556. *The Determination of Acid Strengths of Organic Hydroperoxides.**

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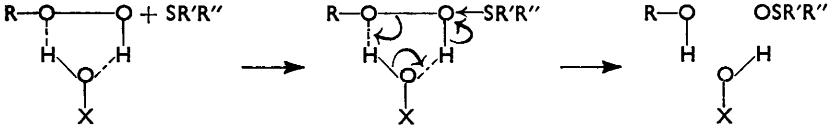
The relative acid strengths of several organic hydroperoxides and alcohols have been determined by an infrared spectroscopic study of their association with *cyclo*hexyl methyl sulphoxide. The equilibrium association constants obtained for a series of hydroperoxides parallel the relative acidities predicted by a kinetic method and enable absolute pK_a values to be derived for those hydroperoxides not amenable to conventional dissociation methods. α-Cumyl hydroperoxide is an exception to this correlation, the anomaly being traced to the intramolecular interaction of the hydroxyl group with the aromatic nucleus.

A kinetic study [1] of the interaction of organic hydroperoxides with saturated sulphides led to the conclusion that the reaction proceeds through a hydrogen-bonded cyclic transition complex :



In this complex, XOH may represent a solvent molecule or, when aprotic solvents are used, a second hydroperoxide molecule. For a given combination of hydroperoxide and sulphide it therefore appears that the reaction rate should increase as the hydrogen lability of the solvent XOH increases, and this was found to be so for a series of alcohols of different acidities. The rate should also depend on the acid strength of the hydroperoxide. For a given sulphide (*cyclo*hexyl methyl sulphide) and solvent (methanol) the second-order rate constants determined under standard conditions for a series of hydroperoxides differ considerably,[1,2] and one object of the present work was to confirm that the variations parallel the relative acid strengths of the hydroperoxides.

Kolthoff and Medalia [3] and Everett and Minkoff [4] determined pK_a values of saturated hydroperoxides by measuring their dissociation in the presence of a strong base. Such methods are not applicable to unsaturated hydroperoxides which are very readily decomposed by alkali; moreover, ionic dissociation does not necessarily reflect the true function of a weak acid in organic solvents.[5] A method was therefore employed whereby the

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[1] Bateman and Hargrave, *Proc. Roy. Soc.*, 1954, *A*, **224**, 389, 399.

[2] Hargrave, unpublished results.

[3] Kolthoff and Medalia, *J. Amer. Chem. Soc.*, 1949, **71**, 3789.

[4] Everett and Minkoff, *Trans. Faraday Soc.*, 1953, **49**, 410.

[5] Davis and Hetzer, *J. Res. Nat. Bur. Stand.*, 1952, **48**, 381.

relative strengths of weak acids could be derived from a study of their association with sulphoxides to form hydrogen-bonded complexes.[6]

If the equilibrium

$$\mathrm{R{\cdot}O{\cdot}OH} + \mathrm{OSR'R''} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{R{\cdot}O{\cdot}O{-}H} \cdots \mathrm{O{-}SR'R''} \quad . \quad . \quad . \quad . \quad (1)$$

is assumed to be the only one operative in dilute solution in carbon tetrachloride, then it may be shown that

$$P_e^{-1} = (P_0 - P_e)^{-1}K_1S_0 - K_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where K_1 is the equilibrium constant $= k_1/k_2$, S_0 is the initial sulphoxide concentration, P_0 is the initial hydroperoxide concentration, and P_e is the equilibrium concentration of unassociated hydroperoxide. With a constant value of S_0 and different values of P_0, the plot of P_e^{-1} against $(P_0 - P_e)^{-1}$ should be linear, with a slope of K_1S_0.

The determination of K_1, as a measure of the acid strength of the hydroperoxide, thus involves only the measurement of a series of values of P_e, which can be accurately carried out by infrared spectroscopy with reference to a suitable calibration curve. Compounds, other than hydroperoxides, having acidic hydrogen can be similarly examined and by a simple adaptation of the method the relative basic strengths of, say, a series of sulphoxides should be determinable.

