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Kinetics of radiative/termolecular associations in the low pressure regime: reactions of bare Au^+ with benzene

Detlef Schröder[a,*], Reuben Brown[b], Peter Schwerdtfeger[b], Helmut Schwarz[a]

[a]*Institut für Organische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany*
[b]*Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand*

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Abstract

Consecutive ion/molecule reactions of gold cation Au^+ with (deuterated) benzene are examined by Fourier-transform mass spectrometry. Primary products upon reacting Au^+ with C_6H_6 are due to charge transfer to afford $C_6H_6^{+\cdot}$ concomitant with neutral gold as well as ligand association to yield the $Au(C_6H_6)^+$ complex. Subsequent reactions of so-formed $Au(C_6H_6)^+$ with benzene result in exclusive formation of the corresponding bisligated complex $Au(C_6H_6)_2^+$. In contrast to a previous report by Ho and Dunbar [Int. J. Mass Spectrom. 182/183 (1999) 175], occurrence of charge transfer from benzene to $Au(C_6H_6)^+$ affording $C_6H_6^{+\cdot}$ concomitant with neutral $Au(C_6H_6)$ is rigorously excluded. Our results are supported by ab initio calculations which predict a strong interaction in the $Au(C_6H_6)^+$ cation, whereas neutral $Au(C_6H_6)$ is best described as a loose van der Waals complex; i.e. $D_0(Au^+–C_6H_6) = 61.1$ kcal/mol versus $D_0(Au–C_6H_6) = 2.0$ kcal/mol. Interestingly, the reaction kinetics for the sequential additions of benzene to cationic gold show irregularities which point to a non-negligible role of excess energy in consecutive bimolecular associations at low pressures. (Int J Mass Spectrom 203 (2000) 155–163) © 2000 Elsevier Science B.V.

Keywords: Benzene; Gold; Ligand association; Radiative processes

1. Introduction

In the last decade, Dunbar and c-oworkers have demonstrated how measurements of radiative association kinetics in the low pressure regime (typically $<10^{-6}$ mbar) can be used as a complementary and versatile method for obtaining accurate binding energies of gaseous metal–ligand complexes [1,2]. In conjunction with appropriate modeling, it is now possible to derive absolute binding energies from such association kinetics [3]. Reactions of bare metal cations M^+ with benzene represent one of the most prominent examples of the virtue of the method [1–3]. At low pressures, association of a metal ion with benzene can occur by means of either radiative association or termolecular processes. Common to both phenomena is the formation of an encounter complex $M(C_6H_6)^{+}*$ which can be assumed to occur at the gas kinetic collision rate k_f because the interaction potential is entirely attractive [4]. In the absence of stabilization mechanisms, however, the encounter complexes $M(C_6H_6)^{+}*$ will undergo rapid unimolecular decay with the backward rate constant k_b, because the whole potential energy of the isolated

* Corresponding author. E-mail: schw0531@www.chem.tu.berlin.de

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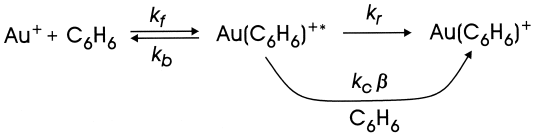

Fig. 1. Kinetic scheme for the radiative and termolecular association of Au^+ with benzene. Variables: k_f, bimolecular rate constant for the formation of the encounter complex $Au(C_6H_6)^+$*; k_b, rate constant for unimolecular dissociation of metastable $Au(C_6H_6)^+$*; k_r, unimolecular rate constant for radiative stabilization of $Au(C_6H_6)^+$*; k_{c3}, rate constant for collisional stabilization of $Au(C_6H_6)^+$* by a gas of the density β acting as a third body.

