complex is twice as stable, and assuming ease of displacement is inversely related to complex stability, the differential rate factor for vanadium–peroxide complex formation is 0.66. A third possibility, that peroxide having displaced amine from a vanadyl complex then proceeds to oxidize *that* amine, thus seems untenable in view of the substantial observed ρ factor.

The above considerations would be less conjectural were it not that the active species in vanadium-catalyzed oxidations by hydroperoxides had been postulated[4] to be not vanadyl but V^V. A more nearly definitive exposition may be expected from further work, now in progress, on vanadium-catalyzed epoxidations, in the presence and absence of amines.

Experimental Section

Materials.—*tert*-Butyl hydroperoxide (Lucidol) was generally used as received, as a 90% aqueous solution; for some of the kinetic experiments, samples were purified to greater than 99.5% peroxide by vacuum distillation, though this made little appreciable difference to the kinetics. All other chemicals were ACS grade and were used as received without further purification.

Analyses.—Initial hydroperoxide concentrations were determined by refluxing an aliquot for 5 min with potassium iodide in isopropyl alcohol–glacial acetic acid (2:1, v/v), followed by thiosulfate titration of the released iodine.

Aniline, substituted anilines, and nitrobenzene were determined by vpc analysis using an F & M Model 700 gas chromatograph equipped with a Model 227 Disc integrator. The column was 6 ft × 0.25 in. 20% SE-54 on 45–60 mesh Chromosorb P, at temperatures from 120–150°. Chlorobenzene was used as an internal standard in each case.

The toluidines were determined by the pmr adsorption of the methyl protons (τ 8.58 for *m*-Me, τ 8.45 for *p*-Me) using cyclohexane as an internal standard. All pmr spectra were run on a Varian A-60 nmr spectrometer.

Kinetic Experiments on Aniline.—Typically, a solution of aniline (2.18 mmol) and *tert*-butyl hydroperoxide (7.84 mmol) in benzene (1.11 ml) and chlorobenzene (0.20 ml) was allowed to equilibriate at reaction temperature; the reaction was initiated by adding 1.00 ml of a freshly prepared solution of vanadium oxyacetylacetonate (2.22 mg) in benzene at the same temperature. Samples were withdrawn at intervals and immediately injected into the gas chromatograph using sample sizes of the order of 10 μl. Exact volume control was unnecessary, because of the use of chlorobenzene as an internal standard.

Kinetic Experiments on Substituted Anilines.—These experiments were carried out as above, the aniline solution containing in addition 2 mmol of the substituted aniline. Determination of the exact initial conditions was, of course, unnecessary.

Registry No.—Aniline, 62-53-3; aniline *p*-Me, 106-49-0; aniline *m*-Me, 108-44-1; aniline *p*-Cl, 106-47-8; aniline *p*-Br, 106-40-1; aniline *m*-Cl, 108-42-9; aniline *m*-Br, 591-19-5; *tert*-butyl hydroperoxide, 75-91-2.

Acidities of Tertiary Alkyl Hydroperoxides

WILLIAM H. RICHARDSON* AND VERNON F. HODGE

Department of Chemistry, San Diego State College, San Diego, California 92115

The pK_a values of several tertiary hydroperoxides were determined in 40% aqueous methanol. The hydroperoxides were chosen to give a maximum span of σ^* values and to be unreactive under the conditions of the measurements. Most of the pK_a values of tertiary hydroperoxides were correlated by the Ingold–Taft equation to give $\rho^* = 0.51 \pm 0.07$ and thus $pK_a = (-0.51 \pm 0.07)\sigma^* + 13.13 \pm 0.02$ with satisfactory correlation ($r = 0.954$). Only a fair correlation ($r = 0.909$) was obtained from a plot of pK_a *vs.* chemical shift of the hydrogen bonded hydroperoxy proton in dimethyl sulfoxide solvent. The utility of these plots is discussed as well as the transmission effect through oxygen in hydroperoxides compared to carbon in alcohols of appropriate structure.

In the course of our study of the basic decomposition of tertiary halo hydroperoxides,[1] it was necessary to estimate the pK_a values of these hydroperoxides. Direct measurement was not possible because of their reactivity in base. Since pK_a values are necessary to interpret kinetic data of various ionic hydroperoxide reactions, we felt that it was desirable to have a convenient method for predicting pK_a values rather than resorting to actual measurements. In many instances, the predicted values need not be highly accurate, but rather approximate values may suffice. Among oxygen containing organic acids, pK_a values of carboxylic acids[2] and alcohols[3] have been correlated by substituent linear free energy relationships. Prediction of pK_a

values for these acids, which bracket the acidity of hydroperoxides, is then possible. Yet, to our knowledge, a substituent linear free energy relationship has not been reported for hydroperoxides. Some effort has been directed to a search for a correlation between pK_a of hydroperoxides and hydrogen bonded OO–H stretching frequencies.[4,5] The utility of the correlation is hampered by intra- and intermolecular hydrogen bonding of the hydroperoxides. Furthermore, the pK_a values of only two hydroperoxides are included in the correlation, one of which is subject to intramolecular hydrogen bonding.[4]

