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# Partial Reduction and Selective Transfer of Hydrogen Chloride on Catalytic Gold Nanoparticles

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Abstract: HCl in solution accepts electron density from Au NPs and partially reduces at room temperature, as occurs with other simple diatomic molecules, such as O_2 and H_2. The activation can be run catalytically in the presence of alkynes to give exclusively E-vinyl chlorides, after the regio- and stereo-selective transfer of HCl. Based also on this method, vinyl chloride monomer (VCM) can be produced in a milder and greener way than current industrial processes.

Hydrogen chloride is a multi-ton produced chemical that is mostly employed in the manufacture of hydrochloric acid but also in the production of vinyl chloride monomer (VCM),[1] alkyl chlorides, and chlorobenzenes.[2] In these processes, the H−Cl bond is generally activated on catalytic metals by oxidation rather than by reduction, despite the σ^*_{H-Cl} lower unoccupied molecular orbital (LUMO) being, in principle, energetically available to accept electron density (Supporting Information, Figure S1).[3] To trigger this process, the metal must enable a symmetry-allowed interaction with the LUMO of HCl while having the lowest affinity towards dissociated HCl, to avoid formation of stable metal–chlorine bonds. These requirements are fulfilled by late-heavy transition metal Au NPs, with one of the lowest M−Cl bond energy tabulated.[4] In fact, this is exactly what occurs when Au NPs activate, dissociate, and transfer on a surface a related diatomic molecule such as O_2,[5] which is particularly productive in the presence of soft electrophiles, such as carbon monoxide,[6] alkynes,[7] and thiols.[8]

Following this initial hypothesis, the possible interaction between a HCl solution in 1,4-dioxane solvent and homo-dispersed (2.8–3.2 nm) Au^0 NPs on TiO_2 (Au−TiO_2), both commercially available, was studied by two different in situ techniques: UV/Vis absorption spectroscopy (UV/Vis) and cyclic voltammetry (CV). The choice of Au−TiO_2 is based on the well-known metallic character of these supported

Au NPs.[9] UV/Vis measurements showed the expected absorption band for the excited reduced state of HCl at about 210–220 nm (ca. 5 eV higher than HCl; Supporting Information, Figure S1),[10] which is well differentiated from the 1,4-dioxane solvent (ca. 190 nm), HCl itself (ca. 180 nm), and Au NPs (> 500 nm; Supporting Information, Figure S2). To check this result, measurements were repeated with the trityl cation (Ph_3C^+) as a probe, which is able to accept in situ generated electrons and sequentially forms the well-defined radical cation ($Ph_3C^{+\cdot}$), anion (Ph_3C^-), and finally the radical anion ($Ph_3C^{\cdot-}$), with its associated oxygenate species ($Ph_3CO_2^{\cdot-}$).[11] The results in Figure 1 A clearly show the
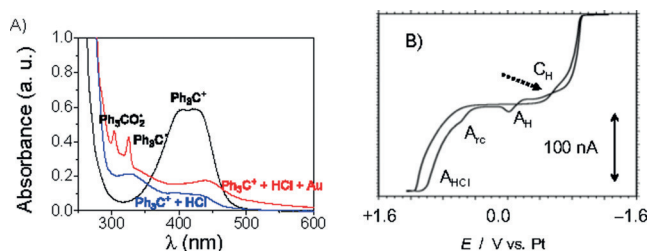
Figure 1. A) UV/Vis spectrum obtained after addition of HCl to a dispersion of Au-TiO_2 and trityl(tetrapentafluorophenyl)borate ($Ph_3C \cdot C_{24}BF_{20}$) in anhydrous 1,4-dioxane under ambient conditions. B) Cyclic voltammogram of Au-TiO_2 contact-probe Pt microelectrode with a HCl solution in 1,4-dioxane (ca. 0.8 M). Potential scan rate 50 mV s^{-1}.

appearance of the radical anion $Ph_3C^{\cdot-}$ and its oxygenated form at expenses of the Ph_3C^+ cation, only when HCl is added to Au NPs. A linear correlation between the HCl added and the formation of the reduced trityl radical species was found in an excess of Au−TiO_2 (Supporting Information, Figure S3), and blank experiments without Au−TiO_2, without HCl or with TiO_2 + HCl do not show any reduced species.

