"Organic Aqua Regia"—Powerful Liquids for Dissolving Noble Metals**

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The dissolution of noble metals is important for metallurgy, catalysis, organometallic chemistry, syntheses and applications of noble-metal nanoparticles, and recycling of noble metals. Aqua regia ("royal water") has been used for centuries as a powerful etchant to dissolve noble metals. The beauty of aqua regia is that the simple 1:3 mixture of concentrated nitric and hydrochloric acids can dissolve noble metals such as gold, palladium, and platinum, although these metals are not soluble in either of the acids alone. We show that simple mixtures of thionyl chloride ($SOCl_2$) and some organic solvents/reagents (pyridine, N,N-dimethylformamide, and imidazole) can also dissolve noble metals with high dissolution rates under mild conditions. We name these mixtures "organicus liquor regius".[1] The discovery of this solvent system is of unprecedented scientific significance and engineering value: Compared with inorganic chemistry, organic chemistry provides precise control over chemical reactivity, and the ability to tailor organic reactions enables the selective dissolution of noble metals. By varying the composition of organicus liquor regius we have for the first time realized the selective dissolution of noble metals, namely, the dissolution of Au and Pd from a Pt/Au/Pd mixture and of Au from an Au/Pd mixture. Selective dissolution is important for many applications, especially for recycling noble metals. The global energy crisis demands green energy technologies, which will undoubtedly require increased resources of noble metals. However, noble metals are scarce on earth; thus, the ability to recover high-purity noble metals by recycling processes will be paramount. Among the noble metals, Pt is used most widely as a catalyst in many green technologies, in particular, proton-exchange membrane (PEM) fuel cells.[2–4] The recycling of Pt, however, has long been a challenging issue: Current recycling technologies are complicated, and rely on the dissolution of Pt in strong inorganic acids and the subsequent separation of the dissolved Pt from solution.[5–7] The nonselectivity of the

inorganic acids results in the dissolution of other noble metals such as Ag, Au, and Pd at the same time as Pt. This lack of selectivity limits the quality of the recycled Pt. Therefore, an improved route for Pt recycling—both in terms of quality and efficiency—requires a selective dissolution process, which would remove the noble metal impurities (Ag, Au, Pd, etc.) before the final dissolution of Pt. Preliminary investigations on a few non-aqueous solutions for dissolving noble metals have been carried out,[8–11] but they showed unsatisfactory solubility,[9–12] selectivity,[9–12] efficiency,[8,10] stability,[11] and simplicity.[8–10] These etchants are not ideal because of the intrinsic inorganic chemistry associated with conventional oxidizers of noble metals (halogens and oxygen).[8,9,11] Organicus liquor regius oxidizes noble metals by a different mechanism.

Figure 1 shows a graph of the dissolution of noble metals in a 3:1 (v/v) mixture of $SOCl_2$ and pyridine (py). The mixture dissolves gold at a rate of $0.3\ mol\,m^{-2}\,h^{-1}$ at room temperature, which is faster than the dissolution of gold in conventional cyanide leaching agents ($< 0.004\ mol\,m^{-2}\,h^{-1}$) and iodide solutions ($< 0.16\ mol\,m^{-2}\,h^{-1}$).[12,13] Silver and palladium can also be dissolved at high dissolution rates ($0.8\ mol\,m^{-2}\,h^{-1}$ and $0.5\ mol\,m^{-2}\,h^{-1}$, respectively); in compar-

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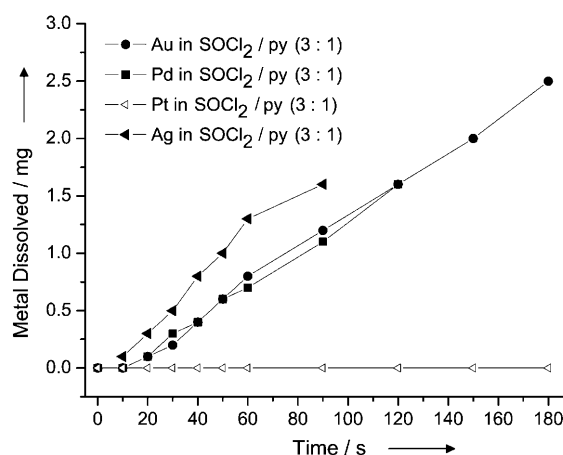   cp.wong@mse.gatech.edu

Figure 1. Kinetic studies of the dissolution of Au, Pd, Ag, and Pt in a 3:1 $SOCl_2$/py mixture. 250 nm thick layers of Au, Pd, Ag, and Pt were deposited onto separate 9 cm² silicon substrates, with 20 nm thick chromium used as the adhesion layer (chromium is not soluble in any of the organicus liquor regius tried) to avoid any error that might be introduced because of peel-off of the noble metal metallization layer. The metallized substrates are immersed in 20 mL of $SOCl_2$/py at room temperature with mild shaking for a preset duration, taken out, rinsed thoroughly, dried, and weighed. No weight loss from a Pt film was detected after it had been immersed in the $SOCl_2$/py mixture at room temperature or even at 70°C (reflux) for 1 week.

ison, platinum is completely inert. We chose to study the Au/SOCl$_2$/py system to obtain insight into the dissolution process.

