

According to Sowa and Nieuwland⁵ amides can be esterficated by alcohols and phenols in the presence of boron trifluoride. It might, therefore, be expected that acetylated amines would be deacylated in the acidic solution formed from boron trifluoride and an alcohol. This was also found to be the case, and 3,4-dinitroacetone-naphthalide and some other acetyl compounds (see Table 1) were easily deacylated when heated in methanol containing boron trifluoride (0.10 g/ml, 4–8 mole/mole acetyl compound) giving the corresponding amine in almost theoretical yield. The time required for complete reaction was determined only approximately. Samples were taken out at suitable intervals and investigated. The relation between the rate of deacylation and the amount of boron trifluoride was not investigated. In the case of *o*-nitroacetanilide, however, an experiment was carried out with one tenth of the above mentioned amount of boron trifluoride; an increase of the time of reaction from 10 to 35 minutes was required.

As can be seen from the Table the sterically hindered 2,6-dimethylacetanilide was very slowly deacylated even at 110 °C, and its *N*-methyl derivative remained unchanged when heated to this temperature for 36 hours. For comparison it may be pointed out that the former compound can not be hydrolysed in boiling concentrated hydrochloric acid but when heated to 200 °C in 70–75 % sulphuric acid it is hydrolysed in about 6 hours⁶. The *N*-methyl derivative remains unchanged when boiled in 80 % sulphuric acid for 9 hours or heated to 220 °C in concentrated alcoholic potassium hydroxide for 11 hours⁷.

Experimental. The acetyl compound (0.30 g) was refluxed in methanol (6 ml) containing boron trifluoride (0.60 g) and at suitable intervals samples were taken out and investigated (m.p. and/or refractive index). When the deacylation was complete the reaction solution was worked up in one of the following alternative ways.

1. After the introduction of ammonia to bind the boron trifluoride as $\text{NH}_3 \cdot \text{BF}_3$ the methanol was evaporated and the residue extracted with ether. Evaporation of the ether yielded the free amine. By treatment of the ether insoluble residue with sulphuric acid as described by Sowa and Nieuwland⁵ practically all the boron trifluoride was liberated.

2. Water insoluble amines forming compounds with boron trifluoride which decom-

pose in aqueous solution (e. g. 2,3-dinitroaniline) were precipitated by diluting the reaction solution with water. The precipitated amine was collected and washed with water.

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The Compressibility of Acetylene at 25.0° C

RAGNAR VESTIN

Swedish Rubber Research Laboratory, LKB Research Laboratory, and Institute for Inorganic and Physical Chemistry, Stockholm University, Sweden

In connection with equilibrium and solubility determinations earlier described¹, the compressibility of acetylene was measured at pressures below 1.5 atm.

It proved advantageous to use the same type of apparatus as for the solubility determinations, even if more accurate compressibility measurements may be performed by other methods. The apparatus consists of a thick-walled glass flask in a water thermostat; the flask is connected to a manometer and a gas-burette, the latter provided with a separate thermostat. The gas contents of ducts and manometer can be calculated from the pressure and the inner reading of the manometer, using a function which has been determined by separate calibration.

During the measurements V and T are kept constant and the relation between p and n is studied. The measurement of the gas quantity (which is volumetrically performed under suitable standard conditions), however, does not give n but $n a$,

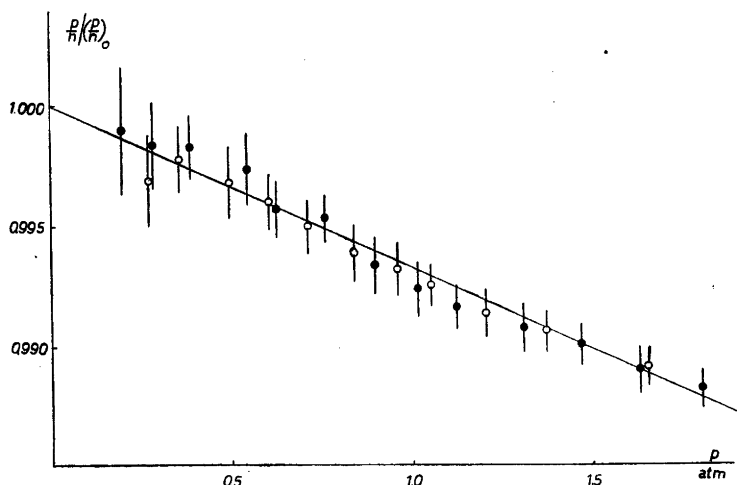


Fig. 1. Compressibility of acetylene.

where a is a constant but unknown factor. The quotient p/na is plotted as a function of p , and by extrapolation to $p = 0$ the limit value $(p/na)_0$ is determined. The results are then expressed by the dimensionless quotient

$$\frac{p}{na} / \left(\frac{p}{na} \right)_0 = \frac{p}{n} / \left(\frac{p}{n} \right)_0 \quad (V \text{ and } T \text{ constant})$$

which is identical with the quotient

$$vp / (vp)_0 \quad (n \text{ and } T \text{ constant})$$

Fig. 1 illustrates the results from two independent series of measurements. The lengths of the vertical lines through the points correspond to the maximum errors, as derived from the numerical accuracy of the experimental data. The straight line corresponds to the relation $vp / (vp)_0 = 1 + k \cdot p$.

A statistical treatment, carried out considering the fact that na contains successively accumulated errors, gives for the one series the value $k = -(6.9 \pm 0.3) \cdot 10^{-3}$ and for the other series $k = -(7.2 \pm 0.4) \cdot 10^{-3}$. By insertion of the k -value, $-7.0 \cdot 10^{-3} \text{ (atm)}^{-1}$, relative vp -values can be computed with a standard error of $\pm 3 \cdot 10^{-4}$.

Both the curve and the statistical computation show a deviation tendency, which indicates that in a general compressibility

function of the type $vp / (vp)_0 = 1 + B \cdot p + C \cdot p^2 + \dots$ there is a positive third virial coefficient, C , and that the correct numerical value for the negative second virial coefficient, B , is somewhat higher than the accepted k -value. An accurate determination of C would demand measurements at higher pressures.

Earlier measurements at 25.0° C, performed by Sameshima² and falling within the interval 1—8.7 atm, give a fairly constant k -value of $-(7.0 \text{ to } 6.6) \cdot 10^{-3} \text{ (atm)}^{-1}$ in the interval 2.4 to 7.3 atm, but within the interval 1.0 to 2.4 atm his measurements seem to give so high a value as $k = -8.5 \cdot 10^{-3}$. Howarth and Burt³ have performed compressibility measurements at 0° C and got $k_0 = -8.8 \cdot 10^{-3} \text{ (atm)}^{-1}$.

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