reactants is still available as excess internal energy of $M(C_6H_6)^+$*. Stabilization, that is formation of long-lived $M(C_6H_6)^+$ ions, can occur by means of either emission of photons from the excited encounter complex with the rate constant k_r or depletion of internal energy in termolecular collisions (either with another benzene molecule or with unreactive buffer gases) with the associated rate constant $k_{c\beta}$, where β stands for the number density of the termolecular collision partner(s). The $M(C_6H_6)^+$ species thus formed can undergo further ligand associations to form the corresponding bisligated $M(C_6H_6)_2^+$ complexes as final reaction products; genuine $M(C_6H_6)_n^+$ complexes with $n > 2$ have not been observed so far [5]. Although radiative association is a strictly bimolecular process, collisional stabilization involves termolecular phenomena. Thus, measurements of the reaction kinetics at different pressures allow to extract the relevant rate constants k_r and $k_{c\beta}$. The resulting kinetic scheme is shown in Fig. 1. Over the years, Dunbar's method has been applied to numerous cases including various metals and ligands, and reasonable agreement with results obtained by other methods lends confidence to the validity of the approach [2].

As an extension, association kinetics have also been used to derive thermodynamic data for bisligated complexes $M(L)_2^+$ formed in consecutive associations [6]. Again, thermal behavior and extrapolation to zero pressure are assumed to provide accurate data in these cases [2,3]. Here, we provide evidence that the latter assumptions are not generally justified; in fact, they appear quite inappropriate in some cases. Instead, a careful analysis of the reaction kinetics is a prerequisite for the concise interpretation of the experimental data. To this end, the reactions of bare Au^+ cation with benzene are studied by means of Fourier-transform mass spectrometry. The experiments are complemented with a theoretical treatment of $Au(C_6H_6)^+$, $Au(C_6H_6)_2^+$, as well as neutral $Au(C_6H_6)$ using density functional theory [7].

2. Experimental and theoretical methods

The experiments were performed with a Spectrospin CMS 47X Fourier transform ion cyclotron resonance mass spectrometer which has been described elsewhere [8,9]. In particular, the instrument has been used in several previous studies of cationic gold complexes [10–12]. In brief, Au^+ cations were generated by laser desorption/laser ionization [13,14] of a gold target in the external ion source of the instrument. The ions were transferred to the analyzer cell which is located within a superconducting magnet (max. field strength 7.05 tesla). After subsequent mass selection of $^{197}Au^+$ and thermalization with pulsed-in argon buffer gas, the ion's reactivity was studied by introducing neutral benzene and other reagent gases by means of leak and/or pulsed valves. The experimentally observed ion intensities were corrected for the noise level as well as contributions arising from the natural abundance of ^{13}C. The experimental second-order rate constants were evaluated assuming the pseudo first-order kinetic approximation after calibration of the measured pressure and acknowledgement of the ion gauge sensitivities [15,16]; the error of the absolute rate constants is $\pm 30\%$, and the ion temperature is assumed as 298 K [17]. Great care is required during the mass selection in order to avoid unintentional kinetic excitation of the ions of interest. As demonstrated previously, these conditions are well-suited to probe ion/molecule reactions occurring at room temperature [10,17–19]. All operations including data accumulation and processing were performed using an ASPECT 3000 minicomputer connected to a personal computer running under WINDOWS NT. The Stuttgart [20] basis set and pseudopotential were used for gold and the double zeta basis sets for carbon and

hydrogen by Dunning and Hay [21,22], all without modifications as implemented in GAUSSIAN 98 [23]. Similar to our previous computational studies of gold compounds [11,12,24,25], full geometry optimizations and frequency analysis were performed by using Becke's 3-parameter fit with the Lee/Yaug/Parr correlation functional [26]. For all molecules a variety of geometries were considered but only the listed structures were found to be minima.

3. Motivation

Our study was initiated by a recent paper of Ho and Dunbar about the association kinetics of Au^+ with benzene [27]. This system had already been studied earlier by Chowdhury and Wilkins [28], and in a different context, we had also previously examined the $Au(C_6H_6)^+$ cation [10]. General consensus is that in the encounter of gold cation with benzene ligand association according to

$$Au^+ + C_6H_6 \rightarrow Au(C_6H_6)^+ \quad (1a)$$

$$\rightarrow C_6H_6^{+\cdot} + Au \quad (1b)$$

competes with electron transfer from neutral benzene to gold in reaction 1b.