CV measurements of Au−TiO_2 in HCl solution show the enhancement of signals at microelectrodes for the one-electron oxidation of Cl$^\cdot$ to Cl_2[12] (+ 0.85 V, A_{HCl}) and the reduction of trace protons[13] (rising cathodic current between + 0.5 and − 0.5 V, C_H/A_H in the Supporting Information, Figure S4, black lines), which is consistent with the catalytic effect exerted by metal NPs in solution[14] and attached to electrodes.[15] Besides, a s-shaped continuous curve with a series of disruptive blip features appears in the linear scan voltammogram, which corresponds to the collision of HCl molecules with Au−TiO_2.[16] To permit a very sensitive record of the process occurring at the immediate vicinity of the electrolyte/solid material/electrode three-phase boundary,[17]

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contact-probe experiments were performed with the Pt microelectrode pressed on a fine deposit of Au−TiO$_2$ at the bottom of the glass cell, and Figure 1B shows that a new oxidation peak (A$_{rc}$) with the expected increase of voltage (+ 0.35 V) for a reduced HCl$^{\delta-}$ species appears, well differentiated from the signals between 0.0 and −0.5 V (C$_H$/A$_H$) associated to hydrogen species generated during the initial oxidation of HCl, and with the characteristic crossover for the Au−TiO$_2$ catalyzed process, marked by a dotted arrow. Thus, the UV/Vis and CV results support the transfer of electrons from Au NPs to HCl.

Alkynes are soft electrophiles that adsorb well on Au NPs and react with activated O$_2$ and H$_2$ on surface.[7,9] Thus, it is possible that the HCl activated on the Au NP could be transferred to an alkyne, thus liberating the Au surface for a next catalytic cycle. The resulting reaction, the hydrochlorination of alkynes, has not found use in the preparation of vinyl chlorides beyond VCM[1] since the non-catalyzed reaction proceeds with low yield and selectivity under harsh reaction conditions[18] and, only very recently, some homogenous metal complexes have shown catalytic activity for the reaction.[19] Vinyl chlorides are naturally occurring products with broad biological activities,[20] and their synthesis still lays on waste-generating stoichiometric halogenating reagents such as thionyl or phosphorus chloride.[21a] Scheme 1 shows that not only different alkynes react well in the hydrochlorination reaction with Au−TiO$_2$ catalyst but also that the reaction proceeds regioselectively, to the Markovnikov product for terminal alkynes (products **2a–j**), and stereoselectively, to the E-alkenyl chloride for internal alkynes (products **2k–n**; see also the Supporting Information, Figure S5). The structure of the hydrochlorination product of deuterated terminal alkyne [D]**1a** (Supporting Information, Figure S6) confirms that the *syn* addition also operates for terminal alkynes.

A Hammett plot for different phenylacetylenes show the generation of a partial positive charge on the internal carbon during reaction (ρ = −1.50; Supporting Information, Figure S7), and whereas electron donor substituents increase the chlorination rate, very strong electron-withdrawing groups decrease the rate and also switch the reaction to the anti-Markovnikov products (products **2o,p**). It is difficult to explain the low reactivity of *meta*-substituted phenylacetylenes, although the so-called *ortho* effect[22a,b] and the possible activation of the Au surface by particularly electron-rich *ortho*- and *para*-substituted phenyacetylenes[22c] may be invoked to explain this reactivity. Other Au catalysts tested including Au^I and Au^{III} salts (halides, oxides, triflates), Au^I complexes (phosphines and carbenes), and bare Au clusters (3–7 atoms)[22d] did not show any significant activity for the reaction. Notice that E-alkenyl products will not be expected on the basis of typical *anti*-hydroadditions to alkynes[9] catalyzed by Au$^+$, but resemble more to the *syn* addition products found for H$_2$ on catalytic metal surfaces.[23]

