ethyl ether, 2-propyl-1-naphthol ethyl ether and 2-aceto-1-naphthol. 2-Propionyl-1-naphthol was active only against *E. typhi*, killing it in sixty minutes. 2-Ethyl-1-naphthol, 4,6-diethylresorcinol and 2-propyl-1-naphthol killed all of the organisms in thirty minutes, except that the last substance did not kill *E. coli*. These more promising substances are being studied further.

Acknowledgment is made to Miss Catherine Ulrich and to the late G. L. A. Ruehle for cultures of the organisms, and to Professor C. M. Brewster for the purification and preparation of the organic compounds studied.

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## Partition Ratios of Some Organic Acids between Water and Ethyl Ether[1]

BY O. C. DERMER, WENDELL G. MARKHAM AND H. M. TRIMBLE

In the course of investigating the use of partition ratios for the identification of organic acids, it became clear that literature dealing with these ratios is fragmentary and even untrustworthy for some common acids. The work here reported concerns the measurement of the distribution of sixteen organic acids between water and ethyl ether at 25°. The results, expressed in the form used by the "International Critical Tables,"[2] are set forth in Table I. The ratios are uncorrected for any difference in association or dissociation in the two phases.

TABLE I

PARTITION RATIOS

| Acid | Concn. in ether layer, $C_e$, $N$ | Ratio $C_w/C_e$ |
|---|---|---|
| Acrylic | 0.0574 | 0.504 ± 0.002 |
| | .115 | .482 ± .002 |
| | .302 | .451 ± .002 |
| | .604 | .440 ± .002 |
| Adipic | .0267 | 1.95 ± .02 |
| | .0670 | 1.90 ± .02 |
| | .108 | 1.88 ± .02 |
| | .138 | 1.84 ± .02 |
| Barbituric | .00080 | 38 ± 3.0 |
| | .00124 | 43 ± 2.0 |
| | .00183 | 43 ± 2.0 |
| Benzenesulfonic | .00028 | 310 ± 40.0 |
| | .00032 | 540 ± 40.0 |
| | .00063 | 690 ± 40.0 |
| | .00115 | 750 ± 40.0 |
| Bromoacetic[a,b] | .0802 | 0.306 ± 0.002 |
| | .163 | .286 ± .002 |
| | .410 | .265 ± .002 |
| | .820 | .250 ± .002 |
| Chloroacetic[a,b] | .0671 | .457 ± .002 |
| | .138 | .439 ± .002 |
| | .351 | .394 ± .002 |
| | .708 | .373 ± .002 |
| Crotonic[a] | .0741 | .253 ± .001 |
| | .151 | .238 ± .001 |
| | .380 | .213 ± .001 |
| | .755 | .188 ± .001 |
| Dichloroacetic[a,b] | .0908 | .176 ± .002 |
| | .190 | .139 ± .002 |
| | .488 | .112 ± .002 |
| | .942 | .102 ± .002 |
| Formic[a] | .0264 | 2.78 ± .03 |
| | .0530 | 2.80 ± .03 |
| | .139 | 2.75 ± .03 |
| | .286 | 2.62 ± .03 |
| Furoic | .0392 | 0.286 ± .003 |
| | .0791 | .265 ± .003 |
| | .203 | .237 ± .003 |
| | .342 | .220 ± .003 |
| Glycine | .00086 | 106 ± 4 |
| | .00108 | 162 ± 4 |
| | .00129 | 313 ± 4 |
| | .00148 | 485 ± 4 |
| Glycolic[a,b] | .00248 | 34.7 ± 0.8 |
| | .00488 | 35.2 ± .8 |
| | .0121 | 35.7 ± .8 |
| | .0244 | 35.5 ± .8 |
| α-Hydroxyisobutyric | .0154 | 4.49 ± .05 |
| | .0313 | 4.39 ± .05 |
| | .0808 | 4.19 ± .05 |
| | .179 | 3.85 ± .05 |
| Succinic[a] | .0100 | 7.75 ± .04 |
| | .0201 | 7.79 ± .04 |
| | .0512 | 7.67 ± .04 |
| | .104 | 7.52 ± .04 |
| Tartaric[a] | .00034 | 280 ± 50 |
| | .00075 | 260 ± 10 |
| | .00172 | 282 ± 5 |
| | .00329 | 294 ± 5 |
| Trichloroacetic[a,b] | .101 | 0.236 ± 0.003 |
| | .187 | .174 ± .003 |
| | .475 | .122 ± .003 |
| | .920 | .101 ± .003 |

[a] For literature see ref. 2. [b] *Cf.* ref. 3.

It is difficult to compare our findings with literature values because nearly all other investigators used either more dilute solutions or differ-

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(1) This paper is based upon a thesis submitted by Mr. Markham in partial fulfillment of the requirements for the degree of Master of Science at the Oklahoma Agricultural and Mechanical College in 1941.

