under the latter conditions if the catalyzed reaction yielded pure nitrogen. This assumption is untenable. It will be noted, however, that the mechanism of the catalysis in this reaction is different from the more usual one which involves adsorption of the metal ions. There is no evidence that the catalyzed reaction involving primarily adsorption of silver ions yields any nitrous oxide.

It was suggested previously that deformation of the adsorbed ions permits the simple removal of the electron from the hydroxylamine ion, thus

$$Ag^+ + NH_2O^- \longrightarrow Ag + NH_2O;$$
$$2NH_2O \longrightarrow N_2 + 2H_2O \quad (4)$$
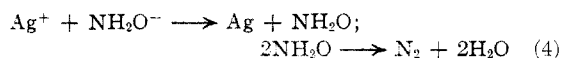
In the absence of catalyst, on the other hand, formation of the nitrosyl radical may occur,[5] as in Eq. 3. The work of Baudisch[14] supplies good evidence for the formation of this radical in the oxidation of hydroxylamine by cupric ion. The nitrosyl radical would yield only nitrous oxide on decomposition. Some nitrogen could be formed in the uncatalyzed reaction by the action of the nitrosyl radical on hydroxylamine.[5]

(14) O. Baudisch, Naturwiss., 27, 768 (1939); Science, 92, 336 (1940).

Summary

1. Mercurous nitrate, under proper conditions, oxidizes hydroxylamine without an induction period and produces chiefly nitrous oxide. Addition of colloidal mercury or silver catalyst produces a progressive increase in nitrogen yield. The product of the catalyzed reaction is predominantly nitrogen.

2. The product of the oxidation of hydroxylamine by silver salts in strongly alkaline solution varies markedly with the nature of the salt and reaction conditions. Nitrogen yields ranging from 5 to 90% were obtained at pH 12.7.

3. The catalyzed reduction of silver thiosulfate complex involves adsorption of hydroxylamine to silver, but not adsorption of silver ions or complex. Kinetic data on the initial uncatalyzed reaction were obtained.

4. The evidence indicates that the metal-catalyzed oxidation of hydroxylamine by mercurous and silver salts yields wholly or predominantly nitrogen. The uncatalyzed reaction yields chiefly nitrous oxide.

Molecular Weights of Hydrogenolysis Products from a Pittsburgh Seam Bituminous Coal

BY J. F. WEILER, J. J. WARD AND H. C. HOWARD

Treatment of a Pittsburgh seam bituminous coal with hydrogen at elevated pressures and at temperatures of 350–425°, in the presence of an oxide catalyst, such as copper chromium oxide, results in degradation to a series of condensed cyclic structures of varying complexity, incompletely saturated and containing some 80% of the carbon and an important fraction of the oxygen, nitrogen, and sulfur of the original coal. The extent of degradation can be measured roughly by the solubility of the reaction products in specific types of solvents. Phenols, and in general compounds of high internal pressure, are "good" solvents and the greater part of the coal becomes soluble in such a solvent after relatively short reaction times but, as is to be expected, the products recovered from such solutions are still highly complex. To obtain complete solubility in a hydrocarbon solvent of low internal pressure such as pentane, it is necessary to continue the reaction for a longer time or to work at a higher temperature.

The present investigation deals with the molecular weights of fractions obtained by solvent precipitation and vacuum distillation from the hydrogenolysis products of a Pittsburgh seam coal. The coal was subjected to intermittent treatment with hydrogen at 350° and extraction with cyclohexane, until further treatment failed to yield significant amounts of material soluble in this solvent. The cyclohexane was distilled off on the water-bath through a column and the remaining viscous residue was subjected to fractionation as indicated below. Molecular weight determinations of the fractions were made cryoscopically in catechol and in diphenyl and ebullioscopically in benzene.