X-ray photoelectron spectroscopy (XPS; see Figure S2 in the Supporting Information) of GTP-160 (see the Experimental Section) shows the Au 4f$_{7/2}$ binding energy at 86.6 eV, which is characteristic of the Au^{III} oxidation state.[14] We used SOCl$_2$/py vapor to etch an Au/Si surface to demonstrate that Au is oxidized to Au^{III} instantaneously. The presence of Au^{III} on the vapor-etched Au/Si surface was confirmed by XPS (see Figure S3 in the Supporting Information) and Raman spectroscopy (in the form of [AuCl$_4$]$^-$; see Figure S4 in the Supporting Information). Vibration modes of Au^{III}–Cl, however, are not observed in the Raman spectrum of either GTP-L (see Figure S5 in the Supporting Information) or GTP-RT (see Figure 3b), probably because they are hidden by the strong background fluorescence. In fact, storing a solution of SOCl$_2$/py (3:1) containing 0.03 mol L^{-1} Au at room temperature in a dark room for 150 days resulted in a large amount of yellow precipitate and the solution turning into a dark suspension. The presence of [AuCl$_4$]$^-$ was confirmed by Raman spectroscopy of the precipitate (see Figure S6 in the Supporting Information). Therefore, we believe that [AuCl$_4$]$^-$ forms as a result of Au dissolution in SOCl$_2$/py mixtures. Furthermore, no chemical shifts resulting from the coordination of py to Au^{III} are observed in the NMR spectra (see Figure S9 in the Supporting Information)[15] and no simple Au^{III} compounds are observed in the mass spectra (see Figures S10 and S11 in the Supporting Information) or the X-ray diffraction pattern (see Figure S12 in the Supporting Information). These results suggest the absence of AuCl$_3$ and its complex with pyridine in the Au/SOCl$_2$/py solution, GTP-L, or GTP-RT.

Oxidation of Au^I to Au^{III} by SOCl$_2$ has been demonstrated under certain conditions;[16,17] however, Au cannot be oxidized by SOCl$_2$ alone.[18] Pyridine undoubtedly plays an important role in the dissolution process. The NMR spectra of the SOCl$_2$/py mixture (see Figure S9 in the Supporting Information) show deshielding of the ^{14}N (ca. $\delta = 5$ ppm), ^{13}C (ca. $\delta = 1.35$ and 2.42 ppm for C3 and C4, respectively), and ^{1}H atoms (ca. $\delta = 0.35$, 0.49, and 0.50 ppm for H2, H3, and H4, respectively), and shielding of C2 (ca. $\delta = -1.77$ ppm) relative to the signals of pyridine in the absence of SOCl$_2$. These chemical shifts can be attributed to a charge-transfer interaction between SOCl$_2$ and py.[19] Charge-transfer complexes between SOCl$_2$ and amines have been prepared by Schenk and Steudel,[20] and studied theoretically by Steudel and Steudel.[21] In our case, the sulfur atom in SOCl$_2$ is an electron acceptor, and the nitrogen atom in pyridine an electron donor. Charge transfer, in general, weakens the bonds within the acceptor molecule,[21] which accounts for the observed red-shifts of both the asymmetric and the symmetric Cl-S-Cl stretching bands in the Raman spectra of SOCl$_2$/py mixtures (see Figure S13 in the Supporting Information). In comparison with pure py and SOCl$_2$, we also observe shifts and changes in the intensity of py-related vibration bands in the FTIR spectra of the SOCl$_2$/py mixture (see Figure S14 in the Supporting Information). Such shifts are mainly attributed to the formation of the charge-transfer complex, SOCl$_2$·py, and is in good agreement with our simulated

vibration spectra (IR; see the Supporting Information). SOCl$_2$·py is observed directly in the mass spectrum of the SOCl$_2$/py mixture (see Figure S15 in the Supporting Information; [SOCl$_2$·py + H$^+$] at m/z 198.1). Therefore, we believe that the charge-transfer interaction activates SOCl$_2$ to oxidize Au.

