SHORT COMMUNICATIONS

MOLECULAR POLARIZABILITY. THE ANISOTROPY OF THE O–O BOND*

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Hydrogen peroxide, irrespective of state, is known to exist as the fixed skew structure[1–5] originally proposed by Penney and Sutherland[6] (see Fig. 1). An electron diffraction study by Shand[7] in 1946 indicated a similar type of configuration for dimethyl peroxide. Rogers and Campbell[8] in 1952 reported the dipole moments of t-butyl hydroperoxide and di-t-butyl peroxide (in benzene at 25°) as 1·87 D and 0·92 D respectively. These were shown to be in accord with hydrogen peroxide-like structures having dihedral angles ϕ of *c.* 100° (for t-butyl hydroperoxide) and *c.* 125° (for di-t-butyl peroxide); the larger ϕ can reasonably be attributed to the mutual repulsions of the bulky t-butyl groups.

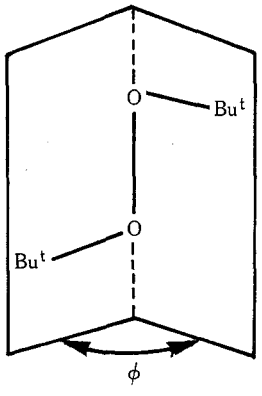

Fig. 1

The present work is concerned with experimental determinations of the dipole moment and molar Kerr constant of di-t-butyl peroxide in benzene solution and with the interpretation of these data to provide (*a*) information on the solute configuration, and (*b*) the anisotropic electron polarizabilities of the O–O group in peroxides.

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[1] Abrahams, S. C., Collin, R. L., and Lipscomb, W. N., *Acta crystallogr.*, 1951, **4**, 15.
[2] Randall, J. T., *Proc. R. Soc.*, 1937, **159**, 82.
[3] Sutton, L. E., *et al.*, Spec. Publ. chem. Soc., No. 11, M 69 (1958); No. 18, M 38s (1965).
[4] Bain, O., and Giguere, P. A., *Can. J. Chem.*, 1955, **33**, 527.
[5] Linton, E. P., and Maass, O., *Can. J. Res.*, 1932, **7**, 81.
[6] Penney, W. G., and Sutherland, G. B. M., *Trans. Faraday Soc.*, 1934, **30**, 898; *J. chem. Phys.*, 1934, **2**, 492.
[7] Shand, W., Ph.D. Thesis, California Institute of Technology, 1946.
[8] Rogers, M. T., and Campbell, T. W., *J. Am. chem. Soc.*, 1952, **74**, 4742.

Experimental

Di-t-butyl peroxide, a commercial sample, was distilled shortly before use (b.p. *c.* 50°/90 mm). Benzene (thiophen-free) was dried with sodium wire. The following solvent constants apply at 25°: $\epsilon_1 = 2{\cdot}2725$; $d_1 = 0{\cdot}87378$; $(n_1)_D = 1{\cdot}4973$; $10^7B_1 = 0{\cdot}410$; $10^{12}{}_sK_1 = 0{\cdot}0756$.

The apparatus, techniques, methods of calculation, and symbols have previously been described.[9-11] The experimental results are shown in Table 1.

TABLE 1

INCREMENTAL DIELECTRIC CONSTANTS, DENSITIES, REFRACTIVE INDICES, AND KERR EFFECTS FOR SOLUTIONS IN BENZENE AT 25°

10^5w_2	1972	5304	7994	9227		
$10^4\Delta\epsilon$	40	106	151	177		
$-10^5\Delta d$	177	419	677	795		
$-10^4\Delta n$	24	64	97	112		
whence $\Sigma\Delta\epsilon/\Sigma w_2 = 0{\cdot}193$, $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}0844$, $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}121$, $\Sigma\Delta n^2/\Sigma w_2 = -0{\cdot}362$						
10^5w_2	1459	2665	4061	6592	7994	8612
$-10^{11}\Delta B$	52	88	154	221	272	280
whence $\Sigma 10^7\Delta B/\Sigma w_2 = -0{\cdot}340$						

Discussion

Our measurements lead to a total polarization of 60·0 c.c., a molar refraction $[R]_D$ of 43·6 c.c., and a dipole moment μ of $0{\cdot}89\pm0{\cdot}06$ D, which is in good agreement with the two previous estimates $0{\cdot}92\pm0{\cdot}05$ D[8] and 0·94 D.[12] In each case μ was calculated assuming the distortion polarization to equal $[R]_D$; an uncertainty in ${}_AP$ (the atomic polarization) of $\pm0{\cdot}05\ R_D$ results in a possible error in μ of $\pm0{\cdot}06$ D. The molar Kerr constant at infinite dilution is $+2{\cdot}9_6\times10^{-12}$.

