out approximately 50% of the contents of the bulbs before the apparatus was sealed off.

A partial check upon the reliability of the results was obtained by means of a direct comparison of the reference acetic acid with an acetic acid obtained by the decomposition of malonic acid. A small difference was observed in the first series of measurements but not in the second.

The four pieces of apparatus were immersed in a large water-bath, fitted with a window for observation. The temperature of the bath could be regulated by hand to within ±0.1° at any point in the temperature range. Observations of the mercury levels, corrected for a layer of acetic acid on each mercury surface, were made with a cathetometer, and are probably accurate to better than ±0.1 mm.

Molecular Weights.—Samples weighing about 50 mg. were titrated with 0.05 *N* sodium hydroxide to a phenolphthalein end-point. The volume at the end-point was less than 20 cc. To ensure high accuracy a weight buret was used, carbon dioxide was carefully excluded, and the end-point was observed in the cold with a uniform quantity of indicator. The error of manipulation was of the order of ±0.03%. Any further error, to a total of about ±0.05%, is to be ascribed to the difficulty of uniformly removing the last traces of water from the solids. Since the measurements are comparative, the alkali solution was standardized with the ordinary malonic and succinic acids.

Summary

1. The preparation and melting points of acetic-d_3 acid-d, acetic-d_3 acid, acetic acid-d, malonic-d_2 acid-d_2, succinic-d_4 acid-d_2, succinic acid-d_2 and succinic-d_4 acid are presented and discussed, together with the vapor pressures of the acetic acids.

2. The hydrogens of the methylene group of malonic acid are easily replaced by deuterium when the acid is dissolved in deuterium oxide. The hydrogens of the ethylene group of succinic acid are not replaced under comparable conditions.

ANN ARBOR, MICHIGAN RECEIVED DECEMBER 27, 1935

[CONTRIBUTION NO. 39 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Molecular Weights of Polymeric Substances in Catechol and their Bearing on the Nature of Coal and Derived Products

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

Catechol has been found[1] to be an excellent solvent for such primary degradation products of bituminous coal as (a) the "humic acids," prepared by mild oxidation; (b) the "solid bitumens," obtained by solvent action, by distillation in high vacuum, and by mild hydrogenation. Cryoscopic measurements gave freezing point depressions corresponding to average molecular weights ranging from 200 to 300. The physical properties of both the "humic acids" and the "bitumens" indicate that these substances are of high molecular weight, and the observed ΔT for the bitumens in diphenyl, a non-polar solvent, leads to values of molecular weight greater than 1000. The present investigation was undertaken in order to determine whether any well-characterized polymeric solutes would give anomalous values for molecular weight in catechol, and, for purposes of comparison, measurements were also made, wherever solubility permitted, in diphenyl.

Method and Materials.—The semi-micro technique used in determining the molecular weights was similar to that already described,[1] except that a stoppered, side-neck test-tube was used to hold the melt. The stopper carried a Koppers Refined Products 1/10° thermometer, 70–120°, and a small sleeve of copper tubing through which the stem of the ring agitator passed. A slow stream of dry nitrogen was passed into the side tube and escaped through the sleeve around the agitator, thus maintaining an inert atmosphere over the solution at all times. Except when freezing point determinations were being made the air-bath was maintained 10–20° above the melting point and the agitator was run continuously. After several hours some of the solvent sublimed from the melt to the cooler parts of the tube; this was of course melted and returned to the solution before the next freezing point was determined. The measurements in diphenyl were carried out in a similar manner except that the freezing points were measured with a 1/10°, U. S. Bureau of Standards Specification, −10 to 100° thermometer.

Concentrations of 1 to 2 g. of solute per 100 g. of solvent were employed. The thermometer was read to 0.01° and, assuming an error of 0.02 in ΔT, the error in the molecular weight of a compound of molecular weight 200 would be 3.5 to 7%. With substances of molecular weight 600 and greater the results are only indicative of the order of magnitude.

Eastman catechol, purified by vacuum sublimation, was employed. The observed, uncorrected, melting points of different lots, after vacuum sublimation, varied from 103.99 to 104.03°. Its stability in an inert atmosphere at temperatures 5–10° above its melting point was satisfactory. When twelve freezing point determinations were made over a period of one hundred hours, the maximum

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[1] Smith and Howard, THIS JOURNAL, **57**, 514 (1935).

deviation of any determination from the average value was 0.04°; in another similar experiment the maximum deviation observed was 0.02°. The value 59, ΔT per mole per 100 g. solvent, was used for the constant.

The melting point of the diphenyl[2] was constant, ±0.01°, and the thermal stability was satisfactory. The reported values[3] of the cryoscopic constant for diphenyl range from 80 to 83.5. Using 4235 cal. per mole as the heat of fusion[4] leads to a calculated constant of 86. Experiments in this Laboratory using naphthalene, dibenzyl and triphenylmethane as solutes, gave values of 76, 80 and 79, respectively. The value 78 was used in the present investigation.