Au−TiO$_2$ could be reused 10 times for the hydrochlorination of **1a** without depletion of the catalytic activity, filtering the solid after complete conversion (19 h), and then calcining the solid in air at 500 °C (Scheme 1; Supporting Information, Figure S8). This calcination temperature was chosen on the
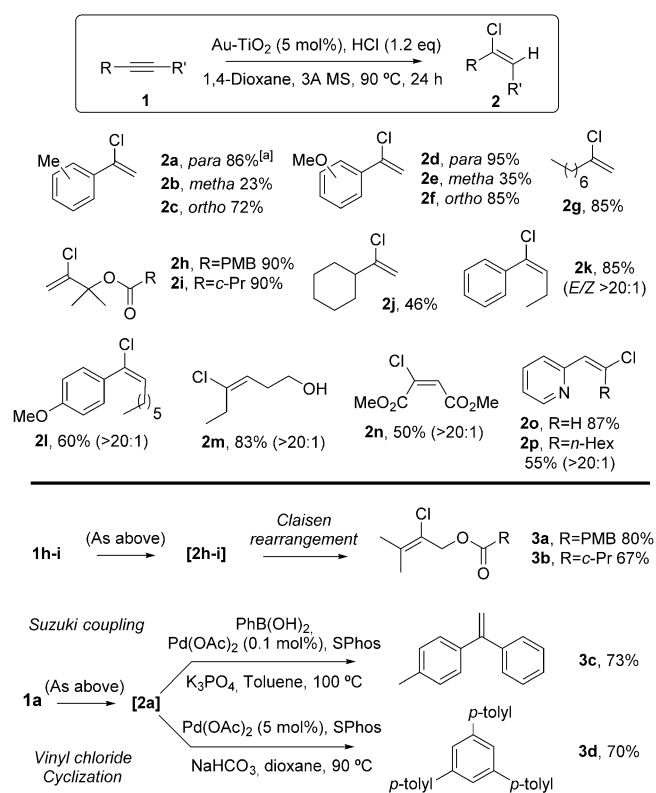
Scheme 1. Top: Au-TiO$_2$ catalyzed reaction of internal and terminal alkynes with HCl. Reaction conditions: 1 mmol of alkyne, 1.2 equiv of HCl in 1,4-dioxane (4 M), 1,4-dioxane (1 mL), 3 Å M.S. and the corresponding amount of Au−TiO$_2$ (5 mol%). Yield of isolated product.[21b] Regioselectivity is > 95% in all cases. [a] Tenth use of the catalyst. Bottom: One-pot hydrochlorination C−C bond-forming reactions, isolated yield for **3a** and GC yields for **3b–d**.

basis of thermogravimetry results (Supporting Information, Figure S9A), where the presence of residues that volatilize at about 450 °C together with about 3 nm Au NPs that melt between 650 and 950 °C was observed.[24] This volatile residue could be assigned to aromatic polyalkynes and polyalkenes strongly adsorbed on the recovered Au−TiO$_2$ catalyst, according to IR spectroscopy (Supporting Information, Figure S9B). Measurements of the reused Au−TiO$_2$ by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), before and after calcination, shows that the size of the Au NPs is not affected throughout the reuse (Supporting Information, Figure S9C), and hot filtration tests and inductively coupled plasma atomic emission spectroscopy analysis of the reused catalyst confirmed that no catalytically active Au species were present in solution during reaction, below the detection limit of the technique (< 10 ppm; Supporting Information, Figure S9D).

The use of vinyl chlorides as starting materials for the synthesis of more elaborated compounds has been severely limited for the unsuitability of synthetic methods available so far and the sensitiveness of the products to polymerization, despite the fact that they present great potential in paramount reactions in organic synthesis, such as rearrangements and cross-couplings.[25] Scheme 1 also shows that the vinyl chloride products **2a,h,i** engage well in C−C bond-forming reactions

such as the Claisen rearrangement to give products **3a,b**, the Pd-catalyzed Suzuki coupling to give product **3c**, and a cyclization coupling to give product **3d**, in one-pot after the hydrochlorination step without need of isolation, to give products otherwise tedious to obtain by multistep synthetic routes.[26] These results illustrate the practicality of activating HCl on Au surfaces.

