kieselguhr catalyst for exchange reactions has been studied. Adsorbed hydrogen and adsorbed water vapor may be removed by evacuation at 218°. Other hydrogen sources of reproducible availability are held tenaciously in the kieselguhr, probably as bound water. These are difficult to remove even at 400–500°, and exchange with deuterium to increasing extents with increase of temperature.

5. The deuterium–ethylene reactions on nickel in the range -80 to 65° results in some exchange as well as the addition reaction. A copper catalyst also shows activity in exchange.

6. Ethylene polymerizes to C_4 and higher hydrocarbons at 0° on nickel, but the breaking of the C–C linkage is negligible.

7. A general discussion in terms of the dissociative adsorption of the saturated hydrocarbons has been given.

PRINCETON, N. J. RECEIVED JANUARY 7, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GREENSBORO COLLEGE]

Aqueous Solubilities of the Isomeric Pentanols

BY P. M. GINNINGS AND RHODA BAUM

An important factor in most investigations of the relationship between molecular structure and aqueous solubility of organic compounds is the molecular weights of the compounds studied. In fact its domination frequently tends to obscure the effect of lesser factors. Evidently, limitation of a study to isomers should simplify considerably analysis of the results and for this reason, a study of the aqueous solubilities of the eight isomeric pentanols or amyl alcohols seemed worthwhile. Search of the literature revealed approximate solubilities for many of these isomers but apparently only two have been measured precisely. Butler[1] using an interferometric method measured the solubility of *n*-pentanol (*n*-butylcarbinol) at 25° as 2.208 weight percentage. Kablukov[2] using the volumetric method of Hill[3] determined the value for isobutylcarbinol (isoamyl alcohol) at a number of temperatures. Values for the latter are also given in the "International Critical Tables."[4]

The solubilities of these two compounds were also determined in the present paper as a check upon our experimental work and the results seem to agree within the accuracy of our method.

Results of our determination of the weight percentage solubilities of these eight isomers are given in the table. The difference between the larger weight percentage for a given temperature and isomer and one hundred represents the solubility of water in that particular isomer. Analysis of the data indicates that the one tertiary isomer is more soluble than any of the three secondary isomers and that these in turn are more soluble than any of the four primary isomers. The solubility increases as the hydroxyl group approaches the center of the molecule (Nos. 1, 5 and 6). If the analysis is limited to either the primary or secondary isomers, it is evident also that the solubility in water increases as the structure of the molecule becomes more compact. However, the most compact primary isomer (No. 4) is not as soluble as the least compact secondary isomer (No. 5). Usually the more soluble the alcohol in water, the more soluble the water is in the alcohol. Of interest also is the fact that as the temperature increases from 20 to 30°, the solubility of all eight isomers decreases.

Experimental

With one exception, the compounds used for the final determinations were prepared by purification of products synthesized by one of the Grignard reactions. *t*-Butylcarbinol was prepared in this Laboratory by the action of *t*-butylmagnesium chloride upon paraformaldehyde with the usual hydrolysis, etc. Dimethylethylcarbinol was prepared by the action of ethylmagnesium bromide upon acetone in the usual Grignard procedure. The other compounds were Eastman best grade of products. The isobutylcarbinol probably was obtained originally as a by-product from a fermentation process and was known to contain some of the active amyl isomer. Approximately seventy-five aqueous extractions, drying with anhydrous potassium carbonate and final fractional distillation over metallic calcium seemed to purify this satisfactorily.

In general, all products from the Grignard syntheses were fractionally distilled with a short column (reflux

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[1] Butler, Thompson and MacLennan, *J. Chem. Soc.*, 674 (1933).

[2] Kablukov and Malischeva, THIS JOURNAL, **47**, 1559 (1925).

[3] Hill, *ibid.*, **45**, 1146 (1923).

[4] "International Critical Tables," Vol. III, p. 388.

