The Dipole Moments of Some Aliphatic Ethers

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Dipole moments of eight ethers were measured in benzene solution. Table I gives the experimental data and the calculated results. The symbols f_2, d and e refer to mole fraction of ether, density and dielectric constant, respectively. The molar refraction MR_D was calculated in each case from the atomic refractions.[2] The dipole moment μ calculated by the method of Hedestrand[3] is given in Debye units. The moment of 1.28 D for diethyl ether in benzene is in good agreement with the value of 1.27 D given by Hassel and Uhl.[4] The values of 1.26 and 1.22 D obtained for di-*n*-butyl ether and ethyl *n*-butyl in benzene, respectively, are to be compared with the values 1.22 and 1.24 D obtained by Li and Terry.[5] Groves and Sugden[6] give the value 1.18 D for the moments of the normal symmetrical ethyl, propyl and butyl ethers in the vapor state. There is a considerable solvent effect in benzene, and the variation of moments reported here may be due to this effect alone. It is perhaps significant, however, that the average of the moments of the symmetrical ethers (1.28 D) is larger than that of the unsymmetrical ethers (1.21 D). Symmetry in ethers might be expected to stabilize hyperconjugation structures which represent polarization of the alkyl groups by oxygen.

TABLE I

DENSITIES, DIELECTRIC CONSTANTS AND DIPOLE MOMENTS AT 25°

f_2	d	ϵ	f_2	d	ϵ
Diethyl ether			Ethyl *n*-propyl ether		
0.006168	0.8726	2.295	0.007026	0.8728	2.297
.01818	.8710	2.327	.01224	.8715	2.300
.04983	.8652	2.372	.03065	.8681	2.331
.08879	.8591	2.442	.05600	.8634	2.352
MR_D 23.00	μ 1.28		MR_D 27.63	μ 1.16	
Di-*n*-propyl ether			Methyl *n*-butyl ether		
0.009158	0.8722	2.295	0.009977	0.8719	2.298
.02006	.8701	2.315	.01305	.8717	2.300
.03587	.8672	2.344	.02713	.8688	2.328
.05300	.8631	2.376	.05846	.8636	2.374
MR_D 31.66	μ 1.31		MR_D 27.06	μ 1.25	
Di-*n*-butyl ether			Ethyl *n*-butyl ether		
0.005780	0.8721	2.293	0.003695	0.8731	2.285
.008948	.8710	2.295	.009879	.8718	2.293
.01881	.8696	2.315	.01905	.8701	2.307
.03748	.8660	2.343	.03682	.8662	2.333
MR_D 41.03	μ 1.26		MR_D 31.76	μ 1.22	
Methyl *n*-propyl ether			*n*-Propyl *n*-butyl ether		
0.009180	0.8714	2.292	0.004597	0.8727	2.293
.01622	.8701	2.304	.009947	.8714	2.296
.03334	.8665	2.336	.02434	.8686	2.317
.06385	.8607	2.365	.04277	.8647	2.340
MR_D 22.35	μ 1.24		MR_D 36.33	μ 1.17	

(1) Department of Chemistry, University of Maryland, College Park, Md.

(2) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Fifth Edition, Julius Springer, Berlin, 1936.

(3) G. Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

(4) O. Hassel and A. H. Uhl, *ibid.*, **B8**, 187 (1930).

(5) N. C. C. Li and T. D. Terry, THIS JOURNAL, **70**, 344 (1948).

(6) L. G. Groves and S. Sugden, *J. Chem. Soc.*, 1779 (1937).

Experimental

Capacitances were measured by the heterodyne-beat method.[7] A modification of the electronic circuit[8] described by Müller, Garman and Droz[9] was used. The dielectric constant of benzene was assumed to be 2.276 at 25°.[10]

Benzene and the Normal Symmetrical Ethers.—Commercial products were purified by refluxing over sodium and distillation. Physical constants are as follows: benzene, b. p. 80.3–80.5°, d^{25}_4 0.8736; diethyl ether, b. p. 34.5–34.6°, d^{25}_4 0.7079; dipropyl ether, b. p. 90.5–91.0°, d^{25}_4 0.7416; dibutyl ether, b. p. 141–142°, d^{25}_4 0.7637.

Asymmetric Ethers.—Sodium was dissolved in an excess of alcohol and an equivalent amount of alkyl halide was added dropwise. After six hours of refluxing the ether was distilled off, treated with sodium over a prolonged period, and redistilled. The following physical constants were obtained: ethyl *n*-propyl ether, b. p. 63.0–63.4°, d^{25}_4 0.7270; ethyl *n*-butyl ether, b. p. 92.0°, d^{25}_4 0.7452; methyl *n*-propyl ether, b. p. 38.3–39.0°, d^{25}_4 0.7230; methyl *n*-butyl ether, b. p. 70.5–71.0°, d^{25}_4 0.7393; *n*-propyl *n*-butyl ether, b. p. 116.5–117.0°, d^{25}_4 0.7531.

(7) C. P. Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Reinhold Publ. Co., New York, N. Y., 1931.

(8) The electronic parts of the apparatus were assembled by Mr. Iwao Miyake of the Physics Department.

(9) R. H. Müller, R. L. Garman and M. E. Droz, "Experimental Electronics," Prentice-Hall, Inc., New York, N. Y., 1942, p. 280.

(10) C. P. Smyth and W. S. Walls, THIS JOURNAL, **53**, 527 (1931).

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Chemical Properties of Californium

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Introduction

In the course of the production and identification of a radioactive isotope of californium (atomic number 98)[1] some evidence as to the chemical nature of this transuranium element was obtained. This isotope was prepared by the bombardment of Cm^{242} with 35-Mev. helium ions in the 60-inch cyclotron of the Crocker Radiation Laboratory and is believed to have the mass number 244. The Cf^{244} has a half-life of about 45 minutes and decays at least partially by the emission of alpha-particles of 7.1-Mev. energy.

It should be pointed out that the first successful identification of the new element depended on the quite accurate prediction of some of its nuclear and chemical properties. The anticipation of the nuclear properties (principally half-life and radiation characteristics) was necessary in order to design adequate chemical procedures of sufficiently short duration and to use suitable instruments for the detection of its radiations. The predic-

(1) S. G. Thompson, K. Street, Jr., A. Ghiorso and G. T. Seaborg *Phys. Rev.*, **78**, 298 (1950).