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Reactions of Au^+ and Au^- with benzene and fluorine-substituted benzenes

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Abstract

Reactions of gold anions and cations generated by laser desorption/ionization were studied in the FTICR spectrometer. Au^- associated with C_6F_6 to give the novel $Au^-(C_6F_6)$ complex, whose binding energy was estimated to be 24 ± 4 kcal mol^{-1} from analysis of the radiative association (RA) kinetics. Au^+ associated with C_6F_5H to give $Au^+(C_6F_5H)$, with binding energy estimated to be 31 kcal mol^{-1}. Au^+ reacted with C_6H_6 to form the well known $Au^+(C_6H_6)$ and $Au^+(C_6H_6)_2$ complexes. The observation of rapid charge transfer from $Au^+(C_6H_6)$ to C_6H_6 was interpreted as showing that benzene binds more strongly to neutral Au than to Au^+. The neutral Au–C_6H_6 bond is accordingly concluded to be stronger than about 70 kcal mol^{-1}. (Int J Mass Spectrom 182/183 (1999) 175–184) © 1999 Elsevier Science B.V.

Keywords: FTICR mass spectrometry; Gold cations; Gold anions; Ion-molecule reactions; Fluorobenzenes

1. Introduction

There is continuing interest in the gas-phase chemistry of metal ions with organic partners [1–5]. Within this expansive field, the importance of metal-ion interactions with π faces in the broad context of gas phase, condensed phase and biological chemistry has been pointed out [6–8]. Quite a lot of work has been done on benzene reactions with gas-phase cations of small main group [9–18] and first-row transition [19–21] metals. Some work has been reported on heavier metal ions reacting with benzene, for instance Y^+, Nb^+ and Ta^+ [22–26], Ag^+ [27,28], Ag^+ and Cd^+ [29]. Of interest here is the interaction of gold ions with benzene-derived molecules, as representative of the behavior of very heavy metal ions.

Early experimental observations of gas-phase gold cation chemistry were reported by Wilkins' group [30,31]. The ion is typically quite reactive, but simple attachment without further reaction was observed to a few neutrals, including benzene, toluene and mesitylene, and at least in the benzene case, attachment of a second ligand to form the benzene dimer complex was also seen. Schwarz's group has studied gold cation complexation quite extensively by experimental and theoretical approaches [32–36]. Their most recent binding energy assignment for Au^+/benzene is 69 kcal/mol [32]. Au^+/C_6F_6 is more weakly bound than Au^+/H_2O (whose binding energy is 38 kcal/mol)

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Dedicated to the memory of Ben Freiser. His imaginative and wide-ranging research, his insistence on the highest standards in all his work, and his infectious enthusiasm, good nature, and friendship enriched us all.

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according to ligand-exchange observations [33], and its binding energy has been estimated as 34 kcal mol^{-1} [32].

The normal sequence of complexation reactions with aromatic π ligands consists of two successive additions,

$$M^+ + L \rightarrow M^+L \tag{1}$$

$$M^+L + L \rightarrow M^+L_2 \tag{2}$$

With aromatic ligands, other reaction channels competing with these seem to be uncommon, with the exception of the charge transfer

$$M^+ + L \rightarrow M + L^+, \tag{3}$$

which is usually fast if it is exothermic. However, a few reactive transition metals (notably Y^+, Nb^+ and Ta^+ [22–26] and Sc^+ [21]) do undergo other reactions, typically dehydrogenation. Transition metal oxide ions also frequently oxidize benzene [37,38].

Fluorine substitution on the benzene ring has a large and easily understood effect on the bond strength of ionic π complexes. The withdrawal of charge from the π cloud by ring-substituted fluorines reduces the binding strength to cations, and (presumably) increases the binding strength to anions. The effect on cation binding was recently demonstrated in a particularly graphic way for the series of Cr^+ complexes with fluorobenzenes [39], showing a systematic decrease in binding energy of the order of 4 kcal/mol for each additional fluorine on the ring. It is in fact doubtful whether the best Cr^+ binding site is still the π site for pentafluoro- and hexafluorobenzenes, which may prefer to bind the metal ion at an electrostatically favored fluorine site. Moreover, those difluoro and trifluorobenzenes having adjacent fluorines were calculated to have fluorine binding sites with the metal bridging the two fluorines with strengths comparable to the ring binding site. The effect of fluorine substitution on anion binding should be the mirror image of the cation trend, giving stronger anion binding with increasing benzene-ring fluorination, but there has been little study of anionic metal-ion/π complexes and this effect has apparently not been verified experimentally. The fact that binding of Au^- to C_6F_6 was observed in the present study with reasonable binding energy, while no Au^- complex has been observed with less highly fluorinated benzenes, is a qualitative confirmation of the expected enhancement of anion π binding by fluorine substitution.