In this respect, the Au^+/C_6H_6 system is a special case compared to almost all other transition-metal cations, simply due to the fact that relativistic effects cause the ionization energy of gold, IE(Au) = 9.226 eV [29], to be almost identical to IE(C_6H_6) = 9.244 eV [29], whereas IE(M) < IE(C_6H_6) holds true for all other *d* elements except mercury and zinc [29]. In congruence with many other monoligated metal cations [2,3,5], however, $Au(C_6H_6)^+$ undergoes subsequent association with neutral benzene to form the corresponding bisligated complex according to

$$Au(C_6H_6)^+ + C_6H_6 \rightarrow Au(C_6H_6)_2^+ \quad (2a)$$

$$\rightarrow C_6H_6^{+\cdot} + Au(C_6H_6) \quad (2b)$$

To our surprise, Ho and Dunbar [27] reported that the major source for formation of ionized benzene in the Au^+/C_6H_6 system is due to reaction (2b) rather than reaction (1b); in fact, their best fits were obtained with $k_{1b} = 0$. Assuming that thermal ions are probed, this conclusion immediately implies that IE($Au(C_6H_6)$) $\gtrsim$ IE(C_6H_6) = 9.244 eV $\approx$ IE(Au) = 9.226 eV. Considering that the interaction between gold and benzene is already quite strong in the cationic species $Au(C_6H_6)^+$—ab initio calculations predict bond dissociation energies $D_0(Au^+–C_6H_6)$ of about 65 kcal/mol [10,30]—this would mean that the neutral is equally or even more strongly bound, i.e. $D_0(Au–C_6H_6) \gtrsim 65$ kcal/mol. Such a magnitude of D_0 appears rather unprecedented when comparing the favorable interaction of the formally closed-shell Au^+ cation ($6s^05d^{10}4f^{14}$) with the polarizable benzene ligand to that of benzene with a neutral gold atom having a $6s^15d^{10}4f^{14}$ configuration. In fact, loss of the electrostatic component in the neutral complex in conjunction with the assumingly repulsive nature of the singly occupied 6s orbital on gold rather suggests that neutral $Au(C_6H_6)$ behaves as a weakly bound van der Waals complex [31]. Similarly, the bond dissociation energies of Au^+ cation to other ligands like ethene or phosphine largely exceed those for neutral gold [18]. These arguments imply $D_0(Au–C_6H_6) \ll D_0(Au^+–C_6H_6)$ and are thus in direct contradiction to the conclusion arrived at in [27]. In view of the distinguished role of gold-benzene complexes [30], we decided to subject the Au^+/benzene system to a more detailed experimental investigation combined with a computational study aimed at resolving this disturbing discrepancy.

4. Results and discussion

The data points in Fig. 2 show the relative abundances of the ionic species observed upon reacting thermalized Au^+ with fully deuterated benzene; C_6D_6 was used to rigorously exclude any interferences which could arise from residual hydrocarbons possibly present as background contaminants in the mass spectrometer. The inset in Fig. 2 demonstrates a clean exponential decay of the Au^+ precursor ion with increasing reaction time, thereby lending support to assume effective ion thermalization. The products