Almost all the vibration modes of pure py and pure SOCl$_2$ remain in the Raman and the FTIR spectra of the SOCl$_2$/py mixture (see Figures S13 and S14 in the Supporting Information). This finding indicates that the parent molecules, although perturbed by the charge-transfer interaction, maintain their basic structural integrity, and that the dominating product is a molecular adduct rather than a rearrangement, elimination, or dissociated product. Neither 1-(chlorosulfinyl)pyridinium chloride nor 1-(chlorosulfinyl)-4-chloro-4-hydropyridine has been identified in the NMR spectra (see Figures S1, S9, S16, and S17 in the Supporting Information).[22–25] Our simulations show that 1-(chlorosulfinyl)pyridinium chloride—the dissociated form of the adduct—is not favorable in terms of energy. Proof of its existence can not be found easily in the FTIR spectra (see Figures S14 and S29 as well as Table S3 in the Supporting Information). However, experimental data on the electrical conductivity of the mixtures suggest the presence of mobile ions as a result of the dissociation (see the Supporting Information). Therefore, 1-(chlorosulfinyl)pyridinium chloride, although a weak electrolyte in SOCl$_2$ (see Figure S30 in the Supporting Information), exists in the solution through dissociation of the SOCl$_2$·py adduct. No known reduction products of SOCl$_2$, such as sulfur, have so far been confirmed.[16,26,27] This is not surprising in view of the complicated mechanism of the reduction reactions of SOCl$_2$.

SOCl$_2$ is consumed nonstoichiometrically on dissolution of Au into the SOCl$_2$/py mixture. This is evident from the reduced Raman intensities of the vibration bands at $\Delta\nu = 200.0$, 288.5, 348.2, 427.5, and 493.0 cm^{-1} in Figure 2. The py-related bands at $\Delta\nu = 657.3$, 1000.9, 1035.4, and 3064.6 cm^{-1} shift to 643.5, 1013.5, 1027.3, and 3101.4 cm^{-1}, respectively. The shifting of the bands is complete at a Au^{III} concentration as low as 0.03 mol L^{-1}. Correspondingly, the NMR spectra
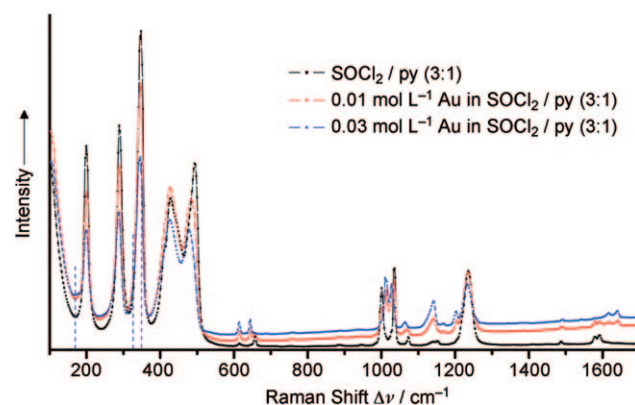

Figure 2. Raman spectra of 3:1 SOCl$_2$/py mixture before and after Au dissolution. The dashed lines indicate the vibrational peak positions of [AuCl]$^-$ at 170, 324, and 348 cm^{-1}, which cannot be distinguished from the ones arising from SOCl$_2$.

(see Figure S9 in the Supporting Information) of the 0.03 mol L^{-1} Au/SOCl$_2$/py solution show fully shifted ^{14}N (ca. $\delta = -10.4$ ppm), ^{13}C (ca. $\delta = -0.46$, 0.14, and 0.50 ppm for C2, C3, and C4, respectively), and ^{1}H signals (ca. $\delta = -0.06$, -0.04, and -0.04 ppm for H2, H3, and H4, respectively) relative to the 3:1 SOCl$_2$/py mixture before Au dissolution. These results suggest a nonstoichiometric chemical reaction in the solution. The solid-state ^{13}C NMR spectrum (see Figure S18 in the Supporting Information) of GTP-RT shows signals for C4, C2, and C3 at $\delta = 147.7$, 142.2, and 129.2 ppm, respectively. This is in very good agreement with the calculated ^{13}C NMR spectra of oligomers of 4-chloropyridine (pyridinium structure; see Figure S19 in the Supporting Information). Protonation of the nitrogen atom can be confirmed by the appearance of the vibration band of NH$^+$ at approximately 3222 cm^{-1} in the FTIR spectra of GTP-RT (see Figure S20 in the Supporting Information) and the Au/SOCl$_2$/py solution (see Figure S7 in the Supporting Information). The pyridinium structure is also reflected in the cyclic voltammogram of the gold/organicus liquor regius solution in acetonitrile, where the reduction peak potential at -1.28 V (see Figure S21 in the Supporting Information) in the cathodic scan falls in the range of the reduction potentials of pyridinium compounds.[28] Dimers and trimers of 4-chloropyridine and their derivatives are present in the mass spectra of GTP-RT (see Figures S10 and S11 in the Supporting Information) and the precipitate from the long-standing Au/SOCl$_2$/py solution (see Figures S22 and S23 in the Supporting Information). We postulate that 4-chloropyridine might form as an intermediate and Au^{III} catalyzes the oligomerization of 4-chloropyridine.[29,30] The oligomeric nature is evident by GTP-L being very viscous. The increased viscosity results in a low mobility of the molecules, and this low mobility could be the reason for the signal broadening observed in the ^{13}C NMR spectrum of the Au/SOCl$_2$/py solution (see Table S1 in the Supporting Information). In agreement with our postulation, different metals such as Au, Ag, and Cu exhibit different catalytic effects (see Figure S24 in the Supporting Information).[30] The oligomerization reaction accounts for the nonstoichiometric feature.

