X = Cl, Br) with Mass-selected Au⁺ cations

	$\Delta_f H(R-X)^c$	ϕ	Products	BR ^b	$\Delta_f H(R^+)^c$	$\Delta E_{thermal}^d$
CH ₃ Cl ^e	-17.5	31	AuCl + CH ₃ ⁺ AuCH ₂ ⁺ + HCl AuH + CH ₂ Cl ⁺	(0.00) (0.95) (0.05)	261 229	-1.3
CH ₂ Cl ₂	-22.9	50	AuCHCl ⁺ + HCl AuCl + CH ₂ Cl ⁺	(0.20) (0.80)	229	-2.4
CHCl ₃	-25.0	77	AuCl + CHCl ₂ ⁺	(1.00)	212	-4.7
CCl ₄	-23.2	74	AuCl + CCl ₃ ⁺	(1.00)	199	-3.4
CF ₂ Cl ₂	-114.1	72	AuCl + CF ₂ Cl ⁺	(1.00)	126	-3.3
<i>i</i> -C ₃ H ₇ Cl	-34.6	69	AuCl + C ₃ H ₇ ⁺ H ₂ /AuCl + C ₃ H ₅ ⁺	(0.94) (0.06) ^e	191	-2.9
C ₆ H ₅ Cl	13.0	86	AuCl + C ₆ H ₅ ⁺ Au + C ₆ H ₅ Cl ⁺	(0.10) (0.90)	269	-3.8
CH ₃ Br ^{fg}	-5.5	10	AuBr + CH ₃ ⁺ AuCH ₂ ⁺ + HBr	(0.00) (1.00)	261	-1.2
CH ₂ Br ₂	0	87	AuBr + CH ₂ Br ⁺	(1.00)	224	-2.4
CHBr ₃	5.7	92	AuBr + CHBr ₂ ⁺	(1.00)	224	-3.6
CF ₃ Br	-155	<1 ^h	AuBr + CF ₃ ⁺	(1.00) ^h	95	-3.2
C ₂ H ₅ Br	-14.9	74	Au(HBr) ⁺ + C ₂ H ₄ Au(C ₂ H ₄) ⁺ + HBr AuBr + C ₂ H ₅ ⁺	(0.20) (0.45) (0.35)	216	-2.4
C ₃ H ₅ Br ⁱ	11.4	77	AuBr + C ₃ H ₅ ⁺ H ₂ /AuBr + C ₃ H ₃ ⁺	(0.85) (0.15) ^e	226	-2.6
<i>t</i> -C ₄ H ₉ Br	-32	84	AuBr + C ₄ H ₉ ⁺ H ₂ /AuBr + C ₄ H ₇ ⁺	(0.87) (0.13) ^e	166	-4.6
C ₆ H ₅ Br	24.9	44	AuBr + C ₆ H ₅ ⁺ Au + C ₆ H ₅ Br ⁺	(0.18) (0.82)	269	-3.8

^aGiven as $\phi = k_r/k_c$ with an estimated error of ± 30 ^bBranching ratios given in brackets.^cHeats of formation at 298 K taken from Ref. [37].^dTerms used to correct 298 K to 0 K values defined as $\Delta E_{thermal} = \Delta_r G_{298} - \Delta_r H_0$ determined by B3LYP calculations^eNature of the neutral product(s) is unclear.^fWhile the [Au,C,H₃X]⁺ products reported in Ref. [9] were also observed in our studies, these are entirely due to consecutive reactions, see text.^gProduct distributions similar to those reported in Ref. [9] are observed when thermalization of Au⁺ by pulsed-in argon buffer gas is omitted.^hOnly observed when thermalization of Au⁺ by pulsed-in argon buffer gas is omitted.ⁱAllyl bromide.

bromide abstraction occurs very fast (R = CH₂Br, CHBr₂, C₃H₅, *t*-C₄H₉) or it is rather slow (R = C₆H₅), if not absent (R = CH₃, CF₃). While halide abstraction occurs to only 35% with bromoethane (R = C₂H₅), this particular value is obscured by competing 1,2-dehydrohalogenations leading to the gold-containing cations Au(C₂H₄)⁺ and Au(HBr)⁺, respectively (Table 3). It is worthwhile to discuss the effect of competition in some

