point of minimum solubility is at about pH 4.6.

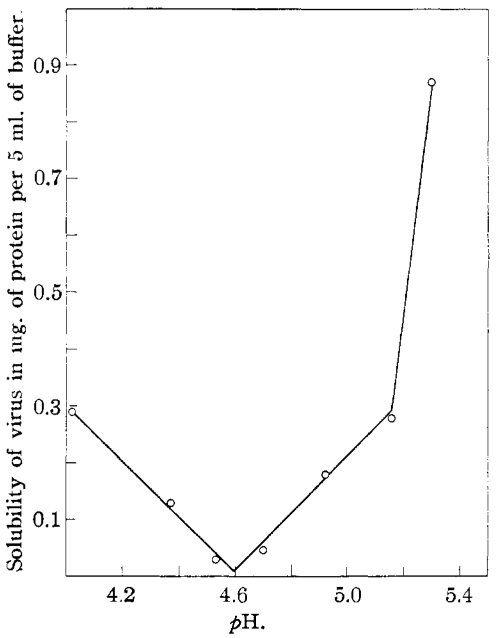

Fig. 4.—Graph showing the variation of the solubility of alfalfa mosaic virus in a "composite buffer" with the pH of the buffer. Point of minimum solubility estimated to be at pH 4.6.

As a general rule derived from the study of other viruses, the pH value of minimum solubility usually approximates the isoelectric point to within a few tenths of a pH unit.

Summary

Alfalfa mosaic virus was found to have a sedimentation constant of 73.9×10^{-13} cm. per sec. in unit centrifugal field, with a probable error of $\pm 5.2 \times 10^{-13}$. The specific volume was determined to be 0.673. Assuming the virus particles to be essentially spherical, an average molecular weight of 2.1×10^6 and an average particle diameter of 16.5 mμ were calculated. In both sedimentation and electrophoresis experiments, evidence was obtained which indicates that the virus preparations are composed of a single kind of particles, in which there is a distribution of frictional coefficients and perhaps electrical charges about a modal value. A portion of the pH mobility curve on the basic side of the isoelectric point was determined and the isoelectric point was estimated from solubility studies to be at about pH 4.6.

PRINCETON, N. J. RECEIVED AUGUST 28, 1940

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Equilibria between Esters, Hydrogen and Alcohols

BY ROBERT BURKS, JR.,[1] AND HOMER ADKINS

Several years ago Lazier, Hill and Amend stated that the reaction of diethyl adipate with hydrogen over copper chromite at 240 to 260° did not go to completion, and suggested a procedure for the removal of esters from the glycol so prepared.[2]

$$(CH_2)_4(CO_2Et)_2 + 4H_2 \xrightarrow{CuCr_2O_4} (CH_2)_4(CH_2OH)_2 + 2EtOH$$

Observations made in this Laboratory had not led to the conclusion that any considerable amount of ester was left after the reaction of hydrogen under the conditions noted above. Indeed, many analyses made upon the products of the hydrogenation of esters had shown that the amount of ester present was less than 1% and in most cases no ester was found. The data presented below show conclusively that reactions of the type, $RCO_2CH_2R' + 2H_2 \rightleftarrows RCH_2OH + R'CH_2OH$, are reversible. There is no justification for assuming that the reversal of the reaction would produce only the original ester, RCO_2CH_2R', for there is an equal possibility for RCO_2CH_2R, $R'CO_2CH_2R'$ and $R'CO_2CH_2R$. In the case of the hydrogenation of diethyl adipate, there are possible one alcohol, one glycol, one hydroxy acid, one monobasic acid and one dibasic acid which might form a very considerable number of different esters.

Obviously it is not easy to determine the amounts of the various esters present in the reaction products, for even under the most favorable conditions for ester formation the total amount of esters is small. However, the effect of the pressure of hydrogen upon the amounts of residual esters in the products of the hydrogenation of diethyl adipate, diethyl glutarate, ethyl laurate

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[1] Wisconsin Alumni Research Foundation Scholar.

