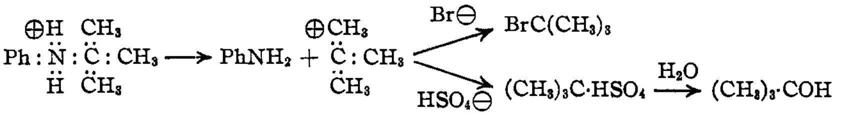
been found that *tert*-butylaniline and other alkylanilines containing *tertiary* alkyl groupings yield aniline on heating with aqueous mineral acids [Hickinbottom, *J. Chem. Soc.*, 1070 (1933); *Nature*, **131**, 762 (1933)]. Under precisely similar conditions, alkylanilines with *normal* alkyl groupings are unchanged. Further, diphenylamine or triphenylamine appears to be stable to hot mineral acid. Yet, according to Kharasch and Flenner [THIS JOURNAL, **54**, 681 (1932)] a *tertiary* alkyl group is less electronegative than the corresponding *normal* alkyl group and each is less electronegative than phenyl.

A more satisfactory basis for arriving at an explanation of such reactions appears to be the theory of chemical reactions developed by Lapworth and Robinson [Robinson, "Outline of an Electrochemical Theory of the Course of Organic Reactions," London, 1932; compare W. A. Noyes, THIS JOURNAL, **55**, 656 (1933)].

In *tert*-butylaniline, the induced effect of three methyl groups attached to a carbon atom is sufficiently intense to cause the transfer of an electron from the *tert*-butyl group to the nitrogen, provided that conditions are suitable and reagents are present to take advantage of this tendency. The hydrolysis of *tert*-butylaniline in acid solution is represented by the following scheme:



$$\mathrm{Ph}:\underset{\mathrm{H}}{\overset{\oplus\mathrm{H}}{\ddot{\underset{..}{\mathrm{N}}}}}:\underset{\ddot{\mathrm{C}}\mathrm{H}_3}{\overset{\mathrm{CH}_3}{\ddot{\mathrm{C}}}}:\mathrm{CH}_3 \longrightarrow \mathrm{PhNH}_2 + \underset{\ddot{\mathrm{C}}\mathrm{H}_3}{\overset{\oplus\mathrm{CH}_3}{\ddot{\mathrm{C}}}}:\mathrm{CH}_3 \begin{cases} \xrightarrow{\mathrm{Br}\ominus} \mathrm{BrC(CH_3)_3} \\ \xrightarrow[\mathrm{HSO_4}\ominus]{} \mathrm{(CH_3)_3C\cdot HSO_4} \xrightarrow{\mathrm{H_2O}} \mathrm{(CH_3)_3\cdot COH} \end{cases}$$

The fate of the *tert*-butyl "ion" obviously depends on the experimental conditions. In concentrated hydriodic acid or hydrobromic acid, the corresponding *tert*-butyl halide is formed, while in more dilute solution increasing amounts of the carbinol result. This has been confirmed experimentally.

The hydrolysis of triphenylmethylaniline [Elbs, *Ber.*, **17**, 702 (1884); Hemilian, *ibid.*, p. 746; Gomberg, *ibid.*, **35**, 1829 (1902)] is represented similarly.

It is evident that, if the induced effect is enhanced by suitable substituents, the tendency to hydrolytic fission is also increased. Recorded examples of this are the elimination of nitrotoluidines from di- and tetranitro-di-*p*-tolylaminobutanes under the influence of hot diluted mineral acid [Morgan and Hickinbottom, *J. Soc. Chem. Ind.*, **43**, 307T (1924); compare Morgan, Hickinbottom and Barker, *Proc. Roy. Soc.*, **A110**, 518 (1926)]; the ready formation of aryl sulfonanilides from the aryl sulfonyl derivatives of *tert*-butylaniline by heating with diluted sulfuric acid.

The same theoretical considerations which have been used to explain the hydrolytic fission of *tert*-butylaniline and triphenylmethylaniline can be applied to account for the sensitivity of the *tert*-butyl halides and triphenylmethyl halides to hydrolysis.

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WILFRED JOHN HICKINBOTTOM

RECEIVED JULY 18, 1934

THE EXCHANGE REACTION BETWEEN DEUTERIUM AND WATER VAPOR ON SURFACES

Sir:

We have observed a rapid conversion of deuterium to hydrogen on catalytic hydrogenating surfaces such as chromium oxide gel and zinc oxide which conversion may be ascribed to the deuterium-water exchange reaction. The existence of this exchange is important, since it may, under favorable circumstances, lead to the practically complete replacement of deuterium by the light isotope in a reaction mixture. In ordinary circumstances it can readily lead to the introduction of hydrogen into what may have been assumed to be pure deuterium.