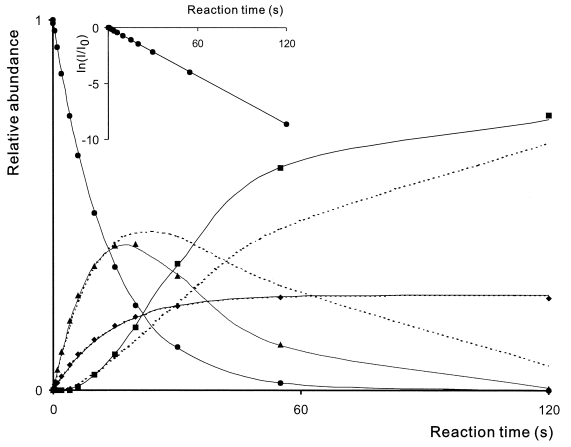

Fig. 2. Data points show the time dependencies of Au^+ (closed circle), $Au(C_6D_6)^+$ (closed triangle), $C_6D_6{}^{+\cdot}$ (closed diamond), and $Au(C_6D_6)_2{}^+$ (closed square) in the presence of 2.8×10^{-9} mbar hexadeuterobenzene. It is important to note that the lines do not connect the data points, but represent the results of two different kinetic models: (1) a conventional kinetic scheme according to Fig. 1 (dotted line) and (2) a scheme assuming an additional thermalization mechanisms for $Au(C_6D_6)^+$ according to Fig. 4 (solid line); see the text for further details. The inset shows a logarithmic plot of the Au^+ intensity (closed circle) vs. time; the linear decay indicates effective thermalization of the Au^+ precursor under the experimental conditions.

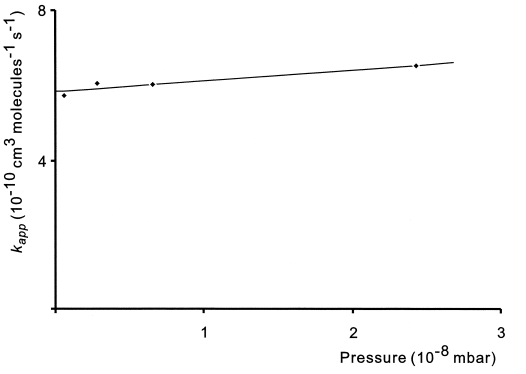

Fig. 3. Apparent rate constant of reaction (3) as a function of C_6D_6 pressure. The solid line is the best fit for the data with $k_{3,app} = k_{r3} + k_{c3}\beta = 5.8 \times 10^{-10}$ cm^3 molecules^{-1} s^{-1} + 1.2×10^{-19} cm^6 molecules^{-2} s^{-1} × $p(C_6D_6)$.

correspond to the deuterated variants of reactions (1) and (2), i.e. $Au(C_6D_6)^+$, $C_6D_6{}^{+\cdot}$, and $Au(C_6D_6)_2{}^+$ are observed

$$Au^+ + C_6D_6 \rightarrow Au(C_6D_6)^+ \quad (3a)$$

$$\rightarrow C_6D_6^{+\cdot} + Au \quad (3b)$$

$$Au(C_6D_6)^+ + C_6D_6 \rightarrow Au(C_6D_6)_2^+ \quad (4a)$$

$$\rightarrow C_6D_6^{+\cdot} + Au(C_6D_6) \quad (4b)$$

Analysis of the reaction kinetics provides a branching ratio of k_{3a}:k_{3b} = 75:25 which differs somewhat from the 94:6 ratio of k_{1a}:k_{1b} reported by Chowdhury and Wilkins [28]. Because a higher yield of the charge transfer according to reaction (3b) might be indicative of excess kinetic energy of the Au^+ precursor, we took great care on this issue and applied various measures to further thermalize any remaining hot Au^+. However, neither when applying excessive argon pulses nor upon variation of the benzene pressure or use of argon as an additional buffer gas significant changes in the branching ratios of k_{3a}:k_{3b} were observed. Further, we have demonstrated recently that gold cations can indeed be thermalized efficiently to room temperature under the experimental conditions [17,19]. Besides our use of deuterated benzene, a possible rationale for the differences are mass discrimination effects operative in the intensity measurements [18,19]. Irrespective of this minor discrepancy, the kinetics clearly reveal that electron transfer occurs as a primary channel in the reaction of Au^+ with benzene, i.e. the quasilinear decay of the Au^+ signal at low conversions coincides with the increases of the $Au(C_6D_6)^+$ and $C_6D_6{}^{+\cdot}$ channels. As ligand association according to reaction (3a) must involve radiative and/or termolecular stabilization mechanisms, the pressure dependence of the apparent rate constant $k_{3,app}$ was examined (Fig. 3). In the pressure regime studied, termolecular association is a minor contributor, and upon extrapolation to zero pressure, $k_{r,3} = (5.8 \pm 1.7) \times 10^{-10}$ cm^3 molecules^{-1} s^{-1} is obtained which corresponds to about (60 ± 20)% of the gas-kinetic collision rate. Failure to reach full collision rate is indeed expected in this case because electron transfer between gold and benzene is practically thermoneutral such that forward and backward reactions have qualitatively similar probabilities. More precisely, the difference ΔIE = 0.018 eV in favor of gold implies that the reverse rate $k_{3b'} = k_{3b}$