Little is known about the possibilities for anion attachment to π faces. Clustering of fluoride [40] and chloride [41,42] ions to some aromatics, including some partially fluorinated benzenes, has been studied, but it is considered that these are hydrogen-bound complexes, and they do not seem very relevant to the present (presumably) π-bound complex of Au^-. Transition metal anion complexes, such as carbonyl and cyclopentadienyl complexes, have been shown to interact with π faces [43,44]. We are unaware of any previous binding-energy information for π-bound transition metal anions.

The present work applied the radiative association (RA) kinetics approach to finding quantitative binding energies. This approach has a restricted window of convenient binding energy values, which, depending on temperature and molecular size, is roughly 1–2 eV (25–45 kcal/mol) around room temperature for metal-ion/benzene types of complexes. The substitution of fluorines offered a nice way of bringing the gold-benzene ion complexes into this range. In the case of Au^+, the unsubstituted Au^+/benzene complex is inconveniently strong (~70 kcal/mol), but pentafluoro substitution brought the bond strength to a convenient value for room-temperature study. Conversely, the (unknown) Au^-/benzene complex is presumably very weak, but the hexafluorobenzene complex is sufficiently strongly bound for convenient study by this technique.

2. Methods

2.1. Experiments

The experiments used methods similar to previous work in our laboratory [29]. They were carried out using the Fourier-transform ion cyclotron resonance mass spectrometer equipped with an IonSpec data

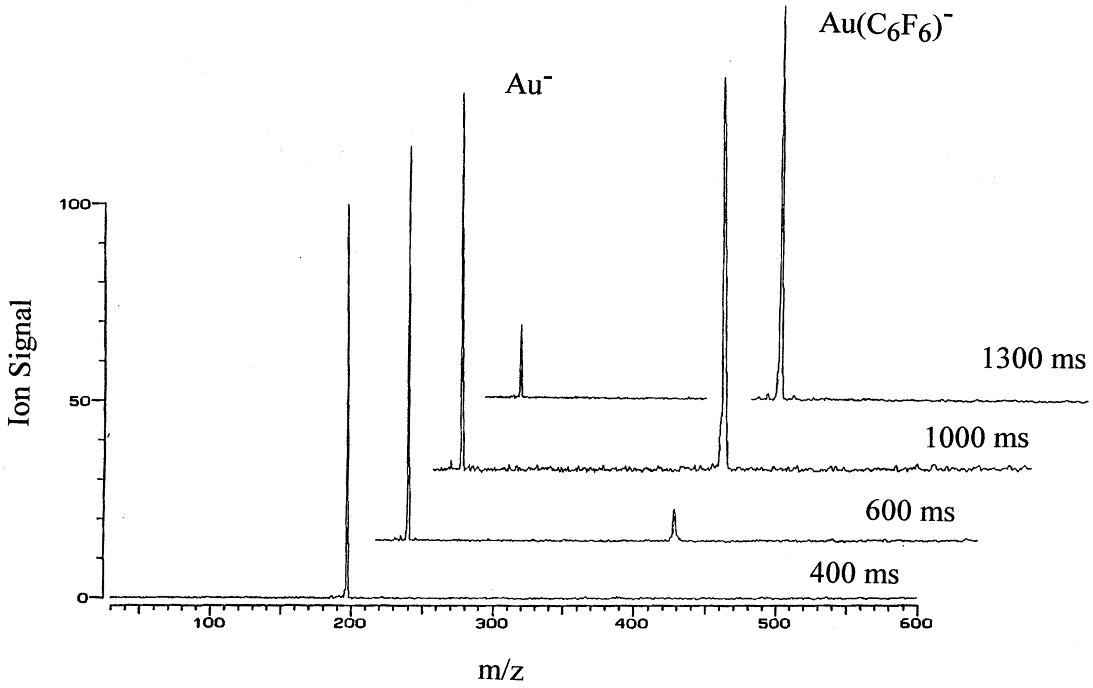

Fig. 1. FTICR spectra showing complexation of Au^- and C_6F_6 at several times following ion formation. 7.7×10^{-7} Torr of C_6F_6.

system. The ions were trapped in a one inch cubical cell with a magnetic field of approximately 1.4 tesla. The metal ions were produced by focusing the 532 nm light pulse (generated by a Nd:YAG laser) onto a gold foil attached to a sample holder near the cell.