Fraction		Per cent. by weight
"A"	Distillate: up to 120° at atmospheric pressure	14.8
"B"	Distillate: 120–200° at 5 mm. pressure	20.2
"C"	Precipitate: the residue from "B" was dissolved in an approximately equal volume of benzene and the solution poured into 5 volumes of pentane at 25°	13.1
"D"	Precipitate: the filtrate from the above precipitation was distilled to remove the greater part of the pentane and the benzene, and the viscous residue poured into 10 volumes of pentane at 25°	7.1
"E"	Precipitate: the filtrate from "D" was cooled to −50°	6.7
	The pentane was then distilled from the filtrate from "E" and the viscous residue transferred to a molecular fractionating still.	
"F"	First cut from molecular still, 150°	18.9
"G"	Second cut from molecular still, 165°	3.4
"H"	Third cut from molecular still, 185°	0.2
"I"	Residue from molecular still	9.8
	Losses and distillate during degasification in molecular still.	5.8

Fractions "A" and "B" were white limpid oils and were reserved for further study in connection with another investigation. Earlier work from this Laboratory has shown that products with these properties are partially and completely saturated, two and three ring, condensed, cyclic structures which exhibit no anomalies in molecular weight determinations.

The results of molecular weight measurements on fractions "C," "D," "E," and "F" are shown in Fig. 1. The data on fraction "C" are typical of results obtained on the primary degradation products of coal. The values in the non-polar solvents are three-to four-fold those in the active phenolic solvent, and large increases in molecular weight with concentration are evident. The data for fraction "D" also show a marked difference in values for molecular weight in the two types of solvents, although of a definitely reduced degree. The extrapolated values in the phenolic solvent are of the same order as those obtained for fraction "C." The material from fraction "E" shows a definitely lower value in the non-polar solvents than that from fraction "D" and the values in these solvents lie close together even at the higher

concentrations. The agreement in the phenolic solvent for the material from fractions "D" and "E," both in the slope of the curve and the infinite dilution value, is striking. The product from the first cut from the molecular still, fraction "F," shows little dependence of molecular weight on concentration and relatively small differences between the two types of solvents. Again the values in the phenolic solvent are of the same order of magnitude as observed in all previous fractions. Data on fractions "G," "H," and "I" have not been plotted. The material from fractions "G" and "H" showed greater deviations again, the infinite dilution values being approximately 260 in catechol and 360 in benzene and diphenyl. Fraction "I," the residue from the still, had properties more nearly like the pentane precipitates. The results of molecular weight measurements in benzene and in diphenyl were irregular and ranged between 540 and 680 for mole concentrations from 0.1 to 1%. The infinite dilution value in catechol, however, was 250.

It is evident that addition of a low internal pressure solvent, such as pentane, to these primary hydrogenolysis products from coal results in selective precipitation of products of higher molecular weight. At increasing ratios of low internal pressure solvent, precipitation of further fractions of decreasing molecular weight is obtained. Temperature, also, obviously plays a part, as is indicated by the precipitation of another fraction, of lower molecular weight, at the same solvent ratio, merely by lowering the temperature. The large variation observed in non-polar and polar solvents in the case of all fractions, except the stable, readily distillable material, shows that the molecular weights of these products in the "poorer" solvents represent an associated state. The appearance in all fractions of units of a molecular weight of 200–250, in the phenolic solvent, strongly supports the point of view that the larger structures which exist in the less active solvents are built up by association or polymerization from some fundamental unit of this average size.

The remarkable dependence of solubility on molecular weight in polymeric homologous series has been discussed recently by Baker, Fuller and Heiss.[1] They showed that in agreement with Schulz' findings for polystyrene systems, there was an approximately linear relation between the