The dissolved Au can be recovered by calcination. In GTP-160, the recovered Au and hexagonal rodlike residuals can be observed by SEM (Figure 3d and f). In comparison with GTP-RT, the Raman intensities of the py-based bands are reduced for the rods (Figure 3e); meanwhile, Au^{III}–Cl bonds are evident. In GTP-230, a complete decomposition of GTP-RT into hexagonal Au discs is observed by SEM (ca. 10 μm in size, Figure 3g and i). These well-shaped Au discs have a {111} orientation (see Figure S25 in the Supporting Information).

Organicus liquor regius can be formulated using not only py but also other organic solvent/reagents, such as *N,N*-dimethylformamide (DMF), imidazole, pyrimidine, and pyrazine. For example, a SOCl$_2$/DMF mixture dissolves Au at a rate of 0.3 mol m^{-2} h^{-1}; in contrast, neither Pd nor Pt are apparently dissolved (see Figure S26 in the Supporting Information). One key feature that all the organic species have in common is that they can undergo charge-transfer interactions with SOCl$_2$.[20,26,31] Although no quantitative
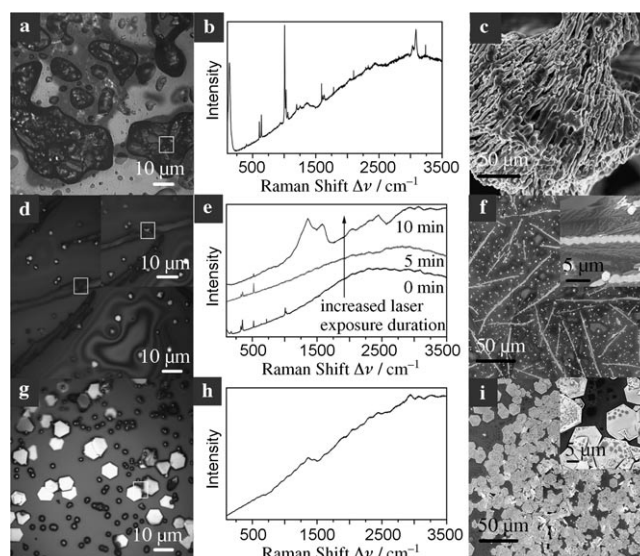

Figure 3. Optical microscope images, Raman spectra, and scanning electron microscope images of GTP-RT (a, b, and c, respectively), GTP-160 (d, e, and f, respectively), and GTP-230 (g, h, and i, respectively). The white squares in (a), (d), and (g) indicate where the laser beam was focused during the Raman measurements. The inset in (d) shows the decomposition of the rod and formation of the gold layer with increased exposure under the focused laser beam (wavelength: 532 nm, 50 mW), with the in situ Raman spectra shown in (e). The insets in (f) and (i) are images at higher magnification.

analysis has so far been carried out to answer the question of why organicus liquor regius with different compositions show different reactivity toward different noble metals, it can reasonably be assumed that the dissolution selectivity derives from the tunable interaction between SOCl$_2$ and the organic solvent/reagents. Further systematic fundamental studies on organicus liquor regius are promising directions for future research.