**Figure 1.** Relative Reaction Efficiencies for Chloride Abstraction from R-Cl Compounds by Mass-selected Au⁺ Cations as a Function of the Derived BDE(Au-Cl).

more detail. By definition, ion/molecule reactions cannot proceed faster than the collision limit, such that competing processes may significantly diminish the relative efficiency of the reaction of interest. Taken to the extreme, even thermodynamically and kinetically allowed processes may be suppressed completely, if other, even more favorable pathways can occur. Hence, competition may heavily disturb the thermokinetic method of Bouchoux et al. [31] which relies on overall reaction efficiencies. Note that competition by alternative channels is much less severe in the kinetic method due to Cooks and coworkers [40], where two mutually competing channels are directly compared with each other. In the same manner, one might therefore argue that also bromide abstraction from bromobenzene is masked by the competing electron transfer (see Table 3). Fortunately, however, the reaction of CF₃Br sets a clear borderline which supports the present analysis. Thus, formation of CF₃⁺ from Au⁺/CF₃Br in analogy to eq 1 was only observed when thermalization of Au⁺ was omitted, and under these conditions it ceased at about 8% conversion with the remaining Au⁺ not reacting at

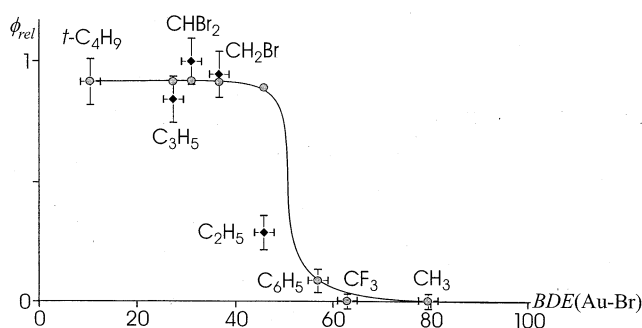


Figure 2. Relative Reaction Efficiencies for Bromide Abstraction from R–Br Compounds by Mass-selected Au^+ Cations as a Function of the Derived $BDE(\text{Au-Br})$. Note that the entry for $\text{C}_2\text{H}_5\text{Br}$ is too low due to effectively competing reactions, see text.

all with CF_3Br . Accordingly, formation of neutral AuBr from the $\text{Au}^+/\text{CF}_3\text{Br}$ system is assigned as an endothermic process.

Excluding $\text{R} = \text{C}_2\text{H}_5$ from consideration, the thermo-kinetic method suggests $BDE(\text{Au-Br}) = 53 \pm 4$ kcal/mol where the increased error bar is due to the lack of an intermediate point which also caused the use of the same parameter b as for $\text{X} = \text{Cl}$ (Figure 2). Accordingly, we arrive at $D_0(\text{Au-Br}) = 50 \pm 5$ kcal/mol after conversion to 0 K as described above.

AuI/AuI^+ . Chowdhury and Wilkins [9] already reported that treatment of Au^+ with iodomethane can be

used to generate AuI^+ cations in the gas phase (eq 2). However, due to the occurrence of the diatomic gold halide as an ionic product, the thermokinetic approach cannot be used unambiguously anymore because the formations of AuI and AuI^+ compete for various groups R (Table 4). Of course, the AuI/AuI^+ ratio might be used for the determination of $IE(\text{R})$ by means of Cooks' kinetic method [40], but in the present context we are not interested in this quantity. Further, several other reactions take place for the iodine compounds, and hence we have to return to the simple bracketing technique.



When thermal contributions are acknowledged, occurrence of eq 2 implies $D_0(\text{Au}^+-\text{I}) > 54$ kcal/mol, while formation of C_6H_5^+ upon reacting Au^+ with iodobenzene suggests $D_0(\text{Au}-\text{I}) > 40$ kcal/mol. However, both processes provide only lower limits. Unfortunately, consideration of consecutive reactions of AuI^+ does not allow for a refinement of these brackets. For example, the reaction of AuI^+ with CH_3I affords an $[\text{Au},\text{C},\text{H}_3,\text{I}]^+$ species with unknown energetics. An upper limit is given by the previously described [41] occurrence of eq 3 under thermal conditions which suggests $D_0(\text{Au}^+-\text{I}) \leq D_0(\text{Au}^+-\text{C}_2\text{H}_4) \sim 69$ kcal/mol.