The intensities of metal ion and ion complex were monitored as a function of reaction time to derive the association rate constant. Fig. 1 illustrates the mass spectra obtained as a function of time for an association reaction, and Fig. 2 shows a typical kinetic plot of the data. Because the metal ions produced by laser desorption were hot in the beginning, initially they either did not react or reacted slower than the thermalized ions did. Fits to pseudo-first-order kinetics were accordingly made to data points at times after the initial nonthermal behavior had died away.

The neutral pressures were read from the ion pump current. The ion pump was previously calibrated for benzene against a Bayard-Alpert gauge. The pressure calibration is considered to be uncertain by a factor of 1.5.

2.2. Ab initio IR frequencies and intensities

The frequencies and intensities used for Au^-/C_6F_6 were calculated at the Hartree–Fock level with the LANL2DZ basis set, which includes a core pseudopotential for gold. Frequencies were scaled by 0.89 as is known to be appropriate for this level of calculation. Calculations used the GAUSSIAN 92 quantum chemistry package [45].

Recognizing that this is a low level of calculation for such systems, we made a comparison with a similar, better studied system to enhance our confidence that the resulting numbers were sensible and usable for our purpose. All-electron DFT results were available for chromium ion with various fluorobenzenes, including both the Cr^+/C_6F_6 and Cr^+/C_6F_5H systems, as well as neutral C_6F_6 and C_6F_5H. (These calculations used the 6-31G* basis on C, H and F, 6-311 + G* on Cr, and employed the B3LYP hybrid functional [39]). These calculations showed rather similar frequencies and intensities for the strongly

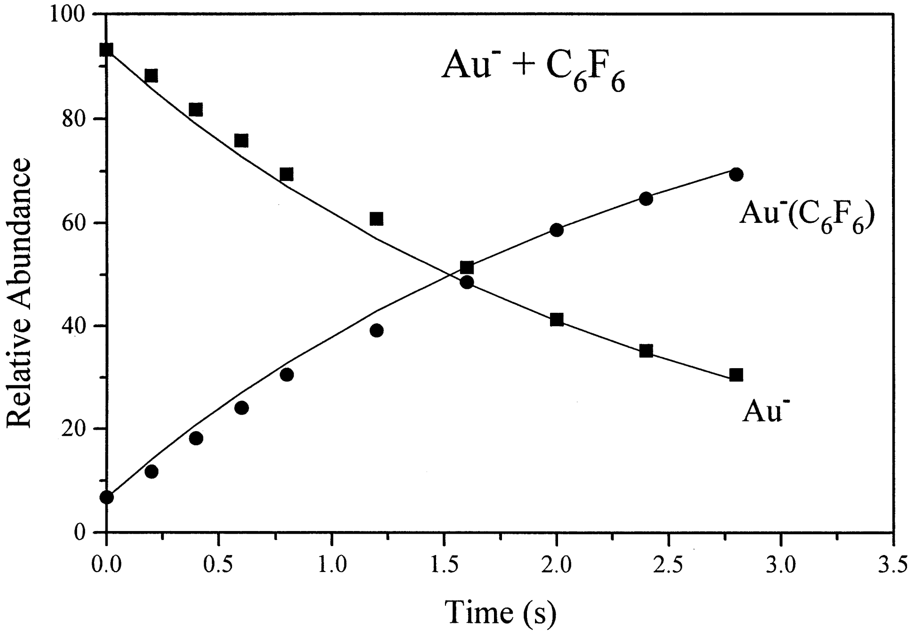

Fig. 2. Kinetic plots for Au^- plus C_6F_6, with fitted curves for a simple association process with rate constant 4.6×10^{-11} cm^3 mol^{-1} s^{-1} at a pressure of 2.8×10^{-7} Torr.