Rogers and Campbell[8] analysed their observed moment (on the basis that $\mu(\overset{+\rightarrow}{\text{C–H}}) = 0{\cdot}40$ D, $\mu(\overset{+\rightarrow}{\text{C–O}}) = 0{\cdot}62$ D, and $\angle$C–O–O = 105°) to indicate that the dihedral angle ϕ in di-t-butyl peroxide is *c.* 125°. Six years later a similar conclusion (*c.* 123°) was drawn by Lobunez, Rittenhouse, and Miller[12] who showed that the measured μ was not compatible with a freely rotating model or with one in which there is "free oscillation outside the region excluded by the barrier to *cis* configuration", i.e. that both the *cis* and *trans* forms are energetically unfavoured. Further evidence for the "rigidity" of the skew structure came from the constancy of the experimental dipole moments (0·94–0·95 D)[12] over the temperature range 30–50°.

[9] Le Fèvre, C. G., and Le Fèvre, R. J. W., Ch. XXXVI in "Physical Methods of Organic Chemistry." (Ed. A. Weissberger.) 3rd Edn. (Interscience: New York 1960.)
[10] Le Fèvre, R. J. W., and Sundaram, K. M. S., *J. chem. Soc.*, 1962, 1494.
[11] Le Fèvre, R. J. W., "Dipole Moments." 3rd Edn. (Methuen: London 1953.)
[12] Lobunez, W., Rittenhouse, J. R., and Miller, J. G., *J. Am. chem. Soc.*, 1958, **80**, 3505.

The proton magnetic resonance spectrum of di-t-butyl peroxide in deuterochloroform consists of a single, sharp absorption 73 c/s downfield from tetramethylsilane (as internal reference) and this changes only to a sharp peak 79 c/s downfield from TMS at the lower limit (−60°) of our spectrometer. The dielectric relaxation time (τ) of $4{\cdot}1\times10^{-12}$ sec recently found[13] for the peroxide in benzene solution (by a single frequency measurement at 3100 Mc/s) would most likely relate to the overall molecular rotation rather than to an intramolecular motion (cf. $\tau = 1{\cdot}2\times10^{-12}$ sec for dimethyl ether in benzene; $\tau = 2{\cdot}0\times10^{-12}$ sec for ethylene oxide in benzene).[13]

The dipole moment of di-t-butyl ether has not yet been recorded. McClellan[14] lists four estimates of μ (di-n-butyl ether) measured in benzene at 25°; all are within the range $1{\cdot}18\pm0{\cdot}09$ D and from these the n-butyl–oxygen group moment is calculable (with $\angle$C–O–C = 110°) as $1{\cdot}03\pm0{\cdot}08$ D. If then μ (di-t-butyl peroxide) = $0{\cdot}89\pm0{\cdot}06$ D and $\angle$C–O–C = 105°, it follows that the dihedral angle ϕ would be $126°\pm8°$. The bond moments of Rogers and Campbell,[8] if used in the present calculations, result in $\phi = 126°$.

The anisotropic electron polarizabilities of the O–O bond can now be derived from the experimental molar Kerr constant of di-t-butyl peroxide and the electron polarization of the O–O link using equations 22, 30, 35, and 36 of Le Fèvre's review.[15] Gillis[16] lists $[R]_D$ for the O–O group as 2·27 c.c. so that ${}_EP$ equals 2·16 c.c. (assuming ${}_EP = 0{\cdot}95R_D$). The following data are necessary for the calculations: b_L(C–C) = 0·97, b_T(C–C) = b_V(C–C) = 0·26,[17] b_L(C–H) = b_T(C–H) = b_V(C–H) = 0·65,[17] b_L(C–O) = 0·89, b_T(C–O) = b_V(C–O) = 0·46,[18] μ(di-t-butyl peroxide) = 0·89 D, ${}_DP/{}_EP = 1{\cdot}05$ (assumed), $\angle$C–O–O = 105°, $\angle$C–C–C = 109·5°, and $\phi = 126°$. The longitudinal, transverse, and vertical polarizabilities of bonds (b_L, b_T, b_V, respectively) are expressed in 10^{-24} c.c., i.e. Å^3 units. Solution of the equations leads to b_L(O–O) = 0·62, b_T(O–O) = b_V(O–O) = 1·04, and a ratio b_L(O–O)/b_T(O–O) of 0·60. Other bonds for which the mean transverse polarizability is known to exceed the longitudinal polarizability are N–H (in ammonia) and N–C (in trimethylamine). Such relationships are understandable if unshared electrons are more polarizable along than across their orbital axes; then, by the method of calculation adopted,[15] the polarizability components for these duplets become incorporated into those of the bond, thus leading to a value of $(b_T+b_V)/2$ which may be greater than that of b_L.

Acknowledgment

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[13] Le Fèvre, R. J. W., and Radford, D. V., unpublished data.
[14] McClellan, A. L., "Tables of Experimental Dipole Moments." (Freeman: San Francisco 1963.)
[15] Le Fèvre, R. J. W., *Adv. phys. org. Chem.*, 1965, **3**, 1.
[16] Gillis, R. G., *Rev. pure appl. Chem.*, 1960, **10**, 21.
[17] Le Fèvre, R. J. W., Orr, B. J., and Ritchie, G. L. D., *J. chem. Soc.* B, 1966, 273.
[18] Le Fèvre, R. J. W., Sundaram, A., and Pierens, R. K., *J. chem. Soc.*, 1963, 479.