jected to an increasing electrical pressure capable of compressing the water. It seems, however, that in experiments such as described in this work, a factor not previously considered should be brought in.

When 85% dry gelatin is permitted to swell at 10°, it is still in the gel condition after eight hours of swelling. It has been demonstrated that a gelatin gel contains many tiny pores filled with liquid.[8] For a 15% gel these openings would have an average radius of about 1 mμ and this value would be correspondingly smaller in more concentrated gels. When water is dispersed into very small droplets, the internal pressure increases according to the formula $P = 2\sigma/r$, in which σ is the surface tension and r is the radius of the spherical drop. In a drop of water 1 mμ in radius, the internal pressure would be about 1440 atmospheres, which pressure is sufficient to cause a 5% compression. In a drop one-tenth this size, the internal pressure would be ten times as great and the resultant compression could be as high as 20% of the original volume.

It is true that when water is dispersed in a gelatin gel it is not dispersed in the form of spherical droplets, nor do we know anything about the interfacial tension between the dispersed water and the solid gelatin walls. Furthermore, nobody knows to what extent the above formula is valid for drops of 1 mμ radius. The above figures can, however, serve as a first approximation demonstrating the possibility that some of the contraction in total volume when protein systems swell may be due to increased internal pressure when the liquid is highly dispersed.

That this factor is actually effective in the experiments herein described is indicated by the fact that the maxima in volume contraction fall nearer the isoelectric point than do the swelling maxima. At the swelling maxima the contraction due to dispersion of the water is at a minimum although the hydration and the electrostatic pressure on the water are probably at maxima at this point.

Summary

Measurements have been made to determine the influence of *p*H on the total volume contractions accompanying the swelling of gelatin at 10°.

A definite minimum in contraction was found at the isoelectric point, maxima at *p*H's 3.5 and 8, and a second minimum at *p*H 2.2.

Contraction in total volume has been attributed (1) to hydration, (2) to increased electrical field around the colloidal micelle as the isoelectric region is left and (3) to compression resulting from dispersion of water in the gel and the resultant increase of internal pressure.

CORVALLIS, OREGON RECEIVED OCTOBER 19, 1934

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[8] I. Friedman and E. O. Kraemer, THIS JOURNAL, 52, 1295 (1930).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Preparation of Ethers in Liquid Ammonia

BY THOMAS H. VAUGHN, R. R. VOGT AND J. A. NIEUWLAND

White, Morrison and Anderson[1] prepared diethyl ether, ethyl *n*-butyl ether and several aromatic ethers by the Williamson method in liquid ammonia at approximately −33° and atmospheric pressure. They obtained ethyl *n*-butyl ether in 19% yield but stated that di-*n*-butyl ether could not be made by this method, presumably due to the insolubility of sodium *n*-butylate in liquid ammonia, and they did not attempt the synthesis of other dialkyl ethers. The present work shows that at higher temperatures and pressures the dialkyl ethers may be readily prepared in liquid ammonia, and that, due to the presence of water or alcohol as impurities, dialkyl ethers frequently occur as by-products in the practical preparation of alkylacetylenes from sodium acetylide and alkyl halides in liquid ammonia.

In most of our experiments a solution of two moles of sodium in 2 liters of liquid ammonia was prepared in the pot of a standard 10-liter aluminum pressure cooker. A high speed Monel metal down-beating propeller stirrer was mounted just beneath the surface of the solution, and 2 mols of an alcohol was run in. A vigorous reaction took place but the foaming could be easily controlled by raising or lowering the stirrer blade. In thirty to forty-five minutes when the formation of the alcoholate was complete, 2 mols of alkyl

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[1] White, Morrison and Anderson, THIS JOURNAL, 46, 961 (1924).

halide was quickly added and the head of the pressure cooker clamped in place. The entire cooker was mounted on a shaker platform and shaken for two hours. The cooker was fitted with a needle valve, a ball release valve and an automatic pressure alarm. Pressures as high as three atmospheres could be readily maintained and controlled within a narrow range in this apparatus. One liter of water was then added and the oil which separated was washed with dilute hydrochloric acid and then with water and dried over calcium chloride. For comparison two runs were made at atmospheric pressure and one in a cadmium-lined autoclave at ten atmospheres.