IR-emitting modes for all the π-Cr^+/fluorobenzene complexes in the region around 1600 cm^{-1} which contributes almost all of the IR emission in these systems, and furthermore the DFT results were quite similar in this regard to the present HF results for Au^-/C_6F_6. It appears that in these complexes the IR emission is dominated by vibrations of the fluorinated ring, and that the frequencies and intensities of these active vibrations can be found well enough by modest level calculations. The three low-frequency metal-ion-dominated vibrational frequencies of the chromium complexes were naturally higher than the gold case, but comparison taking into account some rough mass scaling suggested that the values used for the present gold modeling were not unreasonable. The frequencies assigned to these low-frequency vibrations strongly affect the complex redissociation rate constant k_b, and their uncertainty constitutes an important part of the overall uncertainty in the modeling.

Similar considerations were applied in estimating the IR emission characteristics of the Au^+/C_6F_5H complex. However, the parameters assigned to this species should be regarded with circumspection, because it is quite possible (analogous to the Cr^+ case [39]) that the most stable metal-ion binding is at a fluorine site rather than a π site.

2.3. Kinetic modeling

An association reaction can be analyzed in terms of the detailed mechanism

$$\begin{tikzcd}
A^+ + B \arrow[r, shift left, "k_f"] & (AB)^{+*} \arrow[l, shift left, "k_b"] \arrow[r, "k_r"] \arrow[r, bend right=60, "{[M]}", "k_c\beta"'] & AB^+
\end{tikzcd} \qquad (4)$$

where k_f is the bimolecular rate constant for collisional complex formation, k_b is the unimolecular redissociation rate constant, k_r is the rate constant for IR photon emission from the energized complex, and $k_c\beta$ is the bimolecular rate constant for collisional stabilization of $(AB)^{+*}$ by collision with neutral **M**. $(AB)^{+*}$ is the metastable collision complex. In the low-pressure regime, a simple expression may be written [46] for the apparent bimolecular rate constant for association,

$$k_2 = \frac{k_f k_r}{k_b + k_r} + \frac{k_f k_b k_c \beta}{(k_b + k_r)^2}\,[\mathrm{M}] \tag{5}$$

At the limit of low pressure where three-body collisional stabilization of the complex is negligible, the last term in Eq. (5) vanishes and the overall bimolecular rate constant k_2 becomes k_{ra}, the bimolecular rate constant for radiative association. Following Eq. (5), k_{ra} is clearly the zero pressure intercept of a plot of k_2 versus pressure [M].

2.3.1. VTST-based modeling

Accurate application of this expression to a thermalized population requires a thermal convolution over the energies and angular momenta of the reactants, since the microscopic rate constants are function of these variables. A well developed approach to evaluating k_2 and k_{ra} applies variational transition-state theory (VTST) to the kinetics, using values of k_r derived from ab initio calculations of the vibrational frequencies and infrared emission intensities of the energized complex. Because k_f and k_b correspond to reactions having species in common, the transition-state-theory calculation of the overall rate constant k_{ra} benefits from some cancellation of common factors, as laid out in Ref. [47]. In the limit of low association efficiency per collision, this cancellation leads to the convenient disappearance of all properties of the transition state from the calculation, but the cases considered here were not in this limit and had to be calculated using the full VTST-based expression.

Since the binding energy E_b of the complex is often the unknown quantity of interest and k_{ra} is a very strong function of the assumed value of E_b, the adjustment of E_b to fit experimentally observed kinetics offers a way of determining binding energy values that can be considered "semiexperimental." This approach, termed the RA kinetics method for binding energy determination, has given excellent results in terms of calculating and combining these rate constants to predict binding energies of accuracy comparable to other approaches [10,29,47,48].

2.3.2. McMahon analysis

If the pressure dependence of the apparent bimolecular association rate constant can be experimentally observed, the expressions for the slope [$k_3 = k_f k_b k_c \beta/(k_b + k_r)^2$] and the intercept [$k_{ra} = k_f k_r/(k_b + k_r)$] can be solved (as McMahon's group pointed out [46,49]). This gives "experimental" values of k_r and k_b as functions of the directly measured quantities k_3 and k_{ra}, and of the constants k_f and $k_c\beta$ which can be estimated. Such an "experimental" value for k_r when available provides a good comparison with the calculated numbers, although the quantitative accuracy of these numbers is limited because the assignment of single average values to the microscopic rate constants k_f, k_b and k_r is inherently approximate, and in addition there are uncertainties associated with the estimates of k_f and $k_c\beta$.