Experimental mechanistic studies were performed in order to assess that the selective hydrochlorination of alkynes on Au NPs comes and is controlled by HCl activation. First, cyclic and horizontal touch voltammetry measurements[27] confirm that the transfer of electron density from Au NPs to HCl also occurs in the presence of the alkyne (Supporting Information, Figures S4, S10). Second, the hydrochlorination of **1a** follows a first-order reaction rate for HCl and also Au catalyst (Supporting Information, Figure S11). Third, the hydrochlorination rate increases linearly with the number of Au^0 atoms on the NP, since Au^0 is more prone to give electrons (Supporting Information, Figure S12). For this study, three samples of $Au-CeO_2$ with variable amounts of Au^0 according to X-ray photoelectron spectroscopy (XPS) and in situ CO probe IR spectroscopy (Supporting Information, Figure S13) were prepared, since the metallic-to-cationic Au ratio can be much easily varied on $Au-CeO_2$ than in $Au-TiO_2$.[28] A possible participation of TiO_2 in the hydrochlorination of alkynes was also discarded, since the kinetic profile of the reaction under UV/Vis light (Hg lamp) is very similar to the thermal reaction (Supporting Information, Figure S14). And fourth, an inverse kinetic isotopic effect $KIE_H = 0.71(1)$ was found for the hydrochlorination of phenylacetylene (PA) with DCl catalyzed by $Au-TiO_2$, which strongly supports the idea that the H atom is bound to a heavy atom, Au^0 in this case, during the reaction, in accordance to the location of the σ^*_{H-Cl} LUMO of HCl on the H atom.[3,10]

Density functional theory (DFT) calculations, shown in Figure 2, support the $Au\cdots H-Cl$ electron transfer, since all the optimized geometries for HCl adsorbed on Au_{38} NPs show the H atom pointing to the Au surface, with the Cl atom far from the metal, and the H–Cl bond weakens and increases its length from 1.285 Å in the isolated molecule up to 1.344 Å when adsorbed on Au (Supporting Information, Figure S15). Once the $Au\cdots H-Cl$ interaction occurs, dissociation of H–Cl is an exothermic process by 8–10 kcal mol^{-1}, with activation energy barriers of 5–7 kcal mol^{-1} depending on the presence or not of co-adsorbed alkyne (Figure 2; Supporting Information, Figure S15). The experimental values found for $\Delta H^{\#\#}$ and E_a, obtained by an Eyring plot, are 8.6(8) and 10.0(5) kcal mol^{-1}, respectively, which approach reasonably well the values given by calculations.

After HCl dissociation yielding structure M2, the Cl atom attacks the internal position of the alkyne via transition state TS23, forming the intermediate system M3 with an activation energy of 12.5 kcal mol^{-1}. Then, addition of the hydride occurs stereoselectively via transition state TS34 to give the adsorbed Markovnikov product M4 with an activation barrier of 20.2 kcal mol^{-1}. Initial H addition to form intermediate species M5 involves a higher activation barrier (dotted black line in Figure 2), while initial H addition to the terminal C atom yielding a stable M10 intermediate species is energeti-
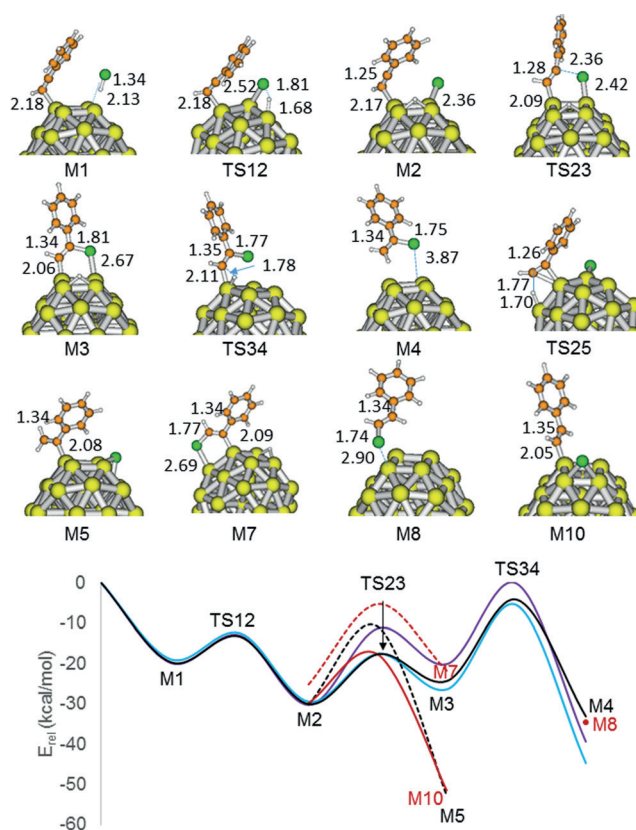

