The Electric Moments of Some Aliphatic Peroxides, Disulfides and Diselenides

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The electric moments of three peroxides, three disulfides and two diselenides have been measured in benzene solution at 25°. The observed moments agree with those calculated for straight chain, hydrogen peroxide-like structures with dihedral angles between 70 and 120°. The presence of larger t-butyl groups decreases the electric moment in each case, indicating that the mean dihedral angle is increased by steric factors. The transannular peroxide, ascaridole, shows an anomalously high electric moment.

The electric moments of organic peroxides have not been studied but should give some information concerning the configurations of these molecules. Hydrogen peroxide has been shown by crystal structure analysis to have a skew configuration with the two OH groups lying in planes making a dihedral angle of 106°, in H_2O_2-urea,[1a] and 94°, in H_2O_2 itself.[1b] The electric moments of di-t-butyl peroxide and t-butylhydroperoxide were measured to determine whether similar structures would account for their moments and whether the larger t-butyl group might increase the mean dihedral angle; a transannular peroxide, ascaridole, was also investigated. Similar studies were made on a series of disulfides and diselenides in which the steric effects of the t-butyl groups should be of diminishing importance. None of these compounds has been investigated previously.

Experimental Part

Materials

Benzene.—Baker C.P. benzene was dried over barium oxide, distilled and stored over sodium, d^{25}_4 0.89345, $n^{25}D$ 1.4979.

t-Butyl Hydroperoxide and Di-t-butyl Peroxide.—Research samples of these were donated by the Shell Development Co., Emeryville, Calif. They were fractionated through an efficient packed column and used immediately; di-t-butyl peroxide, b.p. 52.5° (97.7 mm.), $n^{25}D$ 1.3867, d^{25}_4 0.7926; t-butyl hydroperoxide, b.p. 45° (40 mm.), $n^{25}D$ 1.3975, d^{25}_4 0.8861.

Ascaridole.—A sample from the Eastman Kodak Co. was fractionated *in vacuo*, b.p. 94.5° (10 mm.), $n^{25}D$ 1.4722, d^{25}_4 0.9889.

Di-t-butyl Disulfide.—A sample from Eastman Kodak Co. was fractionated, b.p. 72° (11 mm.), d^{25}_4 0.9194.

Diethyl Diselenide.—Eastman Kodak Co. White Label material was dried and fractionated, b.p. 98° (44 mm.), $n^{25}D$ 1.5806, d^{25}_4 1.6772.

Di-t-butyl Diselenide.—This was prepared by the same method as di-t-butyl disulfide.[2] Crude material was purified by fractionation *in vacuo*, b.p. 63–67° (3–4 mm.), $n^{25}D$ 1.5351, d^{25}_4 1.3529.

Di-n-butyl Disulfide.—Eastman Kodak Co. material was fractionated through a packed column, b.p. 115° (17 mm.), $n^{25}D$ 1.4905, d^{25}_4 0.93245.

Di-i-butyl Disulfide.—Eastman Kodak Co. White Label material was fractionated *in vacuo*, b.p. 97.0° (17 mm.), $n^{25}D$ 1.4847, d^{25}_4 0.92225.

Method.—The dielectric constants and densities of dilute benzene solutions were measured by use of apparatus and technique described previously.[3] The electric moments were calculated from the observed molecular refractions, and the molar polarizations in infinitely dilute solution obtained by extrapolation by the method of Halverstadt and

Kumler.[4] Measurements of dielectric constant and density were usually made on six solutions with mole fraction of solute varying from about 0.001 to 0.020. The probable error in $P_2^∞$ is estimated to be about ±0.02 P, and the probable error in μ about ±0.05 D; where duplicate runs were made the electric moments differed by less than 0.05 D The constants α', β', ϵ_{10}, V_{10} (ref. 4) and the values of $P_2^∞$ for each compound are shown in Table I along with the observed values of the molecular refractions MR_D and the calculated values of the dipole moment.

TABLE I

EMPIRICAL CONSTANTS[a] AND POLARIZATIONS AT 25°, MOLAR REFRACTIONS AND DIPOLE MOMENTS

ϵ_{10}	α'	V_{10}	β'	$P_2^∞$	MR_D	μDebye
		Di-t-butyl peroxide				
2.2713	+0.438	1.14500	+0.194	60.78	43.44	0.92
		t-Butyl hydroperoxide				
2.2690	+4.40	1.14468	+0.0163	95.80	24.52	1.87
		Ascaridole				
2.2695	+11.10	1.14474	−0.292	213.82	47.65	2.85
		Di-t-butyl disulfide				
2.2710	+4.65	1.14490	−0.117	125.94	55.36	1.86
		Di-i-butyl disulfide				
2.2725	+5.42	1.14472	−0.121	127.6	55.396	2.00
		Di-n-butyl disulfide				
2.2725	+5.812	1.14478	−0.156	142.58	55.35	2.06
		Diethyl diselenide				
2.7000	+5.08	1.14480	−1.46	114.38	42.91	1.87
		Di-t-butyl diselenide				
2.2725	+4.875	1.14470	−1.383	132.24	62.636	1.83

[a] Measured values of the dielectric constants ϵ_{12}, and the specific volumes V_{12}, of the solutions were plotted graphically against mole fraction of solute. Within experimental error the points are found to fall on straight lines with slopes α' and β', respectively, and the intercepts at zero mole fraction are ϵ_{10} and V_{10}, respectively. The molar polarizations at infinite dilution P_2, and the dipole moments μ, expressed in Debye units, are calculated from these constants,[4] and are shown in the table.