(2) "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1928, pp. 422–433.

ent temperatures. Since the few known temperature coefficients of partition ratios are low, differences in temperature are not so serious a hindrance to comparison as differences in concentration. On this basis it may be said that our data for bromoacetic acid and the three chlorine-substituted acetic acids agree reasonably well with those obtained at about the same concentrations by Knaus[3] at 18° except for dichloroacetic acid. Fair agreement with the literature[2] may also be noted in our values for succinic acid and formic acid. The work of H. W. Smith,[4] for which the author indeed claimed no high accuracy, seems to be unreliable in the cases of succinic acid, tartaric acid, and probably bromoacetic acid also.

Reference to Table I shows that only glycolic acid has partition ratios which remain practically constant over the tenfold range of concentrations studied. The ratios for most other acids, including all the halogen-substituted acetic acids, decrease with increasing concentration of acid, owing partly to changing ionization in the water layer. The very large ratios for glycine, tartaric acid, and benzenesulfonic acid increase as the acid concentration increases. While this trend is probably real, the absolute values of these ratios are the least trustworthy of our measurements, for the amounts of acid in the ether layer were too small to be titrated accurately.

## Experimental

Ordinary reagent grade ethyl ether was used, preliminary experiments having shown that its further purification had no effect upon partition ratios.

Most of the acids were likewise C. P. reagents, used without purification. Furoic acid was both sublimed and recrystallized, but without altering the value of the partition ratio. "Practical" dichloroacetic acid was fractionated and boiled in the open for a few minutes to expel dissolved hydrogen chloride. Benzenesulfonic acid was prepared by hydrolyzing benzenesulfonyl chloride and removing the hydrochloric acid by evaporation.[5] Acrylic acid was prepared at low temperatures and used immediately to forestall polymerization. A solution was obtained by saponifying methyl acrylate with potassium hydroxide solution at room temperatures, acidifying with hydrochloric acid, evaporating to half volume under reduced pressure at 40–50°, extracting repeatedly with ether, evaporating this to one-fifth its volume, and extracting the acid from the ether with water (70% yield).[6]

In the partition experiments, the acid solutions and the ether were mixed in glass-stoppered bottles and placed in a thermostat at 25 ± 0.2°. After at least thirty minutes the bottles were shaken vigorously for five minutes and then allowed to stand for ten minutes in the thermostat to permit complete separation of the layers. Samples were then pipetted from each layer and titrated with either 0.03219 or 0.1237 *N* carbonate-free standard alkali. That the time allowed for distribution and the amount of shaking were sufficient to establish equilibrium was proved by showing that increasing each did not alter the results. Phenolphthalein was used as indicator in titrating all acids except glycine, which required thymolphthalein and titration in alcoholic solution.[7] Acid in the ether layers was most easily determined by adding excess standard alkali and back-titrating with standard hydrochloric acid. Three samples of each layer were titrated at each concentration, and the mean values, along with the calculated standard deviations, were used to obtain the partition ratios and the indicated precisions of measurement.

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[3] Knaus, Thesis, Basel, Switzerland, 1923; data quoted by "Tables Annuelles," McGraw-Hill Book Co., New York, N. Y., 1924, pp. 260–262, 330.

[4] Smith, *J. Phys. Chem.*, **25**, 616 (1921).

[5] Davies and Davies, *J. Chem. Soc.*, **123**, 2976 (1923).

[6] Preparation by Mr. Jack King.

[7] Harris, *Proc. Roy. Soc.* (London), **95B**, 500 (1923).

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## Catalysts for the Polymerization of Benzyl Chloride

BY O. C. DERMER AND EDWARD HOOPER

Many substances catalyze the reaction of benzyl chloride with itself with elimination of hydrogen chloride.[1] The catalytic activity reported for copper chloride, nickel chloride and barium chloride, which are not known to catalyze other Friedel–Crafts reactions, led us to test some anhydrous chlorides in this reaction under similar conditions. Ten ml. of C. P. benzyl chloride was placed in a dry Pyrex test-tube with a trace (pinhead size) of potential catalyst. The mixture was boiled under a "cold finger" condenser for at least two hours, or else until too little benzyl chloride was left to reflux.

One group of chlorides gave high percentages of the theoretical yield of $(C_7H_6)_x$ polymer, 86–99%, within two hours. This group includes aluminum chloride, antimony pentachloride, boron trichloride, cadmium chloride, columbium pentachloride, ferric chloride, gallium (added as metal), indium (added as metal), manganese dichloride, molybdenum pentachloride, palladium dichloride, platinum tetrachloride, stannic chloride, stannous chloride, tantalum pentachloride, titanium tetrachloride, tungsten hexachloride, uranyl acetate[2] and zinc chloride. All polymers were ther-

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[1] (a) Shriner and Berger, *J. Org. Chem.*, **6**, 305 (1941); (b) Fisher and Eisner, *ibid.*, **6**, 169 (1941).

[2] Used for lack of the chloride, but presumably converted to it in course of the reaction.