3. Results and Discussion

3.1. Au^-/C_6F_6

Fig. 1 shows spectra for the Au^-/C_6F_6 system as a function of reaction time. The monomer complex was formed smoothly, but the dimer complex $Au^-(C_6F_6)_2$ was not observed. The rate constant for the dimer formation Reaction (2) was less than about 10^{-13} cm^3 mol^{-1} s^{-1}. Fig. 2 shows the kinetic plot for this system, with fitted lines using a rate for Reaction (1) of 0.41 s^{-1}, corresponding to a rate constant of $k_2 = 4.6 \times 10^{-11}$ cm^3 mol^{-1} s^{-1}. Plotting the rate constants versus pressure, as in Fig. 3, gives an intercept of $k_{ra} = 1.0 \times 10^{-11}$ cm^3 mol^{-1} s^{-1}. The slope is $k_3 = 2.6 \times 10^{-21}$ cm^6 mol^{-2} s^{-1}.

To apply the McMahon analysis to derive "experimental" k_r and k_b values we may assign k_f and k_c to be equal to the Langevin orbiting rate constants. Using 9.58 A^3 for the polarizability of C_6F_6 gives $k_f = 7.4 \times 10^{-10}$ cm^3 mol^{-1} s^{-1}, and $k_c = 6.4 \times 10^{-10}$ cm^3 mol^{-1} s^{-1}. Using these values in the McMahon-analysis equations gives k_r(McMahon) = 4.6 s^{-1} and k_b = 180 s^{-1}. Comparing k_r(McMahon) with the estimate from the ab initio-derived kinetic modeling [k_r(ab initio) = 12 s^{-1}], we see that there is

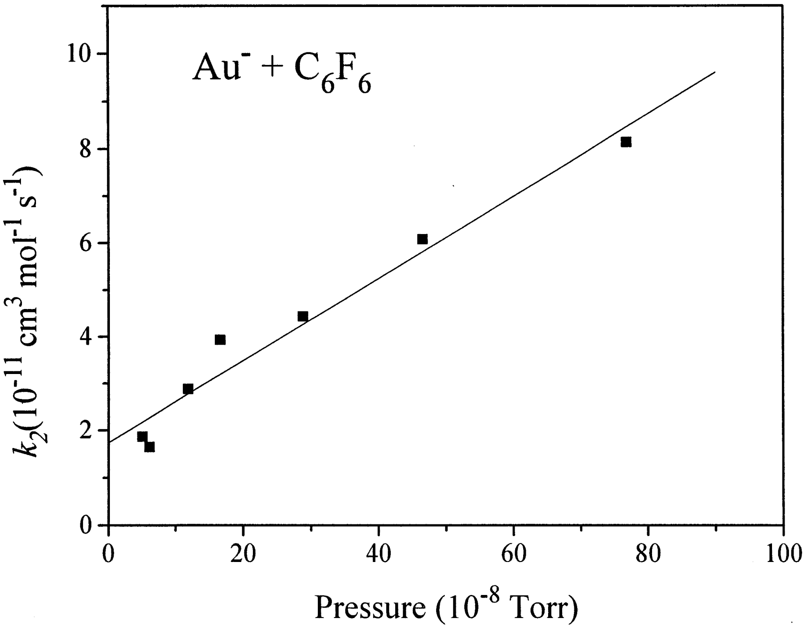

Fig. 3. Apparent bimolecular rate constant for association of Au^- and C_6F_6 as a function of pressure of C_6F_6.

order of magnitude agreement, although not as good agreement as could be hoped. This level of agreement is not worse than can be attributed to uncertainties in the experimental rate constants along with inaccuracies in the low-level ab initio calculations. It is noteworthy that this energized complex emits photons only slowly, at ~5–10 photons s^{-1}, even though it possesses brightly infrared-radiant C–F groups. This reflects its large heat capacity and its low binding energy, which give it a relatively low internal temperature (~800 K).

The binding energy of the complex was derived from the kinetics using the approach described above. A value of 24 ± 4 kcal mol^{-1} was assigned. The uncertainty is based on the combined uncertainties of a number of quantities (the pressure calibration, the ab initio-derived IR radiative intensity, the kinetic effects of uncertain low-frequency vibrational frequencies, the VTST rate expression itself, the assignment of k_{ra} from the data). An uncertainty of 1–2 kcal mol^{-1} might be typical for one of these error sources, leading in combination to the given overall uncertainty.