Figure 2. Optimized geometries of the structures involved in the hydrochlorination of phenylacetylene (PA) over an Au_{38} nanoparticle and calculated energy profiles for PA (black line), methylacetylene (MA; blue line), and dimethylacetylene (DMA; purple line) hydrochlorination yielding the Markovnikov product. Attempts to obtain the anti-Markovnikov product for PA are depicted in red. Distances are given in Å. Optimized geometries of all structures plotted in the energy profile are given in the Supporting Information, Figures S16–S18.

cally competitive (solid red line in Figure 2). However, no transition states could be found for the subsequent attack of Cl to either M5 or M10, suggesting that these highly stable intermediates should accumulate on the gold NPs, in agreement with the spectroscopic observation of aromatic polyalkenes strongly adsorbed on the catalyst surface after reaction. On the other hand, initial addition of Cl to the terminal C atom yielding M7 is energetically disfavored (dotted red line in Figure 2), in agreement with the high regioselectivity experimentally observed. Similar structures and energy profiles were obtained for methylacetylene (MA) and dimethylacetylene (DMA) hydrochlorination (Supporting Information, Figures S17, S18). Experimentally, neither alkenes (hydrogenation product) nor polychlorinated compounds (from Cl_2) are found during reaction, and the lack of reactivity of styrene as a substrate discards the formation and polymerization of simple alkenes from alkynes. These results support that the regio- and stereoselective hydrochlorination event occurs very rapidly on the Au NP surface, without any spillover of the dissociated atoms of the HCl molecule.

Taking into account the experimental and theoretical evidence shown above, a plausible mechanism for the hydro-

chlorination of alkynes in solution catalyzed by Au NPs is shown in Scheme 2. The reaction starts with the transfer of electron density to adsorbed HCl, which then dissociates on the partially charged Au NP to generate a H−Au−(Au)$_n$−Au−Cl species. The presence of co-adsorbed alkyne does not modify significantly this process. Then, the regioselective addition of the Cl atom occurs and the adsorbed transient species stereoselectively captures the H atom, to form the *syn* product and regenerate the Au^0 atoms.
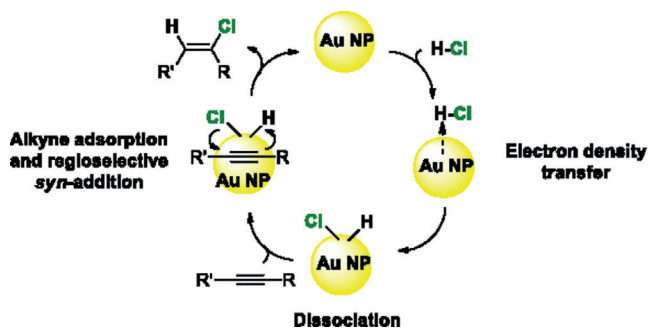
Scheme 2. Proposed mechanism for the *syn*-addition of HCl to alkynes in solution catalyzed by Au NPs.