EXPERIMENTAL

Apparatus and Technique.—A Grubb-Parsons single-beam infrared spectrometer was used with a lithium fluoride prism. To reduce absorption due to atmospheric water vapour in the instrument an activated-alumina air-drier was employed. The absorptions of the test solutions and pure solvent were determined by using matched fused-quartz absorption cells (5 mm.) reproducibly placed in the spectrometer, and all measurements were made at 25·0° ± 0·5°. Calibration curves were derived for each hydroxylic compound, relating the optical density of the 3μ unassociated OH stretching band to the concentration. Over the concentration ranges used for each compound, Beer's law was accurately obeyed, indicating that self-association was negligible—the individual ranges depended on the intensity of absorption of each hydroxylic compound and were within the overall limits 0·002—0·02M. Table 1 gives the frequencies, ν_{OH}, and molecular extinction coefficients, ε, of the OH absorption bands used. It was also shown that *cyclo*hexyl methyl sulphoxide (0·02M in CCl_4) had no absorption in the region 3620—3550 cm.$^{-1}$.

TABLE 1.

	ν_{OH} (cm.$^{-1}$)	ε (mole^{-1} l. cm.$^{-1}$)
Phenol	3609	209
Thymol	3611	183
1-Tetralyl hydroperoxide	3540	75
*cyclo*Hex-2-enyl hydroperoxide	3537	86
α-Cumyl hydroperoxide	3535, 3510	40, 35 *
*cyclo*Hexyl hydroperoxide	3535	87
tert.-Butyl hydroperoxide	3543	87
tert.-Butyl alcohol	3598	55

* Apparent values, $\varepsilon_{app.}$, band overlap being neglected.

For each weak acid, solutions were prepared in carbon tetrachloride containing a standard concentration of *cyclo*hexyl methyl sulphoxide (0·02M) and varying concentrations of the hydroxyl compound such that the equilibrium concentration of the unassociated material fell within the range covered by the appropriate calibration curve. Determinations of the equilibrium concentration were carried out in duplicate.

Materials.—"AnalaR" carbon tetrachloride was further purified by conventional methods, the same spectroscopically pure sample being used throughout. *cyclo*Hexyl methyl sulphoxide [6] had a purity of 99% as estimated by Barnard and Hargrave's method.[7] Phenol and thymol were "AnalaR" samples sublimed in a high vacuum immediately before use. *tert.*-Butyl alcohol had b. p. 82·2—82·3°/760 mm. 1-Tetralyl hydroperoxide was prepared by Nussle,

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[6] Barnard, Fabian, and Koch, *J.*, 1949, 2442.

[7] Barnard and Hargrave, *Analyt. Chim. Acta*, 1951, **5**, 536.

Perkins, and Toennies's method[8] and after five crystallisations from light petroleum (b. p. 40—60°)-ethyl acetate had m. p. 55·2—55·6°. *cyclo*Hexyl hydroperoxide was prepared as described by Walling and Buckler[9] and purified, as were commercial samples of α-cumyl and *tert.*-butyl hydroperoxide, by successive regeneration from the sodium salt followed by fractional distillation. *cyclo*Hex-2-enyl hydroperoxide was isolated from thermally autoxidised *cyclo*hexene as described by Barnard and Hargrave.[10] The purities of these hydroperoxides were respectively 99, 97, 99, 100, and 86% based on their peroxidic oxygen content.[10] For *cyclo*hex-2-enyl hydroperoxide the close agreement of the intensity of its OH stretching band (based on purity) with those of the pure hydroperoxides, together with the absence of bands due to other hydroxylic materials, indicates that the impurity can be considered inert in the bonding equilibria now considered. A similar conclusion was reached by Bateman and Hughes[11] in their study of the kinetics of decomposition of this hydroperoxide.

RESULTS AND DISCUSSION

The Figure shows plots of P_e^{-1} against $(P_0 - P_e)^{-1}$ for a series of hydroperoxides together with phenol, thymol, and *tert.*-butyl alcohol. True linearity is achieved only at low values of P_e. The determination of the correct slope of the line is facilitated, however, by the fact that all lines should theoretically pass through the point $(0, S_0^{-1})$. The deviations suggest the participation of the hydroxylic component in other equilibria, *viz.*, (*a*) by the intermolecular association of the hydroxylic component, $n(\mathrm{ROH}) \rightleftharpoons (\mathrm{ROH})_n$, or (*b*) by the further bonding of the sulphoxide–hydroperoxide complex with unassociated hydroperoxide (or hydroxylic component):

$$\mathrm{RO{-}H \cdots OSR'R'' + R{\cdot}OH \rightleftharpoons (RO{-}H \cdots O - SR'R''),ROH} \quad . \quad (3)$$

Intermolecular association would appear to be negligible in the present instance since Beer's law is accurately obeyed over the whole range of concentration in which P_e falls.