TABLE I

No.	Compound	Temp., C.	Wt., % Alc.		d 25/4 pure alc.	B. p. (760 mm.), °C.	d/4, liq. phases Alc. rich	Water rich
1	*n*-Butylcarbinol	20	2.36	92.52	0.8110	137.6–138.3	0.8317	0.9939
		25	2.19	92.54			.8287	.9930
		30	2.03	92.35			.8253	.9919
2	Isobutylcarbinol	20	2.85	90.53	.8071	131.5–131.7	.8286	.9941
		25	2.67	90.39			.8257	.9932
		30	2.53	90.24			.8188	.9921
3	*s*-Butylcarbinol	20	3.18	91.05	.8106	128.4–129.1	.8311	.9943
		25	2.97	90.81			.8288	.9930
		30	2.83	90.74			.8239	.9928
4	*t*-Butylcarbinol	20	3.74	91.77	M. p.	113.0–114.0	.8243	.9936
		25	3.50	91.64	48–49°		.8216	.9930
		30	3.28	91.46			.8178	.9925
5	Methyl-*n*-propylcarbinol	20	4.86	88.30	0.8056	119.2–119.7	.8317	.9914
		25	4.46	88.21			.8280	.9909
		30	4.13	88.10			.8243	.9898
6	Diethylcarbinol	20	5.61	91.81	.8195	115.4–115.9	.8368	.9920
		25	5.15	91.68			.8330	.9914
		30	4.75	91.42			.8294	.9903
7	Methylisopropylcarbinol	20	6.07	88.12	.8134	111.1–111.9	.8390	.9909
		25	5.55	88.07			.8352	.9902
		30	5.10	87.95			.8348	.9879
8	Dimethylethylcarbinol	20	12.15	75.74	.8055	101.9–102.1	.8662	.9837
		25	11.00	76.53			.8552	.9829
		30	10.10	77.31			.8498	.9828

ratio about 7:1) off metallic calcium, using a precision thermometer, graduated in 0.1° with the range of 100–150°. Dimethylethylcarbinol was distilled off calcium oxide. All boiling points given in the table have been corrected to 760 mm. pressure using Craft's rule when the dT/dp was not known; stem correction was applied when needed.

Compounds 3, 5, 6, and 8 in the table were also obtained in the Technical grade of purity. These had as their origin the isomeric pentenes of petroleum and were quite difficult to purify completely. However, for purposes of comparison these four were purified as carefully as possible by fractional distillation through a 1-m. column, fractionally extracted with water, fractionally salted-out with potassium carbonate and again fractionally distilled through the 1-m. column. In all cases the middle fractions were taken and the extremes discarded. The solubilities of the products were then compared with those obtained on the compounds prepared by the Grignard syntheses and which are given in the table. Agreement was usually close except in the case of the dimethylethylcarbinol; the solubility of the product derived from the Technical was approximately 0.3 wt.% higher than the other at all three temperatures.

Hill's volumetric method mentioned previously in this article was used with some adaptations and refinements to measure the solubilities. A pair of two-bulb graduated and calibrated flasks was constructed mainly from portions of Babcock milk test bottles. The two constricted portions of each double-bulbed flask were made from the graduated necks and so were already graduated in intervals of 0.02 ml. This permitted measurement of the volumes of the liquid phases with an accuracy better than 0.01 ml.

The general procedure was to introduce known weights of the particular alcohol and distilled water (weighings accurate to better than 1 mg.) into the flask stoppered with an excellent grade cork stopper. Flask and contents were then shaken mechanically in a constant temperature water-bath, maintained thermostatically and manually to the desired temperature plus or minus 0.1°. Sufficient time was allowed for the liquids to reach equilibrium, the two liquid phases were allowed to separate and the total volume reading in the flask noted. The flask was then centrifuged in the usual Babcock centrifuge to sharpen the dividing line between the two liquid phases and then returned to the constant temperature bath. After the total volume reading had returned to the same as the original one noted, the reading of the line dividing the two phases was made. From these data, volumes of the two phases were calculated. Ratios of the volumes of the two sections of the two flasks were approximately 1:5 in one and 5:1 in the other. Total volume of each flask was approximately 65 ml. With the weights of the components in both flasks known and both pairs of volumes calculated, sufficient data were in hand to substitute in the pair of simultaneous equations to get the concentrations of each component in each phase. Subsequently, the weight percentages were calculated from the latter values as explained in detail by Hill.

The reliability of the method was better than 0.1 wt. % in practically all of the cases and the authors feel that the validity of the results will approach this limit. Increase of the limits to 0.2 wt.% should probably be allowed in the case of the dimethylethylcarbinol.

Summary

Aqueous solubilities of the eight isomeric pentanols have been determined for 20, 25 and 30°.

The one tertiary isomer is more soluble than any of the three secondary isomers which in turn are more soluble than any of the four primary isomers. The solubility increases as the hydroxyl group approaches the center of the molecule. Limitation of the comparisons to either the primary or the secondary group reveals that the more compact the molecular structure, the greater is the aqueous solubility. The solubility of all eight isomers decreases as the temperature increases from 20 to 30°.