The sources or methods of preparation of the polymers studied are indicated in the table. All, except cellulose and starch, were dried at 100–150° in vacuum to eliminate low molecular weight impurities. No considerable loss in weight was observed with any of the polymers except the tetraethylene glycol. Because of the relatively low molecular weight of this substance, 190, it is probable that the observed loss was due to distillation of the polymer itself.

Results and Discussion.—The polymers investigated included representative samples of such condensation and addition types of polymeric structure as could conceivably be present in coal. The data are summarized in the table.

Solute	Solvent	
	Catechol	Diphenyl
p-Oxybenzid[5]	[a]	[a]
Ethylene succinate[6]	M. w. >2000	[a]
Adipic anhydride[7]	112, 103, 116, 103[b]	790, 467, 794, 467[b]
Lactide[8]	353, 285, 368, 368	770, 770, 814, 814
Tetraethylene glycol[9]	167, 167, 201, 190	198, 198, 238, 220
Cellulose[10]	[c]	[a]
Starch[11]	[c]	[a]
Vinylite resin[12]	M. w. > 2000	M. w. > 2000
Cumar resin[13]	550, 550, 550, 550	1000, 1000, 1400, 1400
Polystyrene[14]	[a]	[c]

[a] Incompletely soluble; no measurement made. [b] Initial, minimum, maximum and final values for mol. wt. [c] Incompletely soluble; measurements gave $\Delta T < 0.02°$.

In the determinations with ethylene succinate, as long as the melt was protected by an inert atmosphere, the observed ΔT was less than 0.02, corresponding to a molecular weight greater than 2000. Under these conditions there was no evidence of degradation of the polymer for periods up to seventy hours. On exposure of the melt to the air, however, ΔT increased rapidly and in ten hours the observed depression corresponded to an average molecular weight of 180. Carothers and Arvin[15] reported values ranging from 2300 to 2900 by boiling point elevation in ethylene chloride and were unable to account for the discrepancy between their figures and those obtained by Vorländer,[16] who found values from 263 to 279 in phenol. No details of Vorländer's experimental technique are available, but it seems probable that the low results are due to absorption of moisture by the hygroscopic solvent followed by hydrolysis of the polymeric ester.

Voerman[17] reported values of 121 and 125 for the molecular weight of adipic anhydride in phenol, but on the basis of physical properties concluded that the substance was of high molecular weight. Hill[18] by boiling point elevation in benzene obtained 860 and 710. He showed that it was possible to isolate diphenyl adipate from a phenol fusion but gave no yield. The cryoscopic data show that the degradation of this polymer in phenolic solvents is complete. The mechanism of the reaction is probably the same as that found for the action of aniline on this substance.[19]

The experiments on cellulose and starch were undertaken because of the discovery, in a series of preliminary measurements on monomeric solutes, that sucrose was split rapidly by catechol. The observed values, theoretical 342, started at 189, fell to 174 in five hours, and remained constant for the duration of the experiment, twenty-one hours. Since the sucrose had been thoroughly dried, and the melt was protected by an inert atmosphere, hydrolysis seems improbable. It has been shown[20] that the hexoses form compounds with the polyhydroxybenzenes and it appears in this case that the weak ether linkage of the sucrose molecule was broken with the formation of one mole of hexose and one of catechol-hexose complex. No evidence for degradation of

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(2) Eastman, used without preliminary purification other than vacuum drying over phosphorus pentoxide at room temperature.

(3) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1926, Vol. IV, p. 184.

(4) Warner, Scheib and Svirbely, *J. Chem. Phys.*, **2**, 250 (1934).

(5) E. Fischer and Freudenberg, *Ann.*, **372**, 32 (1910).

(6) Two samples were used; one kindly supplied by W. H. Carothers and the other prepared according to Carothers, *Chem. Rev.*, **8**, 362 (1931).

(7) Hill, THIS JOURNAL, **52**, 4112 (1930).

(8) Bischoff and Walden, *Ann.*, **279**, 72 (1894).

(9) Obtained through the courtesy of E. W. Reid, Mellon Institute, Pittsburgh.

(10) Whatman filter paper; dried over phosphorus pentoxide at room temperature.

(11) Merck "soluble starch," dried as above.

(12) "A" grade, vinyl acetate, supplied by Carbide and Carbon Chemicals Corp., New York City.

(13) Grade "W-$^1/_2$," kindly furnished by the Barrett Co., Philadelphia, Pa.

(14) A spontaneous polymer from Eastman styrene.

(15) Carothers and Arvin, THIS JOURNAL, **51**, 2563 (1929).

(16) Vorländer, *Ann.*, **280**, 167 (1894).

(17) Voerman, *Rec. trav. chim.*, **23**, 265 (1904).

(18) Hill, THIS JOURNAL, **52**, 4113 (1930).