$\exp(-\Delta\Delta G/RT) \approx 2k_{3b}$ at 298 K [32], thus adding up near to collision frequency for the sum of reactive and unreactive collisions. Due to involvement of $k_{3b'}$ and the weak slope of the apparent rate constant as a function of pressure, k_{c3} is more difficult to determine; an estimate for termolecular stabilization is $k_{c3} = (1.2 \pm 0.8) \times 10^{-19}$ cm^6 molecules^{-2} s^{-1}.

In order to directly probe the occurrence of the charge-transfer process (4b) suggested by Ho and Dunbar [27], $Au(C_6D_6)^+$ generated in reaction (3a) was mass-selected an trapped in deuterobenzene. Proper mass selection provided, electron transfer to afford $C_6D_6{}^{+\cdot}$ was not observed at all under these conditions. This result clearly rules out the occurrence of reaction (4b) to any notable extent. Interestingly, however, the apparent rate constant of reaction (4a) shows dependencies from the mode of ion preparation as well as reaction time; the obvious pressure dependence of $k_{4a,app}$ was not examined. These experiments were performed under the same conditions as those illustrated in Fig. 2 which can thus be used as a direct reference for the experiments described in the following. When $Au(C_6D_6)^+$ was mass selected from the Au^+/C_6D_6 system at a short reaction time, e.g. 5 s, and trapped in deuterobenzene, the initial apparent rate constants $k_{4a,app}$ were significantly lower than those obtained when mass selecting the $Au(C_6D_6)^+$ precursor after longer reaction times, e.g. 20 s, or at longer trapping times, respectively. Likewise, enhanced apparent rate constants $k_{4a,app}$ were found when argon was added to the reaction mixture as an additional buffer gas either via a pulsed valve or continuously leaked-in. Overall, these variations in $k_{4a,app}$ span a factor of about 2. Although we have not attempted to quantitatively analyze the details of the obviously occurring termolecular processes, the different experiments agree upon a maximal value of $k_{4a,max} = (3.8 \pm 1.2) \times 10^{-10}$ cm^3 molecules^{-1} s^{-1} at $p(C_6D_6) = 2.8 \times 10^{-9}$ mbar. Qualitatively, the variation of $k_{4a,app}$ indicates that—even though the sequence begins with thermalized gold cations—the initially formed, long-lived $Au(C_6D_6)^+$ ions contain excess internal energy which is subsequently quenched in further collisions and/or by radiative relaxation. A similar conclusion is derived upon modeling the data points shown in Fig. 2 by different kinetic schemes. The decay of the Au^+ signal as well as the rise of the $C_6D_6{}^{+\cdot}$ intensity can be reproduced accurately using the rate constant k_3 and the branching ratio k_{3a}:k_{3b} = 75:25 given previously. However, irrespective of the choice of k_{3a} and $k_{4a,app}$, the data for $Au(C_6D_6)^+$ and $Au(C_6D_6)_2{}^+$ deviate significantly from the modeled curves. For example, the dotted lines in Fig. 2 are based on a model which is able to reproduce the initial increase of $Au(C_6D_6)^+$, but fails to apply for longer reaction times. The fit used for the dotted lines in Fig. 2 applied apparent rate constants of $k_3 = 0.0718$ s^{-1}, k_{3a}:$k_{3b} = 0.26$, and $k_{4a,app} = 0.023$ s^{-1} at a C_6D_6 pressure of 2.8×10^{-9} mbar. In turn, when larger values of $k_{4a,app}$ are chosen in order to achieve agreement for long reaction times, the $Au(C_6D_6)^+$ channel does not reach the correct maximum and the modeled $Au(C_6D_6)_2{}^+$ channel increases much too early (this model is not included in Fig. 2). Obviously, use of a single value of $k_{4a,app}$ is inappropriate in the modeling. Although related phenomena have previously been noted by Lin and Dunbar [6] in consecutive associations of bare Cr^+ ions, no quantitative analysis of these interesting observations had been attempted.

