Both of these predict correctly pseudo-first order kinetics in excess alkali with a slope varying with the excess alkali and a change to second order kinetics in solutions containing excess salt.

Since for both mechanisms the rate constants in excess alkali and in excess salt differ by a factor of K_h it is possible to evaluate the hydrolysis constant of reaction (2) by dividing (Slope)$(V_e - V_0)(b/a)$ in Table II by k'/b obtained from alkaline solutions at the same temperature. These values are listed in Table II also and it is possible to check the original assumption that $[\mathrm{PP}^{\pm}] = (a - x)$. Actually it can be shown that $[\mathrm{PP}^{\pm}] = (a - x)[\mathrm{OH}^-]/(K_h + [\mathrm{OH}^-])$ which reduces to the assumed form when $[\mathrm{OH}^-] >> K_h$. The rate constants can be corrected for the small amount of hydrolysis by multiplying them by $(K_h + [\mathrm{OH}^-])/[\mathrm{OH}^-]$. This has been done for all of the rate constants finally recorded. The magnitude of the effect is seen in Table I where the column (slope)(2.3)/$[\mathrm{OH}^-]$ gives the uncorrected rate constant and the last column gives the corrected value. This rate constant k is equal to either k_1 or k_2K_h depending upon which mechanism is correct.

It is interesting to compute the values of K_a, the acid ionization constant of the quaternary ammonium cation, from the values of K_h, the hydrolysis constant. Dividing into the ionization product of water at the temperatures indicated we obtain K_a equal to 3.08×10^{-11}, 5.94×10^{-11}, and 39.6×10^{-11} for the phenacylpyridinium, *p*-bromophenacylpyridinium and *m*-nitrophenacylpyridinium cations, respectively. These values are in the same relative order as the corresponding acidities of the substituted benzoic acids.

Summary

1. The alkaline cleavage of enolizable β-ketoalkylpyridinium salts is shown to be pseudo-first order in excess alkali and second order in the presence of excess salt.

2. The mechanism involves either the reaction of a hydroxyl ion with the enol-betaine or the reaction of two hydroxyl ions with the quaternary cation.

3. The rate constants have been determined for the *m*-nitro-, *p*-bromo- and unsubstituted phenacylpyridinium iodides at several temperatures and the activation energies computed.

EVANSTON, ILLINOIS RECEIVED DECEMBER 22, 1947

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The Reaction of Metallic Copper with Titanium(IV) Chloride

BY DONALD E. KOONTZ AND DOUGLAS G. NICHOLSON

During the course of an investigation of the nature of the reaction(s) taking place in the decolorization of commercial titanium(IV) chloride by metallic copper,[1] it was observed that clean dry metallic copper would react with chemically pure titanium(IV) chloride at room temperature. Accordingly, a detailed study was conducted on the interaction of these substances.

Loose rolls of copper foil made from sheets approximately 4 × 6 × 0.0127 cm. were heated to remove carbonaceous matter, cooled, rinsed in dilute hydrochloric acid, then water, and dried. They were then inserted in Pyrex test-tubes containing 5–8 ml. of titanium(IV) chloride, which were tightly closed with lead foil-covered corks.

The purplish-black scale which became evident after two or three hours could be shaken or jarred off, but on continued exposure the bright copper surface again became coated with the scale. After three to five weeks of exposure, the titanium(IV) chloride had entire disappeared, and an appreciable residue of dry, purplish-black material and flakes of unreacted copper remained. Using dry powdered (150 mesh) copper, the process was complete in twenty to thirty hours, but the residue tended to form a hard cake which, because of its expansion, sometimes cracked the tubes.

The rate of scale formation was not appreciably increased by heating the reaction tubes to approximately 100°, unless the metal surface was reexposed. It appeared that the scale tended to protect the metal surface from further action.

Small samples of the dry scale, with adhering flakes of metallic copper, were subjected to the tests and analyses described below.

(a) Exposure to atmospheric oxygen showed a gradual color change, becoming progressively gray, tan, and greenish-blue. The material was hygroscopic.

(b) Treatment with distilled water produced an immediate white turbidity which gradually (five to ten minutes) became reddish-brown in color. The interior surface of the retaining vessel became coated with a very thin mirror-like copper-colored deposit. This coating was insoluble in dilute hydrochloric acid, but was readily soluble in nitric acid or ammonia water–hydrogen peroxide mixture, yielding solutions which gave positive tests for copper(II) ion but negative tests for titanium(IV). The initial water solution gave a positive test for titanium(III) ions.