GREENSBORO, N. C. RECEIVED APRIL 5, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY AND ST. JOHN'S UNIVERSITY]

Equimolar Condensations of Aldehydes with Phenols. The Preparation of Primary Saturated Alkylphenols[1]

BY JOSEPH B. NIEDERL, VICTOR NIEDERL, S. SHAPIRO[2] AND MARTIN E. MCGREAL

Condensation of carbonyl compounds (aldehydes and ketones) with multimolar quantities of a phenol usually results in the formation of the corresponding alkylidene-di-phenol.[3] Dianin and von Braun,[4] however, made the observation that saturated secondary or tertiary alkylphenols are obtained when the intermediate polymeric condensation products resulting from the action of hydrochloric acid upon a mixture consisting of several moles of a phenol and one mole of a ketone, aliphatic (di-*n*-propyl, methyl hexyl ketone and dichloroacetone) as well as aromatic ketones (acetophenone, ω-chloroacetophenone) are subjected to pyrolysis. The formation of saturated alkylphenols from ketone-phenol polymers was a rather unexpected observation and the expression "disproportionation" process was suggested by von Braun for this phenomenon.

In all of the above investigations multimolar quantities of phenol were used. It was the purpose of the research set forth in this communication to investigate equimolar condensations of saturated aliphatic aldehydes with phenols to establish experimentally the following: (a) whether it is possible to obtain mole for mole addition; (b) whether these additions take place analogous to the addition of halogen acids or hydrocyanic acid to the carbonyl bond, or whether the addition takes place as in aldol condensations; (c) to investigate the chemical nature of the intermediate polymer; and (d) to investigate the behavior of these aldehyde–phenol polymers upon pyrolysis, particularly as to the possibility whether a similar "disproportionation" could be observed in the aldehyde series as has already been established in isolated cases in the ketone and indane series.[5] Although the end-products, the saturated primary alkylphenols, could be identified easily, analysis of the intermediate polymeric condensation products did not lead to uniformly interpretable results. Some of these products, when reprecipitated, powdered and completely dried in a vacuum desiccator over phosphorus pentoxide for several months, gave results upon quantitative analysis which corresponded closely to polymeric alkylenephenols. The pyrolysis of the condensation products of phenols and the three cresols with the following aldehydes were studied.

Formaldehyde and phenol yielded a small amount of a cresol. Acetaldehyde and phenol (I) and the three cresols (II, III, IV) gave the corresponding ethylphenol and ethylcresols upon pyrolysis of the Claisen solution soluble polymeric condensation products. Substitution of vinyl acetate for acetaldehyde yielded similar polymers. Propionaldehyde (V), *n*- and isobutyraldehyde (VI, VII), *n*-valeric aldehyde (VIII) and *n*-heptaldehyde (IX) and phenol gave the respective alkylphenols. These primary saturated alkylphenols were purified by repeated fractional distillation, then analyzed and further characterized as crys-

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[1] Presented before the Division of Organic Chemistry at the Pittsburgh meeting of the American Chemical Society, September, 1936.

[2] Several parts are taken from the thesis of S. Shapiro, presented to the Graduate School of New York University in partial fulfilment of the requirements for the degree of Master of Science.

[3] Schmidlin and Lang, *Ber.*, **43**, 2806 (1910); Claus and Trainer, *ibid.*, **19**, 3009 (1886); Moehlau and Koch, *ibid.*, **11**, 283 (1878); L. Claisen, *Ann.*, **237**, 261 (1887); Th. Zincke, *ibid.*, **363**, 255 (1908); E. K. Bolton, U. S. Patent 2,069,573 (1937); H. S. Rothrock, *ibid.*, 2,069,560 (1937).

[4] Dianin, *J. Russ. Phys.-Chem. Soc.*, **23**, 540 (1891); *Ber.*, **25**, 336 (1892); J. v. Braun, *Ann.*, **507**, 15 (1933).

[5] Niederl, Niederl and Reznek, THIS JOURNAL, **58**, 657 (1936); Weissberger, *Ber.*, **44**, 1438 (1911); Weger and Billmann, *ibid.*, **36**, 644 (1903); Kramer and Spilker, *ibid.*, **29**, 561 (1896); **33**, 2260 (1900); **23**, 3278 (1890); Moschner, *ibid.*, **33**, 737 (1900); Stoermer and Boes, *ibid.*, **33**, 3016 (1900).