If an additional time dependence of $k_{4a,app}$ is assumed, however, a reasonable fit of the experimental data is obtained (solid lines in Fig. 2). Here, the quenching is phenomenologically described in an exponential form as $k_{4a,app} = k_{4a,max} \times e^{-(k_q \times t_r)}$, where k_q is a net quenching constant and t_r is the reaction time. The actual fit for the solid lines uses the same set of parameters as for the dotted lines, except that $k_{4a,app}$ is expressed as $k_{4a,app} = k_{4a,max}\, e^{-(k_q \times t_r)}$ with $k_{4a,max} = 0.05$ s^{-1} and $k_q = 0.05$ s^{-1}. In extension to Fig. 1, the resulting kinetic scheme (Fig. 4) assumes that the long-lived adduct ions formed initially contain excess internal energy. Some clarification is necessary in order to differentiate the internal energy contents. The notation $Au(C_6D_6)^+$* is adopted from Fig. 1 and refers to the encounter complexes which have not undergone any kind of stabilization. These species contain the full complexation energy as internal energy $E_{int} = D_0(Au^+–C_6H_6)$ and are thus intrinsically metastable. Radiative and/or termolecular processes removing some internal energy lead to

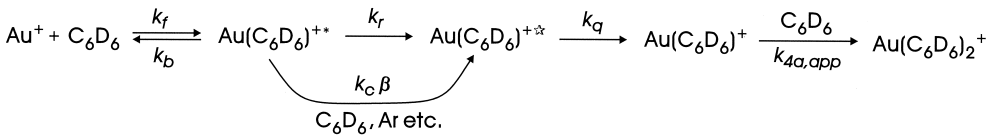

Fig. 4. Simplified illustration of the modified kinetic scheme for the radiative and termolecular association of Au^+ with benzene including an additional quenching rate constant k_q relevant for the formation of the bisadduct $Au(C_6D_6)_2^+$. The notations $Au(C_6D_6)^+$* and $Au(C_6D_6)^{+\star}$ refer to ions of different internal energy contents, see the text. Mathematically, the continuum in terms of internal energy between $Au(C_6D_6)^+$*, $Au(C_6D_6)^{+\star}$, and $Au(C_6D_6)^+$ is expressed as a phenomenological rate constant; see the text for details. For the sake of simplicity, radiative and termolecular processes en route to $Au(C_6D_6)_2^+$ are omitted in the scheme.

complexes which still contain excess internal energy, but with $E_{int} < D_0(Au^+–C_6H_6)$. These ions—though not thermal—are therefore long-lived, i.e. stable within the second timescale of the experiments, and are denoted as $Au(C_6D_6)^{+\star}$. Formation of the bisligated $Au(C_6D_6)_2^+$ adducts by radiative and/or termolecular processes, crucially depends on the internal energy content of the precursor, however, in that association becomes more likely the colder the ions are. Given the magnitude of k_q expressing quenching process of about 0.05 s^{-1}, a combination of radiative and collisional mechanisms in the relaxation of $Au(C_6D_6)^{+\star}$ appears likely. In order to complement the experiments, the cations $Au(C_6H_6)^+$ and $Au(C_6H_6)_2^+$ as well as the neutral complex $Au(C_6H_6)$ were examined theoretically at the B3LYP level of theory (Table 1). The computed structures of $Au(C_6H_6)^+$ are very similar to those reported by Dargel et al. [30], with an almost energetic degeneracy between η^1 and η^2 coordinations. At the B3LYP level of theory, $D_0(Au^+–C_6H_6)$ is computed as 61.1 kcal/mol which also agrees well with the previous results [24,30]. For a further discussion, the reader is referred to the detailed analysis performed in [30]. The structure of the bisadduct $Au(C_6H_6)_2^+$ adopts that of the monoligated complex. The optimized geometry exhibits C_{2h} symmetry with two equally η^2-coordinated benzene ligands surrounding the central gold atom (Fig. 5); η^1 and η^6 coordinations are found higher in energy and bear at least one imaginary mode in frequency analysis leading to the η^2-coordinated system. The computed bond energy amounts to $D_0(C_6H_6Au^+–C_6H_6)$ = 37.8 kcal/mol, i.e. ~60% of the binding energy for the first benzene ligand. In contrast, the geometry of neutral $Au(C_6H_6)$ substantially differs from that of the cationic complexes. Thus, the distance of the gold atom to the nearest carbon atom(s) increases from 2.2 to 2.3 Å in the cationic complexes to almost 2.8 Å in the neutral. The formal η^1 coordination of gold to the aromatic ring is best described as a van der Waals type interaction, i.e. the uncoupled electron is by and large exclusively