We have analyzed by the thermal conductivity method of Farkas and Farkas [*Proc. Roy. Soc.* (London), **144A**, 467 (1934)] the gases desorbed by Dr. H. W. Kohlschuetter from a 15.5-g. sample of chromium oxide gel on which the velocity of activated adsorption of pure deuterium gas at 184° was being measured. In successive experiments, during each of which 25 cc. of pure deuterium was adsorbed, the desorbed gases analyzed, respectively, 98.5, 97.5, 92.5 and 87% of the *light isotope*. The adsorbent was then allowed to take up approximately 550 cc. of deuterium at about 350°, in units of 100 cc., the adsorption of each unit being followed by desorption at the same temperature. The gas desorbed from the surface after a further 25 cc. of deuterium had been adsorbed at 184°, in the manner of the first experiments recorded, now analyzed 41% light isotope, pointing to an exhaustion of the hydrogen source on the surface. The exchange was now repeated at 184° in the reverse direction. Hydrogen to the extent of 25 cc. was adsorbed and the desorbed gas then analyzed. It proved to be 45.5% hydrogen and 54.5 deuterium. The closeness of the analyses in successive experiments using first deuterium and then hydrogen points to the establishment of an equilibrium on the adsorbent surface best explained as an equilibrium between hydrogen, deuterium water and deuterowater, the water being present as a unit in the gel structure of the chromium oxide.

This conclusion is further confirmed by the observed influence of temperature on the reaction. At 0° the gas from a partially deuterized gel treated with deuterium for 12.5 hours showed only 11% hydrogen. This was not due to exhaustion of hydrogen from the surface, since, in succeeding experiments at 100°, samples of deuterium were converted to gas containing 47 and 51.5% of hydrogen, respectively, after nine and fifteen minutes of contact. The experiments of Gould, Bleakney and Taylor [*J. Chem. Phys.*, **2**, 362 (1934)] would lead one to expect a much more rapid interchange at 0° if the process involved only adsorbed hydrogen gas and deuterium.

Similar experiments with zinc oxide (*ex* oxalate), in the preparation of which no hydrogen gas was used, point also to water as the source of the hydrogen. Our experiments indicate a much more rapid exhaustion of the hydrogen source in this case than with the gel structure. Hydrogen production may be renewed on such exhausted surfaces on addition of water vapor. Platinized asbestos when first treated with deuterium also shows hydrogen formation, slower than on the gel and also exhausted by continued treatment with deuterium.

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Received July 17, 1934

LIQUID-LIQUID EQUILIBRIA INVOLVING HEAVY WATER

Sir:

Since deuterium water is not so good a salt solvent as ordinary water [Taylor, Caley and Eyring, This Journal, **55**, 4334 (1933)], we examined the effect of increasing deuterium content on the lower consolute temperature of nicotine and water and on the (upper) consolute temperature of phenol and water. As expected, the former was lowered and the latter raised as the deuterium content of the water increased. The amount of the lowering of the critical solution temperature of nicotine and water was for 3.9% D, 0.28°; and for 10.6% D, 0.72°. For phenol the corresponding increases were as follows: 3.89% D, 0.43°; 4.12%, 0.50°; 5.81%, 0.71°; 10.62%, 1.24°; 47.20%, 5.58°. The temperature increases in the case of phenol are linear in the % D so that an extrapolation to 100% D is possible. The indicated temperature rise is about 11.8°. No attempt was made to determine the extent of the H-D exchange in these experiments, but it is probable that the hydroxyl and amino hydrogen atoms exchanged completely while the rest did not. A single attempt to show a significant change in the isotopic composition of water as a result of consolution with phenol and subsequent unmixing was unsuccessful.

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Received July 16, 1934

OXYGEN ADDITION COMPOUNDS OF ACETYLENES

Sir:

We have recently found that many acetylenes acquire distinct oxidizing properties after coming in contact with air or oxygen. The acetylenes studied have been mainly of the types $RC\equiv CH$, $RC\equiv CR'$ and $RC\equiv CX$, where R and R′ represent alkyl and aryl groups, and X denotes a halogen. Although these acetylenes have been prepared by widely different methods, a large number of them upon exposure to air for several months contain almost the same amount of oxidizing agents. It is improbable, therefore, that the oxidizing properties of the acetylenes are caused by traces of olefins, for equal quantities of olefins would certainly not be formed by the various methods of preparation. It is conceivable that the acetylenes first polymerize, yielding olefinic derivatives which form peroxides. However, mono-alkyl and di-alkyl acetylenes contain very nearly the same amounts of peroxides after exposure to air for equal periods of time. Consequently, it is probable that the acetylenes themselves form peroxides. The similar concentrations of peroxide in many of the acetylenes may be due to a rearrangement of the peroxide into some more stable form when a certain definite concentration is reached. This hypothesis is supported by the ease with