

exists at the end of the reaction an equilibrium mixture of sodium ketyl and sodium pinacolate



in which the equilibrium is preponderantly in favor of the *right-hand* side of the formulation. In other words, the products obtained by addition of sodium to aromatic ketones are *not radicals existing in the monomolecular state, as has been commonly supposed for nearly twenty years*, but consist for the most part of the *dimolecular form*, namely, sodium pinacolate.

In addition, the forthcoming publication will point out the reason why Schlenk, E. Bergmann and others were misled in interpreting as they did the reaction and the structure of the compounds.

CHEMISTRY LABORATORY  
UNIVERSITY OF MICHIGAN  
ANN ARBOR, MICHIGAN

W. E. BACHMANN

RECEIVED JUNE 11, 1932  
PUBLISHED SEPTEMBER 5, 1932

---

#### THE ELECTRODEPOSITION OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

*Sir:*

The possibility of the electrodeposition of molybdenum and tungsten from aqueous solutions is suggested by their position below hydrogen in the electromotive series. Acidic solutions of these elements in various valence states may be prepared with citric acid, glucose or other hydroxyl compounds. Since the procedure for the electrodeposition of molybdenum and tungsten should resemble to a certain extent the methods applicable to chromium, some studies were first made using solutions of trivalent chromium salts and citric acid.

Britton and Westcott [*Trans. Faraday Soc.*, 27, 809 (1931)] have suggested, subsequent to the completion of these experiments, that chromium may be deposited from solutions containing chromium in the form of complexes with organic acids.

The following procedure was found to give bright, adherent deposits of chromium: 2 g. of hydrated chromic chloride and 4 cc. of 2.5 *M* monopotassium citrate solution are diluted in 20 cc., heated to boiling and cooled. A carbon anode is contained in a porous cup and a sheet of copper serves as cathode. Metal is deposited at a current density of 3 amp. per sq. dm. and a voltage drop of 4.5 to 7.5 volts. Too high current density and voltage will cause the deposition of black powder. Chromium was also deposited from a bath in which tartaric acid was employed.

Molybdenum may be deposited from an acid solution: 2 g. of molybdic acid and 15 cc. of 34% hydrobromic acid are evaporated almost to dryness. The dark red-brown residue is dissolved in 6 cc. of 2.5 *M* dipotassium citrate

and diluted to 20 cc. After neutralizing with potassium hydroxide, 1 cc. of 2.5 *M* citric acid is added. A current density three or four times greater than for chromium is used. Tartaric acid and glycerol were substituted for citric acid with less satisfactory results. Molybdenum has also been deposited from solutions of molybdic acid in citric and tartaric acids, but the results have also been less satisfactory.

Tungsten has been deposited from aqueous media [Fink and Jones, *Trans. Am. Electrochem. Soc.*, **59**, 461 (1931)] of alkaline nature. It may also be deposited from acid solutions in bright coherent form. Two grams of tungstic acid is dissolved in potassium hydroxide, 5 cc. of 2.5 *M* citric acid is added, then potassium hydroxide to neutrality and 1 cc. of 2.5 *M* citric acid. The solution is diluted to 20 cc. A platinum foil (5 sq. cm.) is the anode and a copper sheet is used as cathode. Similar results may be obtained if sodium hydroxide and tartaric acid are substituted for potassium hydroxide and citric acid, respectively. Tungsten may also be obtained from solutions containing acetic acid and glycerol or glucose.

Work now in progress has shown the possibility of the electrodeposition of columbium and tantalum by similar methods.

More complete data as to optimum conditions of procedure, current efficiencies and the properties of the deposits will be published at a later date.

DEPARTMENT OF CHEMISTRY  
ST. LOUIS UNIVERSITY  
ST. LOUIS, MISSOURI  
RECEIVED JULY 5, 1932  
PUBLISHED SEPTEMBER 5, 1932

L. F. YNTEMA

---

#### THE DISSOCIATION CONSTANT OF ACETIC ACID

*Sir:*

The new conductivity measurements on acetic acid of MacInnes and Shedlovsky [MacInnes and Shedlovsky, *THIS JOURNAL*, **54**, 1429 (1932)] lead to a dissociation constant that falls off rapidly at concentrations above 0.01 *N*, and the authors are inclined to attribute the effect to a change in the dielectric constant of the solvent. This seems unlikely, if only because such a change would affect both the mobilities and the activity coefficients of the ions, and the resultant effect upon *K* would be extremely small. On the other hand, there are good grounds for thinking that a viscosity correction of some sort should be applied to data such as these, and I have accordingly recalculated the degree of dissociation using the simple viscosity correction, *i. e.*, by employing in place of  $\Lambda$  the value  $\Delta\eta/\eta_0$ ; values for the relative viscosity were taken from "International Critical Tables," Vol. V, p. 20. The results are reproduced in the figure, where the open circles represent the viscosity corrected values, the solid dots are