Table 1
Calculated total energies E_{tot} and zero point energies ZPE (both in Hartree) of Au, Au^+, C_6H_6, $Au(C_6H_6)^+$, $Au(C_6H_6)$, and $Au(C_6H_6)_2^+$ at the B3LYP level of theory and relevant properties derived therefrom

Species		E_{tot}	ZPVE	Property
Au		−135.755 499 0		
Au^+		−135.408 471 0		IE(Au) = 9.44 eV[a]
C_6H_6		−232.213 506 5	0.101275	
$Au(C_6H_6)^+$ [b]	C_s, η^1	−367.720 275 1	0.102172	$D_0(Au^+–C_6H_6)$ = 61.1 kcal/mol[c]
	C_s, η^2	−367.719 167 1	0.102051	$D_0(Au^+–C_6H_6)$ = 60.5 kcal/mol[c]
$Au(C_6H_6)$	C_s, η	−367.969 005 5	0.101480	$D_0(Au–C_6H_6)$ = 2.0 kcal/mol[c]
				IE(Au–C_6H_6) = 6.88 eV
$Au(C_6H_6)_2^+$	C_{2h}	−599.993 682 5	0.204804	$D_0(C_6H_6Au^+–C_6H_6)$ = 36.8 kcal/mol[c]

[a] The deviation of 0.2 eV from the spectroscopic value gives an estimate for the accuracy of the computational approach.
[b] Similar structures and binding energies have been reported in 24 and 30.
[c] Computed bond dissociation energy at 0 K.