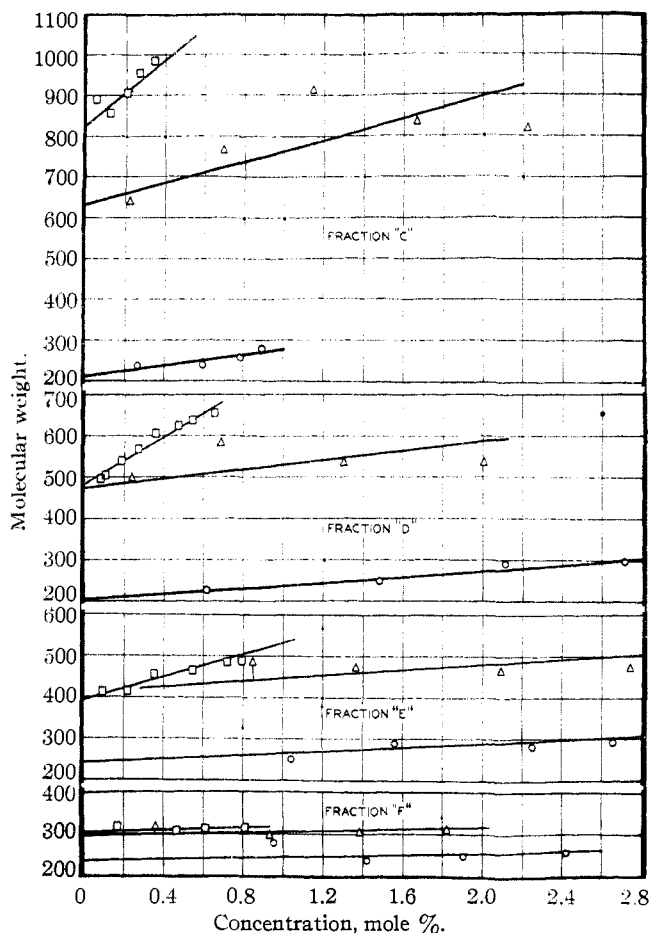(1) Baker, Fuller and Heiss, THIS JOURNAL, 63, 2142 (1941).

Fig. 1.—Molecular weight measurements: ◻, ebullioscopic in benzene; △, cryoscopic in diphenyl; ○, cryoscopic in catechol.

fraction of non-solvent required to produce initial precipitation from an ω-hydroxyundecanoic polyester solution of given concentration and the reciprocal of the average molecular weight. They also pointed out that polymer precipitability frequently exhibits a very strong temperature dependence. In both of these respects the primary degradation products of coal show analogy to the simple, linear polymeric homologous series. In other respects, however, the systems differ. The fractionation in the case of the linear polyester structures is, according to present views, on the basis of differences in molecular weight of structurally identical primary valence units, whereas in the case of the coal degradation products, in which the units are not structurally identical, although of the same general type, the fractionation appears to depend on the ability of certain of the units

present to associate in varying degrees to higher molecular weight structures when placed in a less active solvent medium.

Experimental

The procedures used in the hydrogenolysis of the coal and the recovery of the products have been described in previous contributions from this Laboratory[2] as has also the cryoscopic method of determining molecular weights.[3] A modified Menzies–Wright apparatus similar to that described by Hanson and Bowman[4] was used for the ebullioscopic measurements. The molecular still was a modified form of that used by workers at the Bureau of Standards and at the Gulf Research Laboratories, and will be described in detail in a later publication.

Summary

It has been shown that the primary hydrogenation products from a Pittsburgh seam coal can be separated into fractions of decreasing average molecular weight by the addition of increasing amounts of a solvent of low internal pressure such as pentane. Fractions of lower molecular weight can also be precipitated by lowering the temperature of the pentane solution. The higher molecular weight fractions show large differences in molecular weights in non-polar and polar solvents. All fractions show approximately the same molecular weight, 200–250, in the active solvent catechol, indicating that the higher molecular weight material is built up of units of approximately this size. Distillable fractions of low molecular weight show relatively small differences in molecular weight in polar and non-polar solvents and give flat molecular weight–concentration curves even in the non-polar solvents, showing the absence of association. The analogy between the solvent behavior of these primary degradation products from coal and that of synthetic polymeric homologous series has been pointed out.

(2) Biggs, THIS JOURNAL, 58, 1020 (1936); Biggs and Weiler, ibid., 59, 369 (1937); Leclaire, ibid., 63, 343 (1941).

(3) Smith and Howard, ibid., 57, 512 (1935).

(4) Hanson and Bowman, Ind. Eng. Chem., Anal. Ed., 8, 278 (1936).