If equilibria (1) and (3) are considered together it can be shown that

$$P_e^{-1} = (P_0 - P_e)^{-1}(1 + 2k_3P_e)K_1\,S_0 - K_1(1 + K_3P_e)$$

where K_3 is the equilibrium constant for (3). By fitting this equation to the experimental points, reasonably consistent values of K_3 were obtained, in all cases less than $0{\cdot}1K_1$. At low values of P_e the bracketed terms in the above equation approximate to unity and a sensibly linear plot of P_e^{-1} *versus* $(P_0 - P_e)^{-1}$ should result, as actually found. It seems, therefore, that equilibria of the type (*b*) represent a likely explanation of the departures from the simple theory.

Table 2 presents the values of K_1 derived from the Figure, together with literature values of pK_a where available and, for the hydroperoxides, the second-order rate constants, k_2, for the reaction with *cyclo*hexyl methyl sulphide. It will be observed that the desired correlation exists between these rate constants and the values of K_1 with the exception of those for α-cumyl hydroperoxide. Apart from this exception, log K_1 plotted against pK_a gives a substantially straight line (pK_a = 19·2 — 3·89 log K_1) from which interpolated values of pK_a can be obtained.

TABLE 2.

	K_1 (l. mole^{-1})	pK_a	10^5k_2 (mole^{-1} l. sec.$^{-1}$)
Phenol	314	9·95	—
Thymol	127	10·49	—
1-Tetralyl hydroperoxide	53	—	184
*cyclo*Hex-2-enyl hydroperoxide	43	—	165
α-Cumyl hydroperoxide	22	12·6	126
*cyclo*Hexyl hydroperoxide	39	—	108
tert.-Butyl hydroperoxide	35	12·8	22

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[8] Nussle, Perkins, and Toennies, *Amer. J. Pharm.*, 1935, **29**, 107.

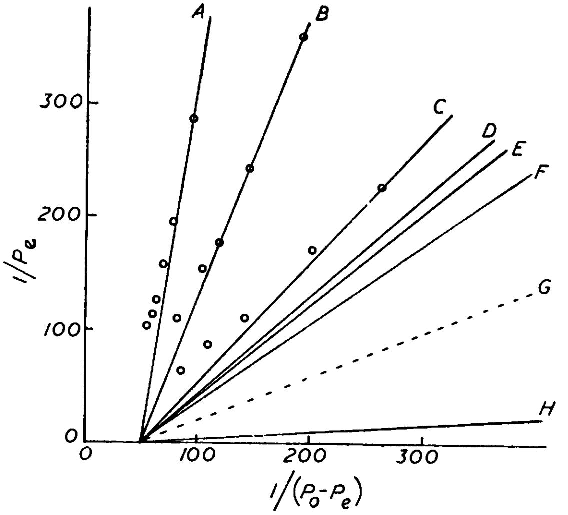
[9] Walling and Buckler, *J. Amer. Chem. Soc.*, 1953, **75**, 4372.

[10] Barnard and Hargrave, *Analyt. Chim. Acta.*, 1951, **5**, 476.

[11] Bateman and Hughes, *J.*, 1952, 4594.

The same value of K_1 for α-cumyl hydroperoxide was derived by relating the intensity of absorption at either of the two frequencies quoted in Table 1 to concentration (P_e). However, since this hydroperoxide alone did not obey the correlation between K_1 and k_2, the significance of the *two* bands at 3535 and 3510 cm.$^{-1}$ was further examined. Repeated purification of the sample, or the use of samples from other sources, did not alter the ratio of the intensities of the two bands, which also remained constant over a wide range of concentration and in the presence of sulphoxide. Significantly, in benzene solution the hydroperoxide exhibited only one band at 3500 cm.$^{-1}$. Other hydroperoxides in benzene gave a shift in the OH band position from that observed in carbon tetrachloride–*cyclo*hex-2-enyl hydroperoxide from 3540 to 3494 cm.$^{-1}$ and *tert.*-butyl hydroperoxide from 3543 to 3496 cm.$^{-1}$.