[2] "Organic Syntheses," Vol. 19, John Wiley and Sons, New York, N. Y., 1939, p. 48. The statement as to the reversibility of the ester hydrogenation is not published, but was contained in a Note accompanying the original manuscript submitted to the Editors.

and methyl myristate has been determined. It was found that for a final pressure at the completion of hydrogenation of 276 atm. there was 0.0039 mole of ester present after the hydrogenation of 0.23 mole of ethyl laurate.[3] With a final pressure of 187 atm. there was 0.0058 mole of residual ester. Methyl myristate showed even less residual ester, there being only 0.0015 mole left after the hydrogenation of 0.21 mole of ester at a final pressure of 265 atm. of hydrogen. In these hydrogenations 0.21 to 0.23 mole of ester was hydrogenated at 260° over 3 to 6 g. of copper chromite. The absorption of hydrogen was complete after about two hours but the conditions for reaction were maintained for two hours longer in order to establish equilibrium concentrations. Diethyl glutarate showed a similar amount of residual ester (0.0017 mole) after the completion of hydrogenation of 0.17 mole of ester at a final pressure of 251 atm. The absorption of hydrogen was complete within forty-two minutes with 5 g. of catalyst at 260°.

All of the analyses referred to above were made upon the whole reaction mixture of the hydrogenation. Since no more than one of the four esters present could contaminate a sample of the alcohol or glycol which had been fractionated, it will be seen that the possible contamination of the alcohol or glycol by esters is exceedingly small.

Diethyl adipate showed a slightly larger amount of residual ester than did the other esters studied. For a final pressure of 177 atm. there was 0.0064 mole of ester after the hydrogenation of 0.17 mole using 2.5 g. of copper chromite at 260°. For a final hydrogen pressure of 271 atm. there was only 0.002 residual ester. The absorption of hydrogen was complete in less than an hour at the higher pressure and in 2.3 hours at the lower pressure. However, shaking and heating were continued for two more hours.

That these amounts of residual ester really represented concentrations at equilibrium was shown by heating a mixture of hexamethylene glycol (0.18 mole) and ethyl alcohol (0.36 mole) under the same conditions as used for the hydrogenation of esters. For a pressure of 177 atm. there was 0.0074 mole and for 269 atm. 0.0018 mole of ester after reaction periods of four hours over 2.5 g. of copper chromite at 260°.

The esters were distributed throughout the boiling range of the products. The moles of ester for the lower and higher pressures were as follows: for the fraction boiling below 90°, 0.0007 and 0.0004; fraction 90–99°, 0.0003 and 0.0001; fraction 90° (740), 133° (7 mm.), 0.0011 and 0.0004; glycol 133° (7 mm.), 0.0008 and 0.0006; residue 0.0033 and 0.0006. All of the figures given above are expressed in moles of the ester submitted to hydrogenation since which particular ester was present was unknown.

A reversal of the ester hydrogenation reaction was also obtained using tetradecanol and methanol. The amount of ester produced was identical with that found after hydrogenation of methyl myristate.

The figures given above clearly substantiate the statement by Lazier, Hill and Amend that the hydrogenation of esters over copper chromite at 240–260° is a reversible reaction. It is also clear why we have seldom found it necessary in this Laboratory to use a chemical method for obtaining pure alcohols and glycols for we almost always carry out hydrogenations at a pressure sufficiently high so that the amount of residual ester left in the product would be very small. A large part of the residual ester is eliminated in the process of fractionation to which we have always subjected the products of hydrogenation, so that in general the amount of ester present in the glycol or alcohol would be at most a few tenths of a per cent. However, hexamethylene glycol prepared by hydrogenation of diethyl adipate at a final pressure of 215 atm. contained after fractionation about 0.9% of ester calculated as diethyl adipate. This value would be considerably decreased if the hydrogenation were completed at 300 atm. and would probably be several per cent. if the hydrogenation were completed at pressures of 100 atm. or less.

It is desirable that for hydrogenations carried out at low pressures of hydrogen, and perhaps with poor samples of catalyst, a method be available whereby hexamethylene glycol can be obtained free of ester. The method given in "Organic Syntheses"[2] is time consuming and laborious. We have found that pure glycol may be obtained by a much simpler process. For example, 30 g. of glycol containing 1% ester was dissolved in 50 ml. of water and extracted with four 50-ml. portions of benzene. The water solution was then distilled through a modified Widmer and 93% of the glycol free of ester was obtained. Ether was also used for extracting the ester. The recovery of glycol was not so high (88%) as with benzene, but the product was also free of ester. Hexamethylene glycol is soluble to the

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[3] The results presented in this paper are based upon over thirty hydrogenations. The data given are in most cases the average of two or more hydrogenations.

extent of 5% in 100 ml. of ether saturated with water. It is soluble in 100 ml. of benzene saturated with water to the extent of 0.3 g. Ester-free glycol may also be obtained by distillation of glycol (40 g.) containing ester from 1 g. of sodium hydroxide. However, the recovery of glycol is poor (78%) and the process has little to recommend it.