Our initial objective was to determine if a correlation existed between hydroperoxide pK_a values and the Taft σ^* substituent constants.[2c] We have attempted to make such a correlation with the existing pK_a values of primary, secondary, and tertiary hydroperoxides;[6,7] however, an unusually large positive ρ^* value resulted and cumene hydroperoxide[7] deviated

* To whom correspondence should be addressed.
(1) (a) W. H. Richardson, J. W. Peters, and W. P. Konopka, *Tetrahedron Lett.*, 5531 (1966); (b) W. H. Richardson, Abstracts of the International Symposium, Chemie der Organischen Peroxide, Berlin-Aldershof, Sept 13–15, 1967; (c) W. H. Richardson and V. F. Hodge, *Tetrahedron Lett.*, in press.
(2) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940, Chapter 7; (b) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); (c) R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.
(3) (a) P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, **82**, 795 (1960); (b) R. W. Taft, *ibid.*, **74**, 4231 (1953); (c) see also, J. R. Robinson and L. E. Matheson, *J. Org. Chem.*, **34**, 3630 (1969).

(4) D. Barnard, K. R. Hargrave, and G. M. C. Higgins, *J. Chem. Soc.*, 2845 (1956).
(5) A. Blaschette and B. Bressel, *Inorg. Nucl. Chem. Lett.*, **4**, 175 (1968).
(6) A. J. Everett and G. J. Minkoff, *Trans. Faraday Soc.*, **49**, 410 (1953).
(7) I. M. Kolthoff and A. I. Medalia, *J. Amer. Chem. Soc.*, **71**, 3789 (1949).

TABLE I

pK_a, pK_h, AND pK_{auto} VALUES FOR TERTIARY HYDROPEROXIDES AND HYDROGEN PEROXIDE IN 40% AQUEOUS
METHANOL AT 25°[a]

| Hydroperoxide	Registry no.	$pK_a{}^b$	$pK_h{}^b$	$pK_{auto}{}^{b,c}$	n^d
HOOH	7722-84-1	12.02 ± 0.01	1.98 ± 0.05	14.00 ± 0.05	9
$(CH_3)_3COOH$	75-91-2	13.27 ± 0.02	0.76 ± 0.04	14.03 ± 0.04	4
$C_6H_5CH_2C(CH_3)_2OOH$	1944-83-8	13.25 ± 0.01	0.76 ± 0.02	14.01 ± 0.02	2
$C_6H_5C(CH_3)_2OOH$	80-15-9	13.08 ± 0.04	0.95 ± 0.04	14.03 ± 0.04	8
$(CH_3)_2C(CH_2Cl)OOH$	14093-73-3	13.2[e]			
$(C_6H_5)_2C(C_2H_5)OOH$	26154-06-3	13.02 ± 0.02	0.99 ± 0.02	14.01 ± 0.02	2
$(C_6H_5)_2C(CH_3)OOH$	2186-29-0	12.94 ± 0.02	1.06 ± 0.02	14.00 ± 0.02	6
$(C_6H_5)_3COOH$	4198-93-0	13.07 ± 0.03	1.00 ± 0.05	14.07 ± 0.05	7

[a] Ionic strength, $\mu = 0.600$. [b] With mean deviation. [c] Calculated from $pK_{auto} = pK_a + pK_h$. [d] Number of determination. [e] $\mu = 1.58$, ref 1b.

considerably from the plot. In the hope of resolving this problem, we selected to determine the pK_a values of a series of tertiary hydroperoxides which would provide a maximum change in σ^*. Tertiary hydroperoxides were selected, since primary and secondary hydroperoxides are reported[8] to undergo decomposition in base to carbonyl compounds. Erroneous pK_a values might then result because of the strongly basic medium that is required for the measurements.

Results and Discussion

Direct pK_a Measurements.—To ensure homogeneity and to generate data comparable to our kinetic data,[1b] 40% aqueous methanol was used as the solvent. To obtain a maximum spread in σ^* values of *unreactive* tertiary hydroperoxides, a series of progressively phenylated hydroperoxides was uniquely suited for the study. The K_a values, defined by eq 1, were obtained from the slope of eq 2.[9] The absorbency of the

$$ROOH \rightleftharpoons ROO^- + H^+, K_a \qquad (1)$$
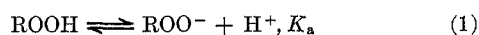
$$A^{eq} = A^- - \frac{[H^+](A^{eq} - A^0)}{K_a} \qquad (2)$$