Table 4. Efficiencies (ϕ in %)^a and products^b in the reactions of (a) several iodine-containing molecules R-I with mass-selected Au^+ cations and (b) of arene ligands L with mass-selected AuI^+

	$\Delta_f H_{298}(\text{R-X})^c$	ϕ	Products	Br^b	$\Delta_f H_{298}(\text{R}^+)^c$	$\Delta E_{\text{thermal}}^d$
(a) $\text{Au}^+ + \text{R-I} \rightarrow \text{Products}$						
$\text{CH}_3\text{I}^{\text{ef}}$	3.7	20	$\text{AuI} + \text{CH}_3^+$	(0.00)	261	-1.2
			$\text{AuI}^+ + \text{CH}_3$	(0.85)		-2.2
			$\text{AuCH}_3^+ + \text{I}$	(0.10)		-1.0
			$\text{AuCH}_2^+ + \text{HI}$	(0.01)		
$\text{C}_2\text{H}_5\text{I}^+$	-2.2	56	$\text{AuH} + \text{CH}_2\text{I}^+$	(0.04)	216	-1.6
			$\text{Au}(\text{HI})^+ + \text{C}_2\text{H}_4$	(0.50)		
			$\text{AuI} + \text{C}_2\text{H}_5$	(0.20)		
			$\text{Au}(\text{C}_2\text{H}_4)^+ + \text{HI}$	(0.10)		
			$\text{AuH} + \text{C}_2\text{H}_4\text{I}^+$	(0.15)		
$i\text{-C}_3\text{H}_7\text{I}$	-9.9	79	$\text{Au} + \text{C}_2\text{H}_5\text{I}^+$	(0.05)	191	-1.8
			$\text{Au}(\text{C}_3\text{H}_6)^+ + \text{HI}$	(0.01)		
			$\text{AuI} + \text{C}_3\text{H}_7^+$	(0.60)		
			$\text{H}_2/\text{AuI} + \text{C}_3\text{H}_5^+$	(0.14)		
			$\text{Au} + \text{C}_3\text{H}_7\text{I}^+$	(0.25)		
$\text{C}_6\text{H}_5\text{I}$	39.4	40	$\text{AuI} + \text{C}_6\text{H}_5^+$	(0.20)	269	-3.8
			$\text{AuC}_6\text{H}_5^+ + \text{I}$	(0.10)		
			$\text{Au} + \text{C}_6\text{H}_5\text{I}^+$	(0.70)		
(b) $\text{AuI}^+ + \text{L} \rightarrow \text{Products}$						
$\text{C}_6\text{H}_5\text{Cl}$			$\text{AuI}(\text{C}_6\text{H}_5\text{Cl})^+$	(0.30)		
			$\text{AuI} + \text{C}_6\text{H}_5\text{Cl}^+$	(0.70)		
C_6H_6			$\text{AuI}(\text{C}_6\text{H}_6)^+$	(0.80)		
			$\text{AuI} + \text{C}_6\text{H}_6^+$	(0.20)		
$1,3\text{-C}_6\text{H}_4\text{F}_2$			$\text{AuI}(\text{C}_6\text{H}_4\text{F}_2)^+$	(0.98)		
			$\text{AuI} + \text{C}_6\text{H}_4\text{F}_2^+$	(0.02)		

^{a-d}See footnotes a–d of Table 2.

^eWhile the $[\text{Au},\text{C},\text{H}_3,\text{I}]^+$ product reported in Ref. [9] was also observed in our studies, it is attributed to consecutive reactions, see text.

^fA product distribution similar to that reported in Ref. [9] is observed when thermalization of Au^+ by pulsed-in argon buffer gas is omitted.