Our kinetic studies demonstrate that the selective dissolution of noble metals is an efficient process (Figure 4). The dissolution selectivity should open up a new avenue toward the recycling of noble metals, in particular, Pt. Besides the application in the recovery of noble metals, organicus liquor
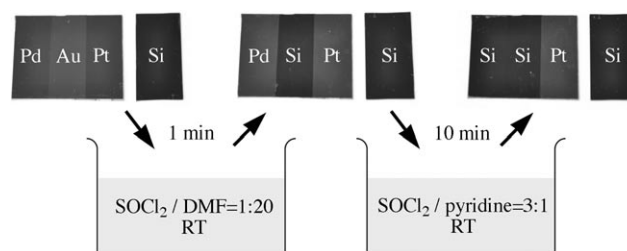

Figure 4. Illustration of an efficient selective dissolution of Au, Pd, and Pt. A silicon substrate was metallized with a Pd/Au/Pt layer (250 nm thick each by electron-beam evaporation or direct current sputtering, with chromium used as the adhesion layer) and the Au and Pd dissolved sequentially in the SOCl$_2$/DMF and the SOCl$_2$/py mixtures, respectively. The top row of images shows the photographs of the Pd/Au/Pt metallization layer on a silicon substrate during the process of selective dissolution.

regius will find wide applications in the microelectronic industry. Figure 5 shows the feasibility of "vapor" etching of Au metallization on a circuit board by vaporized organicus liquor regius. We believe that organicus liquor regius will open a new field of broad interest.
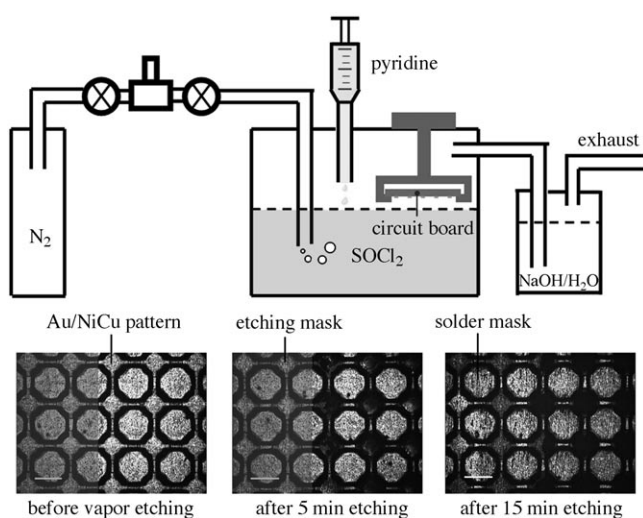

Figure 5. Illustration of a vapor-etching process of Au metallization on a circuit board. The bottom pictures show the optical microscope images of a circuit board during a vapor-etching process.

Experimental Section

Chemicals in the present research were all purchased from Sigma–Aldrich and used without further purification. Organicus liquor regius was prepared by adding organic compounds to $SOCl_2$ in an ice bath. The dissolution process is reproducible irrespective of whether it is carried out in air or under nitrogen. For Au dissolution, a certain amount of Au wire (50 μm in diameter), film (250 nm thick, deposited on silicon substrates by electron-beam evaporation), or foil (50 μm thick) of known mass was tested at room temperature. The dissolution rate of Au depends on the temperature, the composition of the organicus liquor regius, and, slightly, on the form of the Au feed. For comparison and consistency, we used the unit of $mol\,m^{-2}\,h^{-1}$ in the kinetic studies, according to Ref. [13]. After dissolution of Au, the excess of $SOCl_2$ in the $Au/SOCl_2/py$ solution was removed completely by purging the solution with N_2. The as-obtained liquid product was designated as GTP-L. Its solid product (GTP-RT) was obtained by drying at room temperature in a vacuum (15 KPa) for 48 h. GTP-160 and GTP-230 designate the products of the purified GTP-RT after thermal treatments at 160°C for 10 min and at 230°C for 10 min, respectively.

[1] We name the mixtures of $SOCl_2$ and organic solvents/reagents "organicus liquor regius" for the following reasons: 1) the oxidizing capability of organicus liquor regius, as is discussed in the manuscript, is due to the catalysis effect of the organic solvent/reagent rather than $SOCl_2$ itself; 2) $SOCl_2/py$ mixtures with volumetric ratios other than 3:1 are able to dissolve noble metals, so are the other systems; 3) $SOCl_2$ is by nature an inorganic compound but is widely used in organic synthesis and plays a more important role in organic chemistry than in inorganic chemistry. We only present the systematic studies on the $Au/SOCl_2/py$ mixtures because some important properties of py and $SOCl_2$ have been well documented. We focus on the $SOCl_2/py$ mixtures with excess $SOCl_2$ (namely, 3:1) for ease of purification. Moreover, varying the molar ratio of the $SOCl_2/py$ mixtures does not change the nonstoichiometric (as is discussed later) feature of the reactions.

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