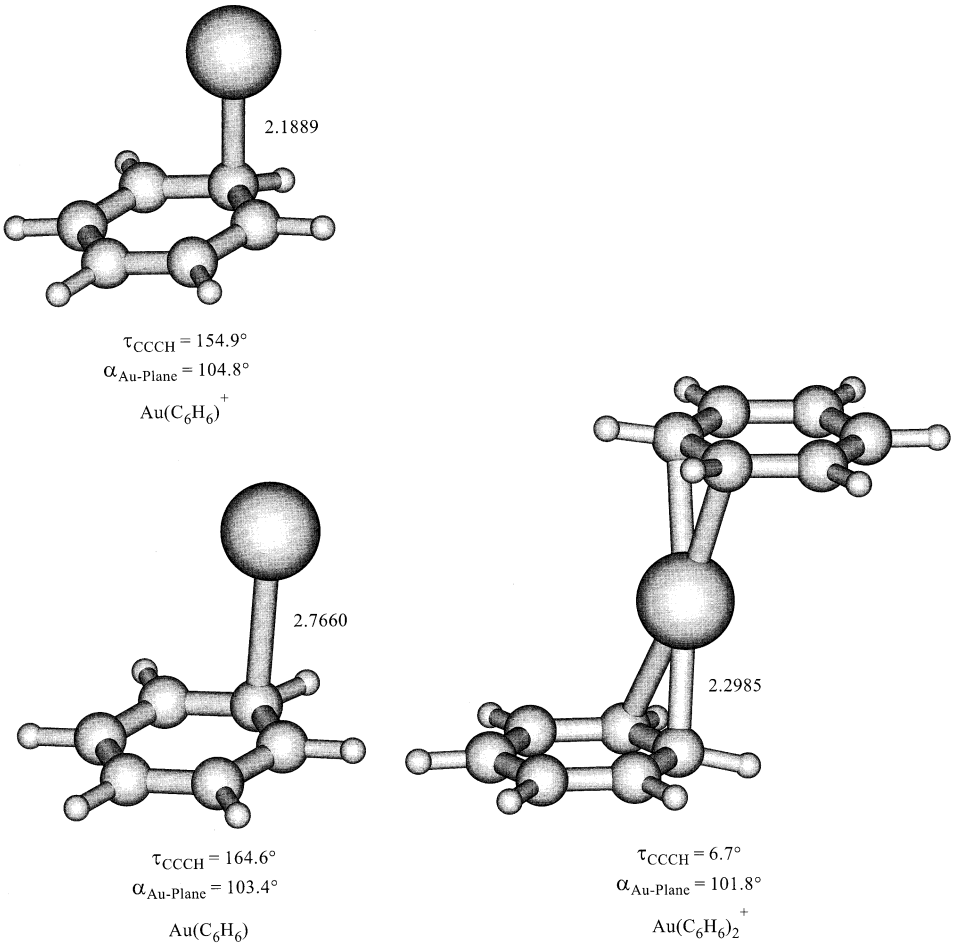

Fig. 5. Optimized structures of $Au(C_6H_6)^+$, $Au(C_6H_6)$, and $Au(C_6H_6)_2^+$ at the B3LYP/SDD level of theory. For the sake of clarity, only the distances (in ansgtrom) of gold to the nearest carbon atom(s), the angle of gold to the plane of the arene ring ($\alpha_{Au\text{-}plane}$), and the dihedron τ_{CCCH} are shown (both in degree). The dihedron τ_{CCCH} reflects the degree of pyramidalization of the carbon(s) attached to gold as a binding partner.

located on gold (spin density: 0.92), and the computed binding energy is rather small, $D_0(Au–C_6H_6) = 2.0$ kcal/mol. Accordingly, the resulting adiabatic $IE(AuC_6H_6) = 6.88$ eV is much below those of benzene and gold. Even though density functional theory does not perfectly describe the dispersive interactions operative in molecules such as neutral $Au(C_6H_6)$ [7], the results clearly support our above expectations for the interaction of neutral gold with a closed-shell arene ligand. In particular, if a low-lying, obviously covalent minimum for neutral $Au(C_6H_6)$ would exist, density functional theory should at least provide a glance of it. However, no indications for such a structure were found despite numerous attempts. For example, a single point calculation of $Au(C_6H_6)$ at the geometry of the $Au(C_6H_6)^+$ cation gives an energy which is more than 70 kcal/mol above the van der Waals-type minimum of the neutral complex.

5. Conclusions

Experimental and theoretical data demonstrate that the previously suggested occurrence of electron transfer from neutral benzene to $Au(C_6H_6)^+$ is invalid. Instead, the reaction of gold cation with benzene follows well-known association kinetics; quite re-

markable is the effectiveness of the radiative stabilization. Although it is beyond our current interest to study the details of the different quenching mechanisms operative in the Au^+/C_6D_6 system, it is to be pointed that consecutive ligand associations in the low-pressure regime must not necessarily obey the simple kinetic scheme as shown in Fig. 1. In fact, modeling of the reaction kinetics with neglect of $Au(C_6D_6)^+$ ions having different internal energy contents might in part explain the erroneous analysis of Ho and Dunbar [27]. Moreover, the present analysis may shed some doubt on other thermochemical properties of bisligated metal complexes derived from association kinetics without explicit appreciation of cooling phenomena in consecutive ligation. This note of caution was also expressed previously by Lin and Dunbar [6] and deserves further attention in studies of radiative associations.

From quite a different, more general point of view, the present results highlight the validity of the previous conclusion that oxidation of gold is dramatically favored by the presence of coordinating organic ligands [18]. Thus, the computed binding energies of neutral and cationic $Au(C_6D_6)^{\cdot/+}$ imply that ionization of gold to the monocationic form is facilitated by more than 2.5 eV in the presence of benzene. Possibly, processing and refinement of gold ores may profit from similarly favorable energetic balances for other organic molecules and solvents.

Acknowledgements

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