3.2. Au^+/C_6F_5H

The experiments and analysis of this system were similar to the preceding case. The best experimental data were at 56 °C, where a k_{ra} of 2×10^{-10} cm^3 mol^{-1} s^{-1} was determined. This leads to a binding energy estimate of 31 ± 4 kcal mol^{-1} for the complexation reaction

$$Au^+ + C_6F_5H \rightarrow AuC_6F_5H^+ \qquad (6)$$

The rate constant for this reaction is not very different from that observed by Schröder et al. [33] for $Au^+ + C_6F_6$, (1.5×10^{-10} cm^3 mol^{-1} s^{-1} at room temperature). They did not carry out a detailed analysis of their results, but the fact that the rate constant of that reaction is similar to that analyzed here for the C_6F_5H reaction suggests that the $Au(C_6F_6)^+$ complex has a similar binding energy in the vicinity of 31 kcal mol^{-1}. This estimate is in accord with the recent assignment of 34 ± 3 kcal mol^{-1} by Schröder et al. for $Au(C_6F_6)^+$ [32].

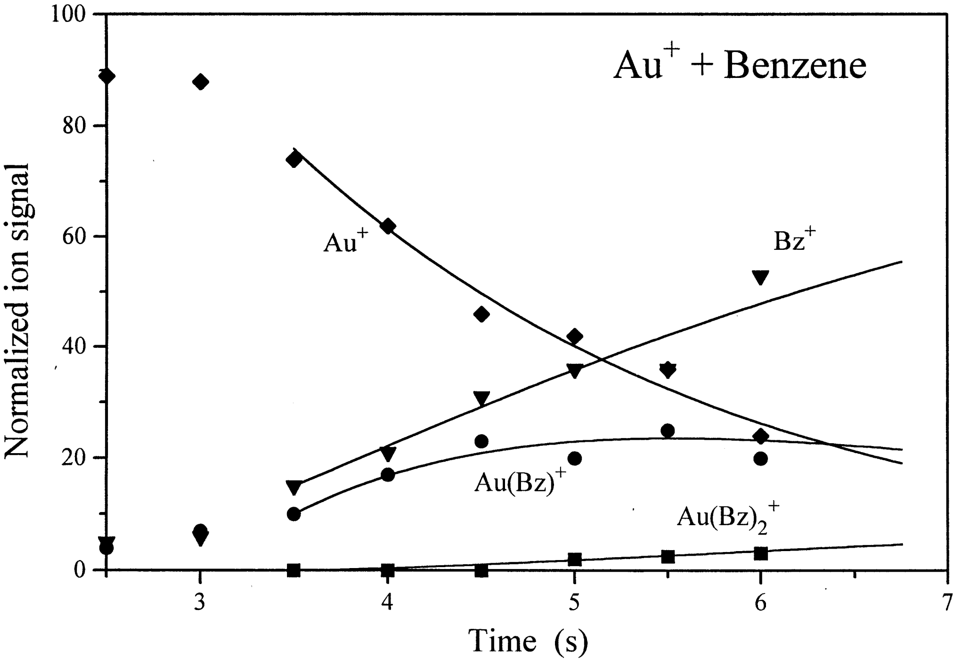

Fig. 4. Kinetic plots for reaction of Au^+ with C_6H_6. The fitted curves are for the reaction scheme (7)–(11), with rate constants (s^{-1}) $k_1 = 0.27$, $k_2 = 0.07$, $k_{c1} = 0.15$, $k_{c2} = 0.30$, and $k_{c3} = 0$.

3.3. Au^+/C_6H_6

It is accepted that gold cation complexes with benzene to form a very strong complex (~70 kcal mol^{-1}) [33], but this system was reexamined to learn more about the kinetics. The expected complexation sequence was observed,

$$Au^+ + C_6H_6 \xrightarrow{k_1} Au(C_6H_6)^+ \tag{7}$$

$$Au(C_6H_6)^+ + C_6H_6 \xrightarrow{k_2} Au(C_6H_6)_2{}^+ \tag{8}$$

and in addition rapid charge transfer occurred, according to one or more of the possible reactions

$$Au^+ + C_6H_6 \xrightarrow{k_{c1}} Au + (C_6H_6)^+ \tag{9}$$

$$Au(C_6H_6)^+ + C_6H_6 \xrightarrow{k_{c2}} Au(C_6H_6) + (C_6H_6)^+ \tag{10}$$

$$Au(C_6H_6)_2{}^+ + C_6H_6 \xrightarrow{k_{c3}} Au(C_6H_6)_2 + (C_6H_6)^+ \tag{11}$$