The crude product was distilled through an air-jacketed Vigreux column 1 meter in length. For example, the product of the reaction of amyl bromide on sodium amylate at 1.7 atmospheres yielded the following fractions: I, 30–50°, 12 g.; II, 50–150°, 163 g.; III, 181–183°, 100 g. Fraction I was brominated and the product purified and shown to be 1,2-dibromopentane in an amount corresponding to 7% of the theoretical yield of pentene-1. Fraction III was refractionated using a standard thermometer and boiled at 183.9–186.40 (31.6% yield of diamyl ether). Fraction II was a mixture of amylene, amyl alcohol, amyl bromide and diamyl ether.

While the amount of ether retained in the middle fraction was not definitely determined the following experiment indicated that it was quite large. A mixture of 80 ml. of amyl alcohol, b. p. 133.5–135.5°, and 15 ml. of butyl amyl ether, b. p. 163°, was distilled through the column used in working up the reaction mixtures. The column holdup was 3 ml. and the dry point was only 143°.

Due to this difficulty of fractionation the yields reported in the following table were probably much below the actual yields.

From this limited material it appeared that the alkyl chlorides are quite unreactive, as they are recovered unchanged in large proportion. The alkyl bromides gave the highest yields of the ethers, along with some amines and 6–8% of olefins resulting from the dehydrohalogenating action of the alkoxides. The amyl iodide was almost totally consumed, producing a lower yield of ether than amyl bromide, along with about 13% of amylene and the remaining material in the form of amyl amines. Under the same conditions amyl iodide dissolved in liquid ammonia alone gave a 95% yield of amylamines.

The alcoholate may also be prepared by adding sodium to the alcohol in ammonia without affecting the yield. The reaction is, however, somewhat slower. When a solution of sodium is added to the alcohol in ammonia the reaction is difficult to control. In the preparation of sodium phenate, sodamide in ammonia[2] was used.

In work for later publication on the reaction of alkyl halides with the sodium compounds of acetylenes[3] in liquid ammonia it was found that the presence of water or alcohols in any of the reagents, or of sodium hydroxide in the sodium or sodamide, or the exposure of the liquid ammonia solutions to moist air, were all conditions which resulted in the contamination of the final product with ethers, often to the extent of 2–4%. On the basis of the quantity of water introduced, the yields of ethers in these reactions appeared to be very high. The reactions may be formulated as follows

TABLE I

	Sodium derivative of	Alkyl halide	Time in hours	Maximum pressure in atm.	Product	Yield, %
1	*n*-Propanol	Propyl bromide	1.5	1	Dipropyl ether	12
2	*n*-Butanol	Butyl bromide	1	1	Dibutyl ether	8
3	*n*-Butanol	Butyl bromide	1	10	Dibutyl ether	28[a]
4	*n*-Pentanol	Amyl chloride	2	2.7	Diamyl ether	3
5	*n*-Pentanol	Amyl bromide	2	2.7	Diamyl ether	32
6	*n*-Pentanol	Amyl bromide	5	2.7	Diamyl ether	33
7	*n*-Pentanol	Amyl bromide	2	1.7	Diamyl ether	32
8	*n*-Pentanol	Amyl iodide	2	2.7	Diamyl ether	17
9	*n*-Pentanol	Butyl chloride	2	3	Amyl butyl ether	0
10	*n*-Pentanol	Butyl bromide	2	3	Amyl butyl ether	28
11	Phenol	Amyl bromide	2	3	Amyl phenyl ether	45

[a] No stirring.

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(2) Vaughn, Vogt and Nieuwland, THIS JOURNAL, 56, 2120 (1934).

(3) Vaughn, Vogt, Sartoretto and Nieuwland, to be published.

$$H_2O \xrightarrow{HC_2Na} NaOH \xrightarrow{RX} ROH \xrightarrow{HC_2Na} RONa \xrightarrow{RX} ROR$$

Similarly, unless extraordinary precautions are taken to exclude all moisture, ethers may be expected to result from any process in which an alkyl halide reacts in liquid ammonia solution on a sodium compound that is decomposable by water.