equilibrium mixture is given by A^{eq}, the absorbency of the hydroperoxide anion is defined as A^- and A^0 is the absorbency of the neutral molecule. The hydrolysis constants (K_h) were calculated from the intercept of eq 4,[10] where $[OH^-]$ is the stoichiometric hydroxide

$$ROO^- + H_2O \rightleftharpoons ROOH + OH^-, K_h \qquad (3)$$
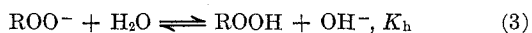
$$\frac{1}{[OH^-]} = \frac{(A^- - A^0)}{K_h(A^{eq} - A^0)} - \frac{1}{K_h} \qquad (4)$$

ion concentration. From the pK_a and pK_h values, the pK_{auto} for autoprotolysis of the solvent may be calculated from $pK_{auto} = pK_a + pK_h$. Since the pK_a is dependent on pK_{auto}, changes in this constant from water are necessary to note. The pK_a, pK_h, and pK_{auto} values obtained in this study for hydroperoxides and hydrogen peroxide are given in Table I. The pK_a of chloro-*tert*-butyl hydroperoxide, which was obtained in an independent study by kinetic methods,[1b] is included for comparison. The autoprotolysis con-

stant of 40% aqueous methanol is indeed constant and essentially the same as that of water. The reported values of pK_{auto} for water and methanol at 25° are 14.0 and 16.7, respectively.[11] A basic solution of one of the hydroperoxides (1,1-diphenylethyl) was neutralized after the pK_a measurement. The resulting ultraviolet spectrum was identical with that of the authentic hydroperoxide, which indicates that no decomposition occurred during the course of measurement. Previously, pK_a values for several hydroperoxides in water were determined by a method similar to that employed here.[6] The pK_a of cumene hydroperoxide was determined by distribution between aqueous base and benzene.[7] These values are given in Table II.

TABLE II

pK_a VALUES OF HYDROPEROXIDES IN WATER

Hydroperoxide	pK_a	Ref
HOOH	11.65[a]	b
	11.6[c]	6
	11.37[c]	d
CH_3OOH	11.5[a]	6
	11.08[c]	d
C_2H_5OOH	11.8[a]	6
$i\text{-}C_3H_7OOH$	12.1[a]	6
$(CH_3)_3COOH$	12.8[a]	6
	12.46[a]	d
$CH_3(C_2H_5)(i\text{-}C_4H_9)COOH$	12.8[a]	6
$C_6H_5C(CH_3)_2OOH$	12.6[c]	7

[a] At 25°. [b] M. G. Evans and N. Uri, *Trans. Faraday Soc.*, **45**, 224 (1949). [c] At 20°. [d] J. E. McIsaac, Jr., H. A. Mulhausen, and E. J. Behrman, Abstracts of the 156th National Meeting of the American Chemical Society, Sept 1968, p ORGN 70.

An Ingold–Taft plot is given in Figure 1 from the data of Table I, Everett and Minkoff,[6] and Kolthoff and Medalia.[7] The σ^* constants are tabulated values[12a] or, if these are not available, they are calculated.[12b] The pK_a values from Table I give a satisfactory[2b,13] correlation $(r = 0.954)$, with the exclusion of chloro-*tert*-butyl and trityl hydroperoxide. The ρ^* value is 0.51 ± 0.07 and the correlation equation is $pK_a = -(0.51 \pm 0.07)\sigma^* + 13.13 \pm 0.02$. Only a satisfactory correlation is obtained because the variation in pK_a values with substituent changes is small as seen from the ρ^* value of 0.51 compared to a corresponding value of 1.42[3a] for alcohols (RCH_2OH).

(8) (a) S. S. Medewedew and E. N. Alexejewa, *Ber.*, **65**, 133 (1932); (b) For similar reactions with dialkyl peroxides, see N. Kornblum and H. E. De La Mare, *J. Amer. Chem. Soc.*, **73**, 880 (1951); R. P. Bell and A. O. McDougall, *J. Chem. Soc.*, 1697 (1958); W. H. Richardson and R. S. Smith, *J. Amer. Chem. Soc.*, **91**, 3610 (1969).

(9) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Wiley, New York, N. Y., 1962, p 85.

(10) (a) E. W. Westhead, Jr., and H. Morawetz, *J. Amer. Chem. Soc.*, **80**, 237 (1958); (b) C. G. Overberger, T. St. Pierre, and S. Yaroslavsky, *ibid.*, **87**, 4310 (1965).

(11) R. G. Bates, "Determination of pH, Theory and Practice," Wiley, New York, N. Y., 1964, p 183.

(12) (a) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 222; (b) p 224.

(13) P. R. Wells, "Linear Free Energy Relationships," Academic Press, New York, N. Y., 1968, p 3.