Fig. 4 shows an example kinetic fit to a data set for this reaction. This figure illustrates the sensitivity of these reactions to thermalization of the reactants. It is seen that reaction of the Au^+ primary ion is slow until about 3 s after ion formation, and only after about 3.5 s do the kinetics give a good fit (shown by the solid lines) to the kinetic scheme. This experiment used a pressure of about 1×10^{-7} Torr of N_2 bath gas, for which 3 s of thermalization corresponds to about 10 collisions. This represents the collisions needed to remove the excess translational energy of the nascent gold ions before the association reaction sequence can proceed with significant efficiency.

Given the complexity of this reaction scheme, a great variety of sets of rate constants can be chosen giving comparably good fits to the data. The fitting procedure was as follows: a starting time was picked (3.5 s in Fig. 4, for instance) at which thermalization appeared to be reasonably complete. The concentrations of the four ions at this time were taken as the initial conditions, and the kinetics of Eqs. (7)–(11) were numerically integrated forward from this time, using a particular set of rate constants. This procedure was repeated with a wide enough range of rate constants to give a good idea of the range of acceptable possibilities. The rate constant information that can be derived from these data fitting trials can be summarized as follows: (i) The monomer complexation rate constant k_1 is large, with a value of $(5.0 \pm 2.5) \times 10^{-10}$ cm^3 mol^{-1} s^{-1}. (ii) The dimer complexation rate constant k_2 is noticeably less than k_1, and has an approximate value of $(1.6 \pm 1.0) \times 10^{-10}$ cm^3 mol^{-1} s^{-1} (depending strongly on the value chosen for k_{c3}). (iii) At least one of the charge transfer reactions (9) and/or (10) is fast, and the sum of k_{c1} and k_{c2} is of the order of 6.0×10^{-10} cm^3 mol^{-1} s^{-1}. It is hard to separate these two rate constants accurately. The best fits have $k_{c2} > k_{c1}$, and $k_{c1} = 0$ gives some of the best fits. However, given the scatter of the data, any combination of k_{c1} and k_{c2} is possible within this constraint. (iv) k_{c3} can have any value, though presumably not greater than the collision rate (10.0×10^{-10} cm^3 mol^{-1} s^{-1}).

The fact that the monomer complexation rate constant k_1 has the same order of magnitude as the collision rate (10.0×10^{-10} cm^3 mol^{-1} s^{-1}) is not surprising, and serves only to confirm that the binding energy of this complex is high. It is also not surprising that the dimer complexation rate constant k_2 is lower than k_1, since many of the collisions of $Au(C_6H_6)^+$ with benzene apparently result in charge transfer rather than complexation. The observed value of k_2 is, thus, consistent with a strongly bound dimer complex. According to the Standard Hydrocarbon model [50] this large k_2 value corresponds to a dimer complex binding energy (for removal of one benzene) of not less than 45 kcal mol^{-1}.

Several arguments suggest that the monomer complex charge transfer, Reaction (10), is fast and accounts for a large fraction of the observed charge transfer products, while the Au^+ charge transfer, Reaction (9), is slower and may have a rate close to zero. In the first place, giving a large value to the charge transfer rate constant k_{c2} gives substantially better data fits than can be achieved if k_{c2} is smaller than k_{c1}, and the smallest k_{c1} values tend to give by far the best fits. Another indication that k_{c1} is very small is that (as seen in Fig. 4) little charge transfer occurs before the Au^+ ions are thermalized at around 3 s, in agreement with what would be expected if Reaction (10) is responsible for the charge transfer products; while Reaction (9), if it were fast, would probably not be inhibited by excess energy of the reactant and would be expected to give rapid formation of $C_6H_6{}^+$ beginning with zero time. Finally, Chowdhury and Wilkins [31] found the Au^+ charge transfer, Reaction (9), to be much slower than the complexation Reaction (7) (by a ratio of 1:15) under their fairly low-pressure conditions; together with our result noted above that $k_{c1} + k_{c2} > k_1$, this again indicates that Reaction (10) must be fast and Reaction (9) must be slow.

These indications that Reaction (10) is rapid suggest that it is exothermic. This is an interesting result in comparison with Reaction (9), which is virtually thermoneutral (actually exothermic by 0.4 kcal mol^{-1} at 0 K). If Reaction (10) is indeed more exothermic than Reaction (9), the following thermochemical argument gives the consequence that benzene is more tightly bound to neutral Au than to Au^+. This in turn suggests a neutral gold/benzene bond strength greater than about 70 kcal.

