TABLE I

PROTEIN CONTENT OF THE BARK FROM 21 LOCUST TREES GROWN IN DIFFERENT SECTIONS

Series R

Samples of Series R were from borer-resistant trees.

Sample no.	Source	Time collected	Age of tree, yrs.	Protein content, %
R_1	Hopedale, Ohio	11-26-34	9	18.12
R_2	Hopedale, Ohio	11-26-34	9	25.34
R_3	Hopedale, Ohio	11-26-34	9	23.23
R_4	Hopedale, Ohio	11-26-34	9	20.38
R_5	Cambridge, Ohio	11-26-34	8	22.41
R_6	Cambridge, Ohio	11-26-34	8	20.93
R_7	Cambridge, Ohio	11-26-34	8	20.93
R_8	Cambridge, Ohio	11-26-34	7	20.81
R_9	Cambridge, Ohio	11-26-34	7	19.46
R_{10}	Cambridge, Ohio	11-26-34	7	22.68
R_{11}	Versailles, Ind.	11- 5-34	13	21.41
			Average	21.43

Series S

Samples of Series S were from borer-susceptible trees.

S_1	Minerva, Ohio	11-26-34	9	27.98
S_2	Minerva, Ohio	11-26-34	9	22.22
S_3	Minerva, Ohio	11-26-34	9	26.62
S_4	Minerva, Ohio	11-26-34	9	24.99
S_5	Minerva, Ohio	11-26-34	9	23.32
S_6	Hopedale, Ohio	11-26-34	10	12.94
S_7	Hopedale, Ohio	11-26-34	10	25.69
S_8	Hopedale, Ohio	11-26-34	10	15.87
S_9	Hopedale, Ohio	11-26-34	10	19.11
S_{10}	Hopedale, Ohio	11-26-34	10	17.06
			Average	21.58

Ohio and Indiana trees was collected the latter part of November. It has been shown[7] that soon before the leaves fall in the autumn their protein is transported to the parenchyma of the bark where it is stored during the dormant period.

[7] E. Schulze, *J. Landw.*, **52**, 323 (1904).

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The Existence of a Maximum in the Gas Solubility–Pressure Curve

BY I. R. KRICHEVSKY

Basset and Dodé[1] have measured the nitrogen solubility in water at 18° and under pressure up to 4500 kg./sq. cm. They detected an excessively interesting phenomenon, that at pressures about 3000 kg./sq. cm. the nitrogen solubility passes through a maximum. Though their determinations are not particularly exact, nevertheless the existence of a maximum is a reality and can be predicted theoretically.

For a case of slightly soluble gases in solvents with small vapor pressure we[2] have deduced a thermodynamical equation

$$\log f_2/N_2 = \log K + \bar{V}_2 P/2303RT \qquad (1)$$

where f_2 is the fugacity of the gas, N_2 its mole fraction in the solution, K Henry's coefficient, $\bar{V}_2$ partial molal volume of the dissolved gas and P total pressure.

The solubility maximum corresponds to that pressure at which

$$\partial \ln N_2/\partial P = 0 \qquad (2)$$

Differentiating the equation (1) with respect to pressure and substituting V_2/RT for $\partial \ln f_2/\partial p$, where V_2 is gas volume, we can readily find that at the maximum solubility

$$V_2 = \bar{V}_2 \qquad (3)$$

The partial molal volume of the water-dissolved nitrogen at 18° is 32.7 cc.[2] For lack of data we shall accept that the partial molal volume of nitrogen does not depend upon pressure. Extrapolating data of Amagat[3] for nitrogen compressibility we found that at 18° the pressure of 3600 kg./sq. cm. corresponds to the volume of 32.7 cc., which is in a fairly good agreement with measurements of Basset and Dodé.

[1] Basset and Dodé, *Compt. rend.*, **203**, 775 (1936).

[2] Krichevsky and Kasarnovsky, THIS JOURNAL, **57**, 2168 (1935).

[3] Amagat, *Ann. chim. phys.*, **29**, 68 (1893).

