[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

A Study of Organic Parachors. X. Parachors of American Petroleum Institute–National Bureau of Standards Hydrocarbons: Benzene and Homologs of Benzene[1]

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As a part of a broad program of determining the parachors of organic compounds, this Laboratory has undertaken the measurement of the surface tensions and the calculation of the parachors of the American Petroleum Institute–National Bureau of Standards pure hydrocarbons. The values found for benzene and twenty homologs are here reported.

Description of Materials

These samples of API–NBS hydrocarbons have been made available by the American Petroleum Institute and the National Bureau of Standards through the API Research Project 44 on the "Collection, analysis and calculation of data on the properties of hydrocarbons." They were purified at the National Bureau of Standards by the API Research Project 6 on the "Analysis, purification and properties of hydrocarbons" from material supplied by the following laboratories: Benzene, 1,2,3-trimethylbenzene (A), and 1,2,4-trimethylbenzene (A) by the API Research Project 6 at the N.B.S. Methylbenzene by the Humble Oil and Refining Company, Houston, Texas. Ethylbenzene (A) and isopropylbenzene by the Monsanto Chemical Company, Dayton, Ohio. 1,2-Dimethylbenzene (A) by the Standard Oil Development Company, Elizabeth, New Jersey. 1,3-Dimethylbenzene (A), 1,4-dimethylbenzene (A), 1-methyl-2-ethylbenzene, 1-methyl-3-ethylbenzene (A), 1,3,5-trimethylbenzene, *n*-butylbenzene (A), isobutylbenzene (A), *s*-butylbenzene (A), and *t*-butylbenzene (A) by the API Research Project 45 at the Ohio State University, under the supervision of C. E. Boord. *n*-Propylbenzene (A), and 1,3-diethylbenzene (A), by the Dow Chemical Company, Midland, Michigan. 1-Methyl-4-ethylbenzene, 1,2-diethylbenzene, 1,4-diethylbenzene by the National Advisory Committee for Aeronautics, Aeronautical Engine Research Laboratory, Cleveland, Ohio.

Results

Surface tensions were measured by the maximum bubble pressure method using a somewhat modified bubbler.[3] Particular care was taken to keep the volume of the system at a minimum.

TABLE I

BENZENE AND HOMOLOGS

Compound	Purity[a] mole % 99+	Densities D^{20}_4 [b]	D^{30}_4	D^{40}_4	$d \times 10^3$ [c] 20°	30°	40°	Surface tensions[d] 20° γ	$\Delta \times 10^3$ [e]	30° γ	$\Delta \times 10^3$	40° γ	$\Delta \times 10^3$	Parachors[f] 20°	30°	40°
C_6H_6	0.963 ± 0.02	0.87903	0.86833	0.85763	0.38	0.56	0.73	28.87	6	27.49	6	26.14	6	206.06	206.11	206.11
$CH_3C_6H_5$	.95 ± .03	.86696	.85766	.84836	.19	.27	.35	28.53	4	27.32	3	26.15	3	245.66	245.67	245.66
$C_2H_5C_6H_5$	.93 ± .05	.86696	.85820	.84944	.12	.17	.21	29.04	6	27.93	5	26.79	2	284.31	284.42	284.41
$C_3H_7C_6H_5$	.71 ± .08	.86198	.85354	.84510	.08	.11	.14	28.99	6	27.91	8	26.81	5	323.57	323.68	323.67
$(CH_3)_2CHC_6H_5$	.96 ± .03	.86175	.85321	.84467	.10	.13	.16	28.20	4	27.17	3	26.09	2	321.42	321.64	321.64
$C_4H_7C_6H_5$	.91 ± .06	.86013	.85201	.84389	.06	.08	.10	29.23	7	28.19	6	27.18	3	362.83	362.98	363.16
$(CH_3)_2CHCH_2C_6H_5$	.86 ± .09	.85321	.84493	.83665	.07	.09	.12	27.47	10	26.50	7	25.55	6	360.17	360.43	360.68
$C_2H_5CH_3CHC_6H_5$	.69 ± .06	.86207	.85387	.84567	.07	.09	.12	28.53	4	27.53	10	26.57	10	359.83	360.07	360.35
$(CH_3)_3CC_6H_5$	.95 ± .03	.86650	.85830	.85010	.07	.09	.12	28.13	4	27.14	6	26.16	5	356.74	356.93	357.08
o-$(CH_3)_2C_6H_4$	.963 ± .013	.88005	.87161	.86317	.10	.14	.18	30.03	33	28.93	2	27.84	6	282.41	282.50	282.55
m-$(CH_3)_2C_6H_4$	.85 ± .05	.86412	.85554	.84696	.11	.15	.20	28.63	5	27.54	4	26.44	2	284.21	284.29	284.29
p-$(CH_3)_2C_6H_4$	.94 ± .03	.86100	.85232	.84364	.11	.16	.20	28.31	5	27.22	4	26.13	3	284.45	284.56	284.58
o-$CH_3C_2H_5C_6H_4$	.76 ± .07	.8809	.8723	.8637	.07	.10	.13	30.20	4	29.13	2	28.11	8	319.88	320.12	320.44
m-$CH_3C_2H_5C_6H_4$	.77 ± .15	.8646	.8560	.8474	.08	.11	.14	29.07	5	27.97	4	26.89	4	322.83	322.93	323.02
p-$CH_3C_2H_5C_6H_4$	.74 ± .03	.8616	.8532	.8448	.08	.11	.14	28.84	3	27.73	3	26.69	5	323.30	323.30	323.39
o-$(C_2H_5)_2C_6N_4$	.97 ± .03	.8805	.8725	.8645	.06	.08	.10	30.30	4	29.25	6	28.24	8	357.64	357.75	357.92
m-$(C_2H_5)_2C_6H_4$	.92 ± .04	.8641	.8561	.8481	.06	.08	.10	29.17	8	28.11	3	27.08	3	361.01	361.01	361.02
p-$(C_2H_5)_2C_6H_4$	.977 ± .020	.8619	.8539	.8459	.06	.08	.10	29.00	4	27.97	7	26.94	4	361.39	361.49	361.48
v-$(CH_3)_3C_6H_3$	.80 ± .04	.8950	.8864	.8778	.06	.08	.10	31.27	7	30.25	6	29.20	3	317.58	318.02	318.32
u-$(CH_3)_3C_6H_3$	.68 ± .20	.8761	.8677	.8593	.07	.09	.12	29.71	6	28.67	5	27.66	39	320.33	320.56	320.79
s-$(CH_3)_3C_6H_3$	.96 ± .02	.8653	.8569	.8485	.07	.10	.13	28.83	4	27.79	3	26.75	1	321.88	322.07	322.19