Summary

1. It was shown that sodium propylate, butylate, amylate, or phenate react with alkyl bromides in liquid ammonia at pressures of from 1 to 10 atmospheres to give fair yields of ethers. Alkyl chlorides or iodides are not as effective as the bromides in this reaction.
2. A similar reaction was found to result in the formation of ethers as by-products in Picon's synthesis of alkylacetylenes and presumably in other procedures of this type.
3. It was shown that sodium alkoxides in liquid ammonia also behave as dehydrohalogenation agents toward alkyl halides.

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[CONTRIBUTION NO. 22 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Equivalent and Molecular Weights of Humic Acids from a Bituminous Coal

BY R. C. SMITH AND H. C. HOWARD

Mild oxidation of bituminous coal with such reagents as oxygen, dilute nitric acid, dilute alkaline permanganate, or peroxides results in nearly complete conversion of the organic material of the coal into alkali-soluble products. The alkaline solutions of these oxidation products are dark brown in color and on acidification brown amorphous so-called humic acids are precipitated. Because of the similar appearance of these products to those obtained by acidification of alkaline extracts of brown coal, lignite, peat and other partially decomposed organic material, they have been designated "regenerated" humic acids.[1] While the humic acids obtained from peat and similar materials have been investigated quite extensively, little work has been done on the amorphous acids produced by the oxidation of bituminous coal, with the result that almost no information is available as to even such general properties as equivalent and molecular weights. Since these products are obtained in high yields, through reactions which probably do not result in profound internal structural changes, information as to their properties is obviously of importance from the standpoint of our knowledge of the nature of the units composing bituminous coal.

Previous investigations,[1,2] which have dealt for the most part with acids directly extracted from peat or brown coal, have resulted in values ranging from 134 to 345 for equivalent and 733 to 1445 for molecular weight.

Experimental

Preparation of the Acids.—All humic acids used in this study, except where otherwise noted, were prepared by the oxidation of a bituminous coal[3] by refluxing with 1 *N* nitric acid for approximately a week in the presence of air. The reaction is chiefly an oxidation, since 85–90% of the nitric acid consumed appears in the gaseous products as nitric oxide, when air is excluded from the system. More nitrogen is found in the humic acids than can be accounted for by the original coal. The nature and significance of this nitrogen has not yet been determined.

The acid-soluble oxidation products were separated by filtration and the insoluble residue washed with water until peptization started. This residue was then treated with an excess of ammonium hydroxide and suspended inorganic and organic material separated by sedimentation or filtration. The dark brown alkaline humate solution freed from suspended material was then acidified and the resulting precipitate of humic acids separated by filtration and washed until peptization started. Final purification was carried out by electrodialysis. It was found that inorganic impurities were retained very tenaciously, more than a week usually being required for the complete removal of the precipitating agent by electrodialysis. The mixture of water and purified acids (part of the acids remained in suspension and part deposited on the anode diaphragm) was removed from the cell and evaporated to dryness on the water-bath. The acids

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(1) Francis and Wheeler, *J. Chem. Soc.*, **127**, 2236 (1925).

(2) Odén, "Die Huminsäure," Theodor Steinkopff, Dresden, 1922, p. 86; *ibid.*, p. 91; Bahr and Ehrenberg, *J. Landw.*, **61**, 427 (1913); Biesalsky and Berger, *Braunkohle*, **23**, 197 (1924–25); Erdtmann, *Svensk Kem. Tid.*, **38**, 201 (1926); Kawamura, *J. Phys. Chem.*, **30**, 1364 (1926); Fuchs, Stengel, and Bangert, *Brennstoff-Chem.*, **9**, 181 (1928); Stadnikoff and Korschew, *Kolloid-Z.*, **47**, 138 (1929); Samec and Pirkmaier, *ibid.*, **51**, 96 (1930); Thiessen and Engelder, *Ind. Eng. Chem.*, **22**, 1131 (1930); Stach, *Braunkohlenarch.*, **40**, 1 (1933).

(3) For a detailed description of this coal see U. S. Bureau of Mines, Technical Paper 525 (1932).