(19) Hill, *ibid.*, **52**, 4111 (1930).

(20) E. Fischer and Jennings, *Ber.*, **27**, 1355 (1894).

either starch or cellulose in catechol was found. The small ΔT which was observed at first in both cases disappeared in a few hours and was undoubtedly due to moisture.

Except where there is definite evidence for chemical degradation, none of these polymers shows anomalous behavior to the degree exhibited by the products derived from coal. However, both the lactide and the cumar resin polymers show significant differences in the two solvents which cannot be ascribed to any known chemical reaction.

The small ΔT observed in diphenyl for the products derived from coal can be explained by assuming that a large part of the solute is colloidally and not molecularly dispersed, but such a distinction, in a system of this type, between a colloid particle and a macromolecule appears of little significance. The large values of ΔT in catechol may ultimately be found to be due to degradation of the polymer by some chemical reaction, but if such a mechanism is later discovered it will not affect the conclusion that these primary breakdown products of a Pittsburgh seam bituminous coal, the regenerated humic acids and the bitumens, must be polymers built up of relatively small units which are held together by such weak forces that as mild a "chemical reagent" as fused catechol can effect degradation. It is probable that the original coal itself is such a polymer, but degradation of coal by solvents only becomes considerable at relatively high temperatures.

Summary

Cryoscopic determinations in catechol and, where solubility permitted, in diphenyl, of a number of polymeric solutes have been made. Except where there is definite evidence of chemical degradation, none of these polymers shows anomalous behavior to the degree exhibited by products derived from coal. It has been pointed out that the cryoscopic behavior of these primary degradation products of coal shows them to be polymers built up of relatively small units.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF MOUNT HOLYOKE COLLEGE]

Preparation and Physical Constants of 2-Methylbutene-1

BY MARY L. SHERRILL AND GERTRUDE F. WALTER[1]

Unsymmetrical methylethylethylene, 2-methylbutene-1, has been reported by a number of investigators as one of the products of dehydration of commercial amyl alcohol,[2] active amyl alcohol,[3] and tertiary amyl alcohol.[4,5] It has also been obtained from the iodide derivative of active amyl alcohol,[6,7] from tertiary amyl iodide[8] and by the electrolysis of sodium dimethyl glutarate.[9] In no case was pure 2-methylbutene-1 obtained but the boiling point of the compound was shown to be within the 31–34° range.

An investigation of the ultraviolet absorption spectra of olefins has been in progress in this Laboratory for several years. Trimethylethylene has been prepared from tertiary amyl alcohol by the action of iodine, of oxalic acid and of 15% sulfuric acid. In every case a low-boiling fraction, b. p. 30–34°, n^{20}_{D} 1.3774–1.3809, d^{20}_{4} 0.6505–0.6570,[10] was obtained but careful fractionation failed to separate pure 2-methylbutene-1 and the preparation of that hydrocarbon by the nuclear synthesis of olefins developed by Boord and co-workers[11] was undertaken. The reactions involved in this synthesis are as follows

$$CH_3CHO + C_2H_5OH + HCl \longrightarrow CH_3CHClOC_2H_5 + H_2O \quad (1)$$

$$CH_3CHClOC_2H_5 + Br_2 \longrightarrow CH_2BrCHBrOC_2H_5 + HCl \quad (2)$$

$$CH_2BrCHBrOC_2H_5 + CH_3MgCl \longrightarrow CH_2BrCH(OC_2H_5)CH_3 + MgClBr \quad (3)$$

$$CH_2BrCH(OC_2H_5)CH_3 + KOH \longrightarrow CH_2{=}C(OC_2H_5)CH_3 + KBr + H_2O \quad (4)$$

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[1] Presented before the Organic Division at the New York meeting, April, 1935.

[2] Leendertse, Tulleners and Waterman, *Rec. trav. chim.*, **52**, 515 (1933).

[3] Norris and Joubert, THIS JOURNAL, **49**, 873 (1927).

[4] Bourguel and Piaux, *Bull. soc. chim.*, **51**, 1041 (1932).

[5] Church, Whitmore and McGrew, THIS JOURNAL, **56**, 176 (1934).

[6] Wassilijeff, *Chem. Zentr.*, **70**, 1, 775 (1899); *J. Russ. Phys.-Chem. Ges.*, **30**, 993 (1897).

[7] Michael and Zeidler, *Ann.*, **385**, 251 (1911).

[8] Le Bel, *Bull. soc. chim.*, [2] **25**, 546 (1870).

[9] Walker and Wood, *J. Chem. Soc.*, **89**, I, 604 (1906).

[10] Master's theses and Honor papers, Mount Holyoke College: A. Jackson, 1929; R. Comroe, 1931; E. Burkey, 1933; M. Adams, C. Monod, 1935.

[11] Boord and co-workers, THIS JOURNAL, 1930, to date.