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Mechanism of the Reduction of Unsaturated Compounds with Alkali Metals and Water

BY CHARLES BUSHNELL WOOSTER AND KENNETH L. GODFREY

A number of valuable methods for reducing unsaturated organic compounds involve the use of a combination of an alkali metal or its amalgam with water or some other hydrolytic solvent, and the various interpretations which have been offered for these reactions are based on one, or the other, of two rival hypotheses. The earlier of these hypotheses attributes the reduction to "nascent" hydrogen liberated by the reaction between the alkali metal (or its amalgam) and the hydrolytic solvent.[1] In more general terms, this hypothesis requires that the actual reduction is effected by the *combination* and not by the metal alone. The more recent hypothesis attributes the

[1] Kekulé, *Ann. Suppl.*, **1**, 129 (1861); Herrmann, *Ann.*, **132**, 75 (1864); von Baeyer, *ibid.*, **269**, 145, 170, 174 (1892).

actual reduction to the alkali metal alone; that is, the primary reduction process is assumed to be addition of the alkali metal to the unsaturated compound. It is considered that the function of the solvent is merely to replace the metal in the addition compound with hydrogen by a hydrolytic process and that direct reaction between the solvent and the free alkali metal (or its amalgam) is a side reaction.[2] It has been shown definitely that certain specific reduction processes actually follow the course prescribed by the second hypothesis.[3]

We have now discovered another specific reduction reaction which appears definitely to follow the course prescribed by the *first* hypothesis. This reaction is the reduction of toluene with sodium (or potassium) and water in liquid ammonia. Toluene is not attacked by solutions of these alkali metals in liquid ammonia in the absence of water for the blue color of the alkali metal solutions is not discharged by addition of a large excess of toluene even when the mixture is allowed to stand for several hours. Furthermore, the presence of the total amount of metal in the free state may be demonstrated by the addition of ethyl bromide, ammonium chloride or a catalyst (iron rust) which initiates reaction between the metal and the solvent ammonia. Under these conditions the theoretical amount of ethane or hydrogen is always evolved and the toluene may be recovered. On the other hand, when water is added to the mixture much less than the theoretical amount of hydrogen is evolved and there is obtained a highly unsaturated liquid product which boils over the range 110–115°, chars with fuming sulfuric acid, reacts vigorously with liquid bromine and rapidly decolorizes a solution of bromine in carbon disulfide.

It is evident that although toluene does not react with liquid ammonia solutions of these alkali metals, it is immediately attacked (doubtless reduced) when water also is added. These facts are especially significant because under such conditions a very appreciable concentration of toluene is always present in the same phase with the ammonia and the alkali metal so the action of water cannot be ascribed to any purely surface phenomenon. It is also noteworthy that the effective combination is relatively specific, thus the hydrogen produced by reactions between the alkali metals and ammonia or ammonium chloride does not attack the toluene.

Finally, these observations have an important bearing on the technique of studying reactions in liquid ammonia, because two common practices are the use of toluene as a diluent to facilitate the reaction of organic substances sparingly soluble in ammonia, and the measurement of the hydrogen evolved on addition of water to determine the amount of excess free alkali metal remaining at the end of a reaction. It is now clear that a combination of these two practices will give misleading results, and that ammonium chloride (or an ammonolysis catalyst) should be used instead of water under such circumstances.

These studies are being continued in the hope of obtaining further significant information regarding the mechanism of such reduction processes.

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[2] Willstätter, Seitz and Bumm, *Ber.*, **61**, 871 (1928).

[3] Wooster and Smith, THIS JOURNAL, **53**, 179 (1931).

COMMUNICATIONS TO THE EDITOR

OCCURRENCE OF ACETOVANILLONE IN WASTE SULFITE LIQUOR FROM CONIFEROUS WOODS

Sir:

Investigation of the products of alkaline degradation of waste sulfite liquor from the pulping of coniferous woods (mixture of spruce and balsam) on a large laboratory scale has disclosed the presence therein of acetovanillone (3-methoxy-4-hydroxyacetophenone) identical in every way with the synthetic product made from guaiacol acetate. *Anal.* OCH_3, 18.65; calcd. 18.68; m. p. 114.5°. Synthetic acetovanillone: m. p. 115°; mixed m. p. 114–115°. Semicarbazone: m. p. 165.5–166°; mixed m. p. 164.5–165.5°.

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