[a] A. P. I. Project 6 and A. P. I. Project 44 at N. B. S. Status Report, Sept. 30, 1948. [b] A. P. I. Research Project 44 at N. B. S. "Selected Values of Properties of Hydrocarbons." Density of liquid. [c] Density of vapor. Calculated. [d] Dynes per cm. Each recorded value is an average of at least seven determinations. [e] Average deviation of the several determinations from average surface tension values. Surface tension values rounded off to second place. Deviations given as calculated to third place. [f] $P = \gamma^{1/4}[M/(D - d)]$.

Table I gives the purity of the various samples

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[2] From material to be presented by Raymond E. Donaldson to the graduate faculty of Emory University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Quayle and Smart, THIS JOURNAL, **66**, 935 (1944).

and the density data necessary for the calculation of parachors by the formula $P = \gamma^{1/4}[M/(D-d)]$, where M is molecular weight, γ is surface tension, D is the density of the liquid at the temperature of measurement of surface tension, and d is the density of the vapor at that temperature. Values of d are approximated from the empirical formula[4]

$$\log \frac{d_t}{d_f} = 5\left(\frac{T}{T_b} - 1\right)$$

in which d_t is the density of the vapor at the chosen temperature T, T_b is the boiling point absolute, and d_f is the density of the vapor at the boiling point. Approximate values of d_f are obtained from the formula $d_f = 0.0122 \times M/T_b$.

Of interest are the values for toluene, ethylbenzene, *n*-propylbenzene, isopropylbenzene and *n*-butylbenzene reported by Vogel.[5] Although a different method of measuring was used (cap. rise), only in case of isopropylbenzene is there a parachor variation as great as 0.1%. In this one case Vogel obtained a parachor 0.2% lower.

Although broader and more valid generalizations will be possible when values are available from additional and related compounds, there are certain constitutional variations that should be pointed out, particularly in the ortho, meta, para relationships. It was considered at one time that such position isomers showed no change. The meta isomer shows a parachor decrease of from 0.7 to 1.0% compared with the ortho. The para isomer shows a further decrease of from 0.1 to 0.15% in the parachor value. This latter decrease is admittedly of the order of magnitude of the experimental error. However the direction of the change is the same in three cases. The numerical values are shown in Table II.

TABLE II

PARACHOR DIFFERENCES IN POSITION ISOMERS

Compounds	Ortho to meta	% Change	Meta to para	% Change
Xylenes	1.80	0.6	0.24	0.1
1,2,3-Trimethylbenzene and 1,3,5-trimethylbenzene	2.15	0.7	..	..
Methylethylbenzenes	2.95	1.0	.47	0.15
Diethylbenzenes	3.37	0.9	.38	0.1

It may be noted in considering the series of normal monoalkyl compounds that the CH_2 increment from methyl- to ethylbenzene is abnormally low, 38.65. An abnormal low value for the CH_2 increment is also shown in comparing methyl- and ethyl-*p*-xylenes.[6]

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Summary

1. The surface tensions and parachors of benzene and twenty homologs are reported at 20, 30 and 40°.

2. The variations in parachors of ortho, meta and para isomers are pointed out.

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[4] Sugden, Reed and Wilkins, *J. Chem. Soc.*, **127**, 1540 (1925).

[5] Vogel, *J. Chem. Soc.*, **40**, 3390 (1948).

[6] Unpublished data, this Laboratory.

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Oxygen Isotope Exchange in the Electric Discharge

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Introduction

The problem of the enhanced O^{18} content of the atmosphere discovered by one of us in 1935[2] and more recently discussed by Kamen and Barker[3] has never been satisfactorily solved, either through a photosynthetic[4] or bacterial[5] explanation.

In this note we give for the first time what appears to be a possible explanation. We believe that the O^{18} enhancement takes place in the stratosphere under the influence of ultraviolet rays and by means of a random isotopic exchange between carbon dioxide and water. In order to give this idea a laboratory test, we decided to investigate the possibility of oxygen isotope exchange between carbon dioxide and oxygen and

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[2] M. Dole, THIS JOURNAL, **57**, 2731 (1935); *J. Chem. Phys.*, 4, 268 (1936); J. A. Swartout and M. Dole, THIS JOURNAL, **61**, 2025 (1939).

[3] M. C. Kamen and H. A. Barker, *Proc. Nat. Acad. Sci.*, **31**, 8 (1945). This effect is called by Kamen and Barker, the "Dole Effect."

[4] C. H. Greene and R. J. Voskuyl, THIS JOURNAL, **58**, 693 (1936); M. Dole and G. Jenks, *Science*, **100**, 409 (1944).

[5] M. Dole, R. C. Hawkings and H. A. Barker, THIS JOURNAL, **69**, 226 (1947).