The mechanism proposed here resembles more the metal-catalyzed pairwise addition of H$_2$[23] than the classical electrophilic activation of alkynes.[29a] In the described mechanism, the electron density flows from the metal to the nucleophile (HCl) and then to the electrophile (alkyne), thus the nucleophile is activated before the electrophile. This mechanism bypasses the typical protodemetalation step in Au-catalyzed electrophilic hydroadditions that leads to *anti* addition products. Indeed, this reaction mechanism occurs for the *cis* addition of some heteroelements (Het−Het and Het−H bonds) to alkynes with Au−TiO$_2$[29b,c] and Au nanopore[29d–f] catalysts.

The Minamata Convention in 2013 states that mercury catalysts will not be allowed in new VCM plants and that all plants will have to remove them definitively in 2022. Thus, the search of eco-friendly alternative catalysts for VCM production is mandatory.[30] Despite exothermic in nature, the hydrochlorination of acetylene is currently run at > 150 °C, to partially desorb the acetylene molecules of the alkynophilic Hg^{2+} or Au^{3+} catalytic sites and allow HCl to interact with the metal. In clear contrast, here it is shown that the adsorption and activation of HCl on Au NPs occurs prior to the alkyne at lower temperatures. Thus, VCM production was attempted with Au-TiO$_2$ catalyst either in a continuous flow stirred-tank reactor (CSTR) or in a fixed-bed tubular reactor (FBTR). Figure 3 shows that the process works well, and acetylene transforms at 80 °C to vinyl chloride monomer (VCM) and other chlorinated products, including C2 polychlorides and vinyl chloride oligomers, in high conversions after long reaction times on stream. Considering that polyvinyl chloride (PVC) is the third worldwide plastic in terms of production volume per year (> 30 million tons),[31] the results here shown might constitute a step forward towards the development of a more efficient and greener production of the precursor of PVC.
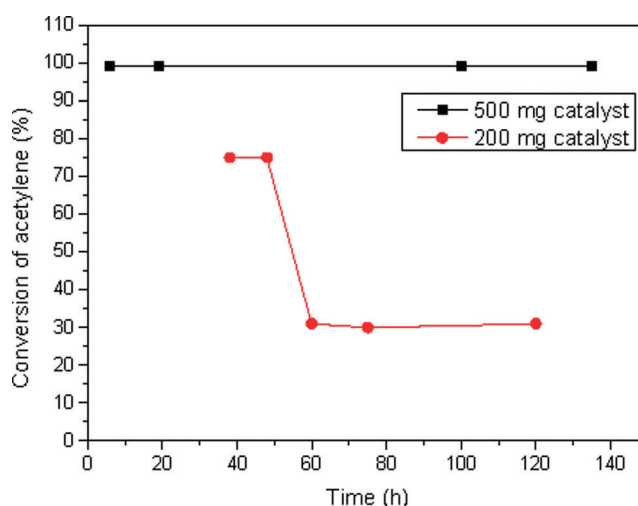
Figure 3. Hydrochlorination of acetylene in flow by feeding a gas mixture of HCl and acetylene in a continuous flow stirred-tank reactor (CSTR) of Au-TiO$_2$ catalyst dispersed in 1,4-dioxane at 80 °C, for two different catalyst masses. Data could be reproduced in a second run. A mixture of pure acetylene, pure HCl, and part-per-million amounts of toluene as additive passed through a fixed-bed tubular reactor (FBTR) with supported Au-TiO$_2$ gave very similar results.

In conclusion, catalytic Au^0 atoms in supported Au NPs adsorb and dissociate HCl in anhydrous organic solvents at room temperature, to give H−Au−(Au)$_n$−Au−Cl transient species that reacts regio- and stereoselectively with alkynes adsorbed on surface, leading to *E a*-vinyl chlorides (*syn*-hydrochlorination products). The solid catalyst can be reused and employed in flow for the conversion of acetylene to VCM under much milder reaction conditions than currently employed in industry. Notice that although the hydrochlorination of acetylene on carbon-supported Au catalysts was already proposed by Hutchings in 1985,[1] and subsequently brought to industrial scale, the approach presented herein is clearly different, since the reaction is in a liquid rather than in the gas phase, the H−Cl bond is activated by reduction rather than by oxidation, and Au^0 active sites rather than Au$^+$ are involved.

Conflict of interest

The authors declare no conflict of interest.

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