(c) Treatment with 6 *N* hydrochloric acid produced a clear purplish-pink solution containing

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[1] From a thesis submitted to the Graduate School of the University of Pittsburgh by Donald E. Koontz in partial fulfillment of the requirements for the Master of Science degree, January, 1948.

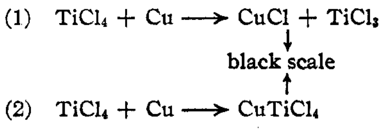
suspended flakes of copper. This solution gave a positive test for titanium(III) ions. After filtering to remove the suspended copper, samples of this solution were analyzed to determine the copper:titanium ratio present. This was done as follows: (1) atmospheric oxidation for twenty-four hours; (2) titanium was determined by double precipitation by ammonia water followed by ignition of the precipitate to the dioxide; (3) after removal of ammonia from the combined titanium filtrates, copper present was precipitated by the addition of sodium hydroxide, followed by ignition to the oxide. Analyses of solutions of five different scale samples gave an average weight ratio of the elements copper:titanium of 1.39:1.00. Theoretical weight ratio of these elements (based on one atom of each) is 1.33:1.00. It thus appeared that the black residue was composed of compounds of copper and titanium whose metallic ratio contained one atom of each.

(d) Samples of the metal-free, 6 *N* hydrochloric acid solution of the scale become a pale bluish-green color after exposure to atmospheric oxygen for approximately twenty hours.

A sample of freshly prepared copper(I) chloride was added to a solution of titanium(III) chloride, prepared by electrolytic reduction of aqueous titanium(IV) chloride. A water-clear purplish-pink solution resulted. On standing several minutes after dilution with a 4–5 fold excess of distilled water, the initial color of the solution faded and an adherent copper-like deposit coated the interior surfaces of the vessel. This deposit exhibited the same characteristics as that produced when a sample of purplish-black residue was added to distilled water (b, above).

Discussion

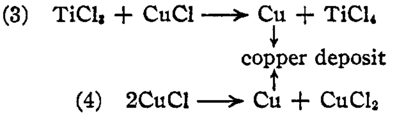
Based on the above-described tests and observations, it appears that the purplish-black scale is a mixture and/or a compound containing a ratio of one atom each of titanium(III) and copper(I) chlorides. Either or both of the following reactions are postulated as the means by which the scale is produced.



$$\begin{tikzcd} \text{(1)} & TiCl_4 + Cu \arrow[r] & CuCl + TiCl_3 \arrow[d] \\ & & \text{black scale} \\ \text{(2)} & TiCl_4 + Cu \arrow[r] & CuTiCl_4 \arrow[u] \end{tikzcd}$$

The white precipitate produced immediately on addition of the scale to distilled water was probably copper(I) chloride (a product in reaction (1), or produced by aqueous decomposition of $CuTiCl_4$ formed in reaction (2)) in a solution of titanium(III) chloride hexahydrate.

The gradual color change which took place (with passage of time) in the aqueous mixture of titanium(III) and copper(I) chlorides was probably due to either or both of the two reactions

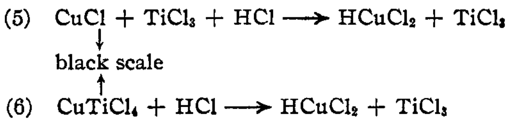


$$\begin{tikzcd} \text{(3)} & TiCl_3 + CuCl \arrow[r] & Cu + TiCl_4 \arrow[d] \\ & & \text{copper deposit} \\ \text{(4)} & 2CuCl \arrow[r] & Cu + CuCl_2 \arrow[u] \end{tikzcd}$$

Of these two equations, (3) and (4), reaction (3) appears to be more probable since reaction (4) indicates that one-half of the total copper initially present would be in solution after the reaction was complete. Tests conducted on the residue and filtrate indicated that only a very small fraction of the total copper initially present was soluble in 6 *N* hydrochloric acid.

It is interesting to note that reaction (3), in aqueous solution, is the reverse of reaction (1) in non-aqueous medium.

The solubility of the purplish-black scale in 6 *N* hydrochloric acid producing a clear purplish-pink solution can be explained by either or both of the following equations



$$\begin{tikzcd} \text{(5)} & CuCl \arrow[d] + TiCl_3 + HCl \arrow[r] & HCuCl_2 + TiCl_4 \\ & \text{black scale} & \\ \text{(6)} & CuTiCl_4 \arrow[u] + HCl \arrow[r] & HCuCl_2 + TiCl_3 \end{tikzcd}$$

Conclusions

A detailed study of the reaction of metallic copper with titanium (IV) chloride has been undertaken. This reaction produces a purplish-black scale which contains copper (I) and titanium(III) ions.

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