Discussion of Results

The dipole moment of hydrogen peroxide[5] combined with the values $\angle HOO = 105°$, and dihedral angle $H–O–O–H = 100°$ (mean of two reported values[1,2]) leads to the value 1.71 for the OH bond moment in H_2O_2; the value 1.51 for OH in the water molecule is presumably lower because of group interactions. By combining this with the C–H moment of 0.40 and the CO moment of 0.62, calculated from di-n-propyl ether, we calculate the moments 1.78 and 1.27 for t-butyl hydroperoxide and di-t-butyl peroxide, assuming $\angle COO = 105°$ and dihedral angle $C–O–O–H = 100°$. The

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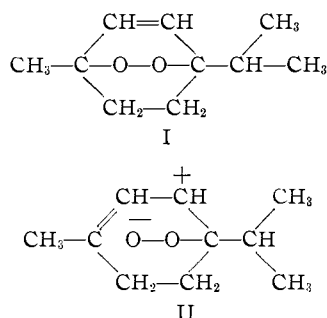(2) H. Rheinboldt, F. Mott and E. Motzkus, J. prakt. Chem., **134**, 257 (1932).

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agreement between calculated and observed moments in the case of the hydroperoxide is within experimental error but the observed moment of di-t-butyl peroxide is 0.35D less than calculated; this may be interpreted as indicating a larger mean dihedral angle as a result of steric repulsion of the large t-butyl groups, the value calculated being about 125° (with large probable error). If, as might have been anticipated, the C–O moment were somewhat larger in the peroxides than the ethers, then the moment of di-t-butyl peroxide should be larger than calculated.

Ascaridole is a transannular peroxide to which structure I has been assigned. The C–O–O–C group must be more or less *cis*-planar and, assuming a C–O moment of 0.62, the maximum moment

$$CH_3—\overset{CH=CH}{\underset{CH_2—CH_2}{C—O—O—C}}—\overset{CH_3}{\underset{}{CH}}—CH_3$$

I

$$CH_3—\overset{+}{\underset{CH_2—CH_2}{C}}\overset{CH—CH}{\underset{}{O—O—C}}\overset{CH_3}{\underset{CH_3}{CH}}$$

II

expected for ascaridole would be about 2.04 D. It seems difficult to account for the observed value, which is 0.8 D higher; perhaps some contribution to the normal state of the molecule from structures such as II tends to increase the moment of the molecule.

Dimethyl disulfide and dimethyl trisulfide have been studied by the electron diffraction method; for the former $\angle$ C–S–S = 107° was reported,[6] with no information concerning the dihedral angle, and for the latter[7] $\angle$ C–S–S = 104 ± 5° was found with the dihedral angle C–S–S–C = 106°. The values $\angle$ C–S–S = 98° and dihedral angles S–S–S–C = 85° were found in crystalline 2,2'-diiododiethyl trisulfide.[8] If we assume a chain structure for the disulfide with $\angle$ C–S–S = 104° the dipole moment

calculated for free rotation (or 90° dihedral angle) would be 1.74, using the value 0.87 for the C–S bond moment calculated from the electric moment of n-butyl sulfide. The observed values 2.06 D for di-n-butyl disulfide and 2.00 D for di-i-butyl disulfide are higher than calculated for free rotation and could be accounted for by a *skew* configuration with dihedral angle C–S–S–C about 70°. The moment of di-t-butyl disulfide, 1.86 is lower than that of di-n-butyl disulfide, indicating a dihedral angle larger by about 10°, as might be expected from steric repulsions of the larger t-butyl groups. If the C–S moment in the disulfides were slightly larger (0.20 D) than in the sulfide, where group interaction may lower the dipole moment, then the dihedral angles calculated would be close to the values reported for other disulfides.[7,8,11] Although dipole moment measurements cannot distinguish between the free rotation model and a *skew* configuration in which terminal groups oscillate with a mean dihedral angle 90 ± 30°, the latter is favored since Pauling[9] has shown theoretically that repulsion of the p π-electrons on the sulfur atoms should lead to a chain structure for these molecules, with dihedral angles C–S–S–C about 90–100°.

The value 2.06 reported here for di-n-butyl disulfide agrees well with the electric moments of dimethyl disulfide[10] (1.96), diethyl disulfide[10] (1.99), dipropyl disulfide[10] (1.96) and di-n-hexyl-disulfide[11] (2.00), reported previously.

The moment of di-t-butyl diselenide is similarly lower than that of diethyl diselenide. However, the difference is now within experimental error so the steric effects must be small as would be expected for the greater separation between the groups in the selenides. No simple aliphatic selenides have been studied but a value C–Se = 0.8 is estimated for the C–Se moment from the observed dipole moments of phenyl selenide and diphenyl diselenide. The dihedral angles C–Se–Se–C in diethyl diselenide and di-t-butyl diselenide are then calculated to be 83 and 85°30', respectively.

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