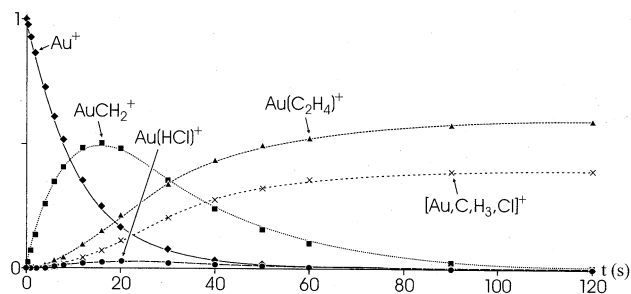
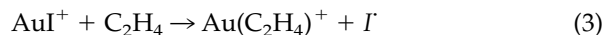


Figure 3. Time dependence of the ionic species in the reaction of mass-selected Au^+ with chloromethane ($p = 4 \cdot 10^{-9}$ mbar); dots: experimental data, lines: kinetic fit.



Note, however, that the experimental estimation of $D_0(\text{Au}^+-\text{C}_2\text{H}_4)$ was inter alia based on eq 3, and can therefore not serve as an independent reference for the determination of $D_0(\text{Au}^+-\text{I})$. Instead, the value given above refers to several theoretical studies which suggest $D_0(\text{Au}^+-\text{C}_2\text{H}_4)$ between 65 and 75 kcal/mol [41–43]. Further, in the case of eq 3 the thermal correction due to involvement of an atomic species works in the opposite direction, and accordingly we derive a bracket of 54 kcal/mol $< D_0(\text{Au}^+-\text{I}) < 66$ kcal/mol.

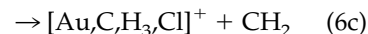
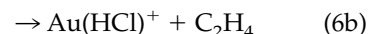
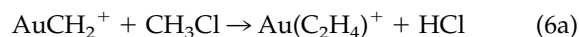
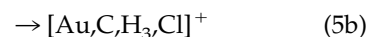
In order to gain further insight into the thermochemistry of gold iodide [44], a different strategy was pursued. To this end, cationic AuI^+ was reacted with neutral arenes L having appropriate ionization energies $IE(\text{L})$, in order to observe a competition between electron transfer eq 4a and mere association eq 4b.



For L = benzene ($IE = 9.24$ eV), eq 4b predominates, whereas electron transfer according to eq 4a prevails for L = chlorobenzene ($IE = 9.07$ eV). By reference to thermokinetic approaches [31, 40], $IE(\text{AuI}) = 9.15 \pm 0.1$ eV is derived accordingly being in certainly fortuitous match with the CCSD(T) value of 9.18 eV. While the association eq 4b may obscure electron transfer according to eq 4a, the derived figure is further supported by the weakness of eq 4a with L = 1,3-difluorobenzene ($IE = 9.33$ eV) for which also association is much slower than for L = C_6H_6 and $\text{C}_6\text{H}_5\text{Cl}$. With $IE(\text{AuI}) = 9.15 \pm 0.1$ eV being rather close to $IE(\text{Au}) = 9.2255$ eV, it is also concluded that $BDE(\text{Au}-\text{I}) \sim BDE(\text{Au}^+-\text{I})$ or, more precisely, 52 kcal/mol $< D_0(\text{Au}-\text{I}) < 64$ kcal/mol.

The $\text{Au}^+/\text{CH}_3\text{Cl}$ system. While we mostly deal with thermochemical aspects of the primary halide abstraction reactions, one particular detail of the consecutive reactions in the $\text{Au}^+/\text{CH}_3\text{Cl}$ system is worth more detailed consideration. Figure 3 shows the time evolution of the gold-containing product ions upon reacting

Au^+ with CH_3Cl ; for the sake of clarity, minor carbocationic products are omitted (see Table 2). Thus, the gold-carbene cation AuCH_2^+ is formed first in eq 5a, and then $\text{Au}(\text{C}_2\text{H}_4)^+$ as well as $[\text{Au,C,H}_3,\text{Cl}]^+$ are generated which persist with a more or less constant ratio at longer reaction times. Except for a minor channel leading to $\text{Au}(\text{HCl})^+$, a more or less superimposable graph has been reported by Chowdhury and Wilkins [9], nicely demonstrating the reproducibility of ICR kinetics. Quite different are the interpretations of these data, however, as far as the origin of the $[\text{Au,C,H}_3,\text{Cl}]^+$ species is concerned. In particular, Chowdhury and Wilkins attributed the formation of $[\text{Au,C,H}_3,\text{Cl}]^+$ cation to a direct association (eq 5b).