The thermochemistry of the charge transfer of the monomer complex can be thought about in terms of the following cycle:

$$\begin{tikzcd} Au^{+} + 2L \arrow[r, "\Delta H(CT1)"] \arrow[d, "\Delta H(AuL^{+})"] & Au + L^{+} + L \\ AuL^{+} + L \arrow[r, "\Delta H(CT2)"] & AuL + L^{+} \arrow[u, "-\Delta H(AuL)\ )"'] \end{tikzcd} \tag{12}$$

where L is benzene, ΔH(CT1) and ΔH(CT2) are the enthalpies of the indicated charge transfer reactions, and $\Delta H(AuL^+)$ and ΔH(AuL) are the enthalpies of attachment of benzene to cationic and neutral gold, respectively. This cycle shows that

$$\Delta H(CT2) = -\Delta H(AuL^{+}) + \Delta H(CT1) + \Delta H(AuL) \tag{13}$$

which is more informative written in the form

$$E(\mathrm{CT2}) - E(\mathrm{CT1}) = D(\mathrm{AuL}) - D(\mathrm{AuL}^+) \qquad (14)$$

where E(CT) is the exothermicity of the indicated charge transfer, and D(AuX) is the bond strength of the indicated complex. Thus, the charge transfer of the ligated metal ion is more exothermic than the charge transfer of the bare metal ion by an amount equal to the difference in binding energies of the neutral and the cationic forms of the metal. Because other things being equal, the binding energy of the cationic metal is normally substantially larger than that of the neutral metal (because of electrostatic effects), charge transfer from the ligated metal ion is usually less exothermic than that from the bare metal ion to the same neutral acceptor. However, this is evidently not the case for the gold/benzene system, leading to the unusual result that the charge transfer of Reaction (10) is fast while that of Reaction (9) is slow.

3.4. Other reactants

Au^- was found not to react at all with a number of other neutrals, namely benzene, mesitylene (1,3,5-trimethylbenzene), fluorobenzene, trifluorobenzene, pentafluorobenzene, acetone, and nitrobenzene. (Rate constants for these reactants estimated to be below 10^{-12} cm^3 mol^{-1} s^{-1}). Chlorobenzene did react to give Cl^-. For comparison, Weil and Wilkins [30] did not observe attachment of Au^- to any of the neutrals they looked at. For those few neutrals showing any reactivity, typically they saw reactions leading to formation of AuH as the neutral product, reflecting the great strength of the Au–H bond (70.6 kcal). With halides, Chowdhury and Wilkins [31] observed S_N2 displacements, analogous to the reaction we observed with chlorobenzene.

Au^+ was found to react with acetone by CH_3^- abstraction to give CH_3CO^+. This is not surprising, as Weil and Wilkins [30] found this to be a frequent reaction type with alcohols. Reaction of Au^+ with naphthalene gave only charge transfer products, which was not unexpected in view of the 25 kcal mol^{-1} exothermicity of this reaction. It can be noted that attachment in competition with exothermic charge transfer was observed in the case of some metal ions reacting with coronene even with exothermicities of the order of 24 kcal mol^{-1} [51], but the fact that attachment did not compete successfully with charge transfer in the present case is not particularly surprising.

4. Conclusions

The observation of $AuC_6F_6^-$, and the estimate of its binding energy as 24 kcal mol^{-1}, are probably the most notable results of this study, given the scarcity of previous characterizations of anionic π complexes. The characterization of $Au(C_6F_5H)^+$ with an estimated binding energy of 31.0 kcal mol^{-1} is useful, in that it expands the limited body of information about cationic gold complexes, and compared with the much stronger (70 kcal mol^{-1}) $Au(C_6H_6)^+$ complex, clearly points up the strong destabilizing influence of the benzene-ring fluorine substituents. No new understanding is contributed by the observation of rapid addition of Au^+ to C_6H_6, which was already well known as a strongly bound complex. However, the observation of fast (and presumably exothermic) charge transfer from $AuC_6H_6^+$ to benzene is interesting in that it suggests that benzene is more strongly bound to neutral Au than it is to Au^+. The neutral Au–C_6H_6 bond can, thus, be assigned as stronger than about 70 kcal mol^{-1}.

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