Summary

Experimental evidence has been presented in support of Lazier's conclusion that the hydrogenation of esters over copper chromite at 240 to 260° is a reversible reaction. The concentration of esters at equilibrium is a function of the pressure of hydrogen and is for pressures of 200 to 300 atm. of the order of 1%. Alcohols and glycols prepared at such pressures and separated from these reaction products by the ordinary methods of fractionation should contain at the most a few tenths of a per cent. of ester. Simple methods for obtaining ester-free hexamethylene glycol have been described.

MADISON, WISCONSIN RECEIVED AUGUST 19, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. IX. The Vapor Phase Fluorination of Methane[1]

BY ELBERT H. HADLEY AND LUCIUS A. BIGELOW

We have described before[2] the vapor phase fluorination of ethane, and the influence of nitrogen dilution upon this reaction. Methane was not investigated first, among other reasons, because preliminary experiments had shown that unexpected difficulties would probably be encountered. The present paper contains the results of a study of the fluorination of methane, in which these difficulties have largely been overcome.

The reactions were carried out in the usual way over a copper gauze catalyst[2] and the products rectified in the Booth–Podbielniak fractionating unit, to which we have added a differential manometer attached to the top and bottom of the distilling column, and provided with adequate mercury traps and a shunt. This device was to indicate immediately any obstruction of the distilling tube by subliming silicon tetrafluoride, or carbon dioxide, which could otherwise lead to disastrous consequences.

Table I shows the results obtained from a series of runs, expressed, as usual, in liquid volume per cent. of the total condensate, and calculated on a ten-hour basis. The figures, except for the total volumes, have been rounded off to the nearest 5%.

TABLE I

THE PRODUCTS OBTAINED BY RECTIFYING FLUORINATED METHANE

Liquid vol. % of material boiling	Gas volume ratio of fluorine to methane to nitrogen					
	1:1:0	1:1:1	2:1:0	2:1:2	2:1:4	2:1:10
All < −128° (mostly CH_4)	65	60	30	25	20	10
−128° (CF_4)	30	30	45	50	40	45
All > −128°	10	10	20	30	35	45
Total vol. of condensate for 10 hr. in ml.	26	25	14	14	11	11

These results show definitely that when the volume ratio of fluorine to methane was 2:1, and the dilution ratio of fluorine to nitrogen was 1:5, the proportion of the product boiling higher than carbon tetrafluoride rose to a maximum of 45 liquid volume per cent. of the total condensate. This value could not practicably be increased, since at still higher dilution ratios the low boiling gases could not be condensed efficiently.

A large amount of this higher boiling product was collected, passed four times through a 10% sodium hydroxide solution to remove most of the carbon dioxide and silicon tetrafluoride, dried, and finally rectified.

Runs were made under different operating conditions but the fractionation of the product obtained when the volume ratio of fluorine to methane to nitrogen was 2:1:10 will be described as typical. It is of interest that under these conditions no pure compounds distilled at first. Instead there was obtained a series of definite, heterogeneous constant boiling mixtures, with constant molecular weights.

In the distillation, some carbon tetrafluoride came over first and was discarded, leaving a 30-ml. sample. Then a minor fraction distilled, doubtless containing silicon tetrafluoride, followed by 8.5 ml. of mixture E (b. p. −89°, mol. wt. 85). After this came 6.5 ml. of mixture Z (b. p.

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(1) This paper has been constructed from portions of Mr. Hadley's Doctorate Thesis, presented to the Graduate School of Duke University in May, 1940.

(2) Calfee, Fukuhara and Bigelow, THIS JOURNAL, **61**, 3552 (1939); Young, Fukuhara and Bigelow, *ibid.*, **62**, 1171 (1940).