These observations suggest that in dilute solution in carbon tetrachloride an equilibrium exists between two forms of α-cumyl hydroperoxide. One form is completely unassociated and gives rise to the absorption at 3535 cm.$^{-1}$. The other, in which an intramolecular interaction between the OH group and the benzene ring occurs, is responsible for the absorption at 3510 cm.$^{-1}$. Support for this interpretation was obtained by examining the following closely related compounds (0·02M solutions in CCl_4). Phenethyl alcohol has a doublet at 3627 and 3608 cm.$^{-1}$, whereas 2-*cyclo*hexylethyl alcohol has only one band at 3630 cm.$^{-1}$. αα-Dimethylbenzyl alcohol has one slightly asymmetric band at 3618 cm.$^{-1}$, but 2-benzylpropan-2-ol has a doublet at 3615 and 3600 cm.$^{-1}$. These results indicate that (1) the presence of a benzene nucleus is necessary for the splitting of the OH band, and (2) the relative position of the OH group and the benzene nucleus is critical. Models of 2-benzylpropan-2-ol, 2-phenylethyl alcohol, and α-cumyl hydroperoxide indicate that, unlike αα-dimethylbenzyl alcohol, these can attain a configuration in which the OH group and the benzene nucleus are very close.



Determination of K_1.
A, phenol.
B, thymol.
C, 1-tetralyl hydroperoxide.
D, cyclo*hex-2-enyl hydroperoxide.*
E, cyclo*hexyl hydroperoxide.*
F, tert.*-butyl hydroperoxide.*
G, α-cumyl hydroperoxide (uncorrected).
H, tert.*-butyl alcohol.*

Experimental points relating to A, B, and C only are shown but the remainder show the same form of curvature.

Although such interaction between an OH group and an aromatic ring is well recognised, little is known about its precise nature. Fox and Martin [12] and Tuomikoski [13] discussed the splitting of the OH band in benzyl alcohol with reference to this type of interaction and Buswell, Rodebush, and Whitney [14] interpreted the spectra of some phenyl-substituted vinyl alcohols on this basis. Mecke [15] observed a splitting of the second overtone of the νOH band in phenol when examined in dilute solution in benzene. He attributed this to

[12] Fox and Martin, *Trans. Faraday Soc.*, 1940, **36**, 897.
[13] Tuomikoski, *Suomen Kem.*, 1950, **23**, *B*, 44.
[14] Buswell, Rodebush, and Whitney, *J. Amer. Chem. Soc.*, 1947, **69**, 770.
[15] Mecke, *Discuss. Faraday Soc.*, 1950, **9**, 161.

the fact that the solvent molecule may have its molecular plane either perpendicular or parallel to the OH bond.

If, in the bonding equilibrium of α-cumyl hydroperoxide with *cyclo*hexyl methyl sulphoxide, the hydroperoxide in its normal configuration, R·O·OH, is also in equilibrium with the intramolecular bonded form $[\text{R·O·OH}]_A$:

$$\text{R·O·OH} \rightleftharpoons [\text{R·O·OH}]_A \text{; equilibrium constant, } K_4$$

then equation (2) becomes $(1 + K_4)P_m^{-1} = (P_0 - P_m)^{-1}K_1S_0 - K_1$, where P_m is the value of the hydroperoxide concentration derived from the linear relation between concentration and the optical density at either band maximum. If it is assumed that the true molecular extinction coefficient ($\varepsilon_{st.}$) of the unassociated OH band at 3535 cm.$^{-1}$ is 87 (see below) then K_4 may be evaluated from the expression $(\varepsilon_{st.}/\varepsilon_{app.}) - 1$ as 1·175. Plotting $(1 + K_4)P_m^{-1}$ against $(P_0 - P_m)^{-1}$, K_1 for α-cumyl hydroperoxide now becomes 41, a value which places it, in terms of acid strength, between *cyclo*hex-2-enyl and *cyclo*hexyl hydroperoxides in agreement with the kinetically determined order.

In assuming the value 87 above for the molecular extinction coefficient of the unassociated OH band at 3535 cm.$^{-1}$, 1-tetralyl hydroperoxide was ignored because of the slightly asymmetric nature of its OH band. This suggests the occurrence of an intramolecular association similar to that proposed for α-cumyl hydroperoxide and examination of the structure confirms that such a possibility exists. However, in view of the very small shift, which is insufficient to enable the bands to be resolved, K_4 must be negligibly small and hence the true value of K_1 for 1-tetralyl hydroperoxide will approximate very closely to that given in Table 1.

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