molecule, and this free hydroxyl group is essential for the cleavage of the carbonyl group with alkaline hydrogen peroxide. It follows therefore that this group is not present in dehydrorotenol. Rotenol gives a color test with ferric chloride, whereas dehydrorotenol does not. Thus it follows that the hydrogen atom of the free hydroxyl group is involved in the formation of dehydrorotenol. If the original ether linkage in rotenone was reformed in the formation of dehydrorotenol from rotenol, dehydrodihydrorotenolic acid and *dl*-dihydrorotenonic acid [H. L. Haller and F. B. LaForge, THIS JOURNAL, 53, 3426 (1931)] should be identical as the asymmetric center I [*ibid.*, p. 3427] is racemized in the formation of rotenol. Besides, dehydrorotenol does not react with iodine and alcoholic potassium acetate to lose two hydrogen atoms and to form dehydrodihydrorotenone. It is possible, therefore, that the structure for dehydrorotenol is either VI or VII.

The product obtained from dehydrodihydrorotenolic acid and acetic anhydride, which was thought to be a mixed anhydride [H. L. Haller and F. B. LaForge, THIS JOURNAL, 53, 2271 (1931)], is in fact a true acetyl derivative, the hydroxyl group in the 4 position having been acetylated.

VI   VII
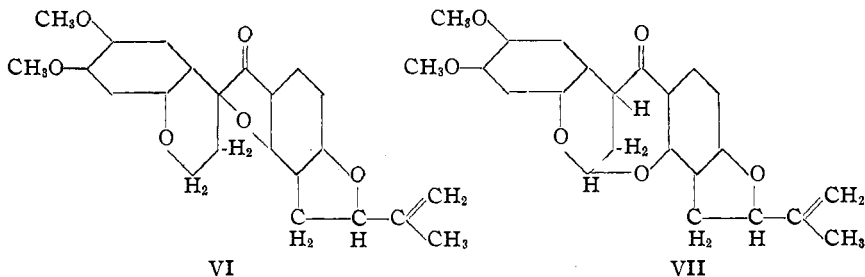
INSECTICIDE DIVISION
BUREAU OF CHEMISTRY AND SOILS
WASHINGTON, D. C.

H. L. HALLER

THE RELATION BETWEEN THE DISSOLUTION OF METALS IN ACIDS AND THE ELECTROLYTIC EVOLUTION OF HYDROGEN

Sir:

The finding of Brönsted and Kane [THIS JOURNAL, 53, 3624 (1931)] that the velocity of the reaction of sodium amalgam with aqueous solutions is proportional to a fractional power of the concentration of sodium in the amalgam suggests strongly that the rate of hydrogen evolution on a sodium amalgam surface is essentially the same as on a mercury surface polarized electrically to a potential equal to that established by the sodium–sodium ion equilibrium. From the precise and definitive work of Bowden [*Trans.*

Faraday Soc., **24,** 473 (1928)] we know that the coefficient n in the Tafel polarization equation

$$E = \frac{RT}{nF} \ln I + \text{constant}$$

is 0.5 on mercury surfaces at current densities below about 10^{-4} amp. per sq. cm., and changes discontinuously at higher current densities to 0.27. Since

$$E = \frac{RT}{F} \ln \frac{a_{Na^+}}{a_{Na}} + E_0$$

and since current is proportional to reaction velocity, the above hypothesis indicates such a fractional order of reaction as was found.

$$v \propto \frac{[Na]^n}{[Na^+]^n}$$

This assumes, of course, that these amalgams are so dilute that there is approximate proportionality between activity and concentration of the sodium.

It also follows that the reaction velocity should vary inversely as the same fractional power of the sodium-ion activity. While Brönsted and Kane seem not to have expected any such effect, and report no quantitative results on the effect of sodium ion, they do report that addition of sodium chloride decreases the reaction velocity.

It should therefore be possible to apply to the amalgam reaction all of the electrochemical evidence that the reaction $H^+ + e \rightleftharpoons H$ is reversible and very rapid compared with the process of formation of H_2 from the atomic hydrogen or its alloy with the metal. In particular it is extremely difficult to understand the saturation effects observed in the electrochemical oxidation of hydrogen to hydrogen ion [see Hammett, THIS JOURNAL, **46,** 7 (1924)] on the basis of any other mechanism.

The contrary conclusion of Brönsted and Kane that the first step in the formation of molecular hydrogen from hydrogen ion is the rate-determining one depends upon their observation of a direct effect of the concentration of the reacting acid upon the velocity. This would be strong evidence if it could be proved that diffusion was not a factor in the determination of the reaction velocity in their experiments and in those of Kilpatrick and Rushton [*J. Phys. Chem.*, **34,** 2180 (1930)]. Certainly Bowden showed that the electrolytic evolution of hydrogen on mercury is determined by hydrogen-ion concentration and is subject to no generalized acid effects when the reaction velocity is so low that diffusion is not a significant factor.

DEPARTMENT OF CHEMISTRY   LOUIS P. HAMMETT
COLUMBIA UNIVERSITY   ARTHUR E. LORCH
NEW YORK, N. Y.