Kinetic modeling of the time dependencies of the ionic species is incompatible with eq 5b, however, in that $[\text{Au,C,H}_3,\text{Cl}]^+$ is obviously formed in a consecutive reaction. Further, the primary product AuCH_2^+ is unlikely to afford $[\text{Au,C,H}_3,\text{Cl}]^+$ upon reaction with CH_3Cl , because that would require loss of a free CH_2 fragment (eq 6c). Therefore, the products generated from AuCH_2^+ are considered next. Equation 6a generates a $[\text{Au,C}_2\text{H}_4]^+$ species which is identified as the genuine ethene complex $\text{Au}(\text{C}_2\text{H}_4)^+$ because rapid formation of $\text{Au}(\text{C}_2\text{D}_4)^+$ is observed upon addition of C_2D_4 [45]. Formation of $[\text{Au,C,H}_3,\text{Cl}]^+$ via eq 7 can be ruled out, however, because the $\text{Au}(\text{C}_2\text{H}_4)^+$ trace remains constant at longer reaction times though CH_3Cl is leaked-in continuously and C_2H_4 is practically absent, thus suggesting $BDE(\text{Au}^+-\text{CH}_3\text{Cl}) \gg BDE(\text{Au}^+-\text{C}_2\text{H}_4) \approx 69$ kcal/mol [41–43]. Instead, kinetic analysis of the data reveals that formation of $[\text{Au,C,H}_3,\text{Cl}]^+$ can fully be explained by involvement of the $\text{Au}(\text{HCl})^+$ cation generated in eq 6b, even though this product never exceeds a few percent of all ions. In fact, due to its low abundance, Chowdhury and Wilkins might have neglected it as a minor channel. Notwithstanding, formation of $\text{Au}(\text{HCl})^+$ as a reactive intermediate via eq 6b and its depletion in eq 8 can account for the $[\text{Au,C,H}_3,\text{Cl}]^+$ species which contributes to about 40% of all products at long reaction times. Such a kinetic phenomenon that an “almost invisible” intermediate

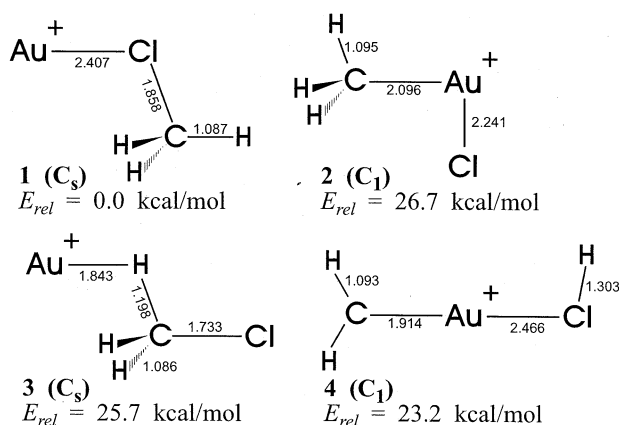
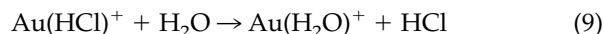


Figure 4. Structures of $[Au,C,H_3,Cl]^+$ isomers calculated at the B3LYP/SDD level of theory (selected bond lengths given in Å).

determines the outcome of a major pathway in ion/molecule reactions has been analyzed previously [46], and it can occur if the rate constant for the generation of the intermediate is much lower than those of its consecutive reactions. In the present case, the kinetic fits suggest that k_{6b} is ca. 18 times lower than k_8 .



For the sake of completeness, we note that in addition to eq 5–8, also eq 9 and 10 were observed due to the presence of water in the background of the high-vacuum system. Accordingly, $D_0(Au^+-HCl) < D_0(Au^+-H_2O) \approx 38$ kcal/mol [41, 42, 47, 48] is implied; our B3LYP calculations predict $D_0(Au^+-HCl) = 30$ kcal/mol. This result is by no means unusual as, for example, also the proton affinity of HCl is significantly lower than that of water [49]. In turn, however, it is fair to ask, why $Au(HCl)^+$ is formed at all in eq 6 if ethene is that much a better ligand for ionized gold. A rationale is provided by inspection of the thermochemistry of eq 6. Thus, with $D_0(Au^+-CH_2) \approx 89$ kcal/mol as suggested by Metz and coworkers [38], formation of the ethene complex $Au(C_2H_4)^+$ in eq 6a is predicted to be 63 kcal/mol exothermic, and eq 6b is still exothermic by about 20 kcal/mol. Hence, formation of $Au(HCl)^+$ can be attributed to the large amount of energy released upon C–C bond formation in the reaction of $AuCH_2^+$ with CH_3Cl .

So far, we deliberately used the formula $[Au,C,H_3,Cl]^+$ which shall only reflect the elemental composition of the ionic species without any structural specification. In order to gain some structural insight, several conceivable $[Au,C,H_3,Cl]^+$ species were examined by means of exploratory B3LYP calculations (Figure 4). The association complex 1 with gold attached to the chlorine atom corresponds to the most stable species ($E_{rel} = 0.0$ kcal/mol). Three other isomers are located ca. 25 kcal/mol higher in energy and correspond to the

C–Cl bond insertion species 2, the ion/dipole complex with gold binding to one of the hydrogen atoms 3, and the carbene complex 4. Despite some uncertainty in the level of theory used, it is quite safe to assume that isomer 1 is formed in the Au^+/CH_3Cl system. This conclusion fully confirms the previous assignment of structure 1 by Chowdhury and Wilkins, based on the observation that $[Au,C,H_3,Cl]^+$ undergoes ligand exchange to yield AuL^+ and neutral CH_3Cl when reacted with benzene and acetonitrile, respectively [9]. At the B3LYP level of theory, $D_0(Au^+-CH_3Cl)$ is computed as 42 kcal/mol which is consistent with the significantly larger affinities of gold to benzene and acetonitrile, respectively [41, 42]. Finally, also the occurrence of eq 10 is consistent with structure 1 as well as $D_0(Au^+-CH_3Cl) > D_0(Au^+-H_2O) \approx 38$ kcal/mol [41, 42, 47, 48].

Conclusions

Guided by theoretical studies, experimental measurements of gold halides lead to an improved set of $BDEs$ for neutral gold(I) halides as well as the AuI^+ cation, i.e. $D_0(Au-Cl) = 66 \pm 3$ kcal/mol, $D_0(Au-Br) = 50 \pm 5$ kcal/mol, as well as the brackets 52 kcal/mol $< D_0(Au-I) < 64$ kcal/mol, and 54 kcal/mol $< D_0(Au^+-I) < 66$ kcal/mol at 0 K. With respect to the previous experimental and theoretical data (Table 1), the following conclusions can be drawn. (i) The earlier experimental data of Chowdhury and Wilkins [9] are fully consistent with the present results. (ii) Inclusion of entropy effects is essential for a quantitative analysis of ion/molecule reactions when an atomic species is involved on only one side of the reaction. (iii) The values derived from vibrational spectroscopy are somewhat overestimated. (iv) Most of the computational approaches slightly underestimate the bond strengths.

Despite of the improved accuracy of the present experiments, the error margins are still considerable, and further refinement would be desirable. In particular, the fact that $D_0(Au-Br)$ is at the lower limit of $D_0(Au-I)$, though within the error margins, appears surprising. Further, it needs to be stressed that the thermokinetic methods used here crucially rely on the accuracy of the auxiliary thermochemistry used for anchoring, and changes in the heats of formation of the carbocationic species involved would, of course, also affect the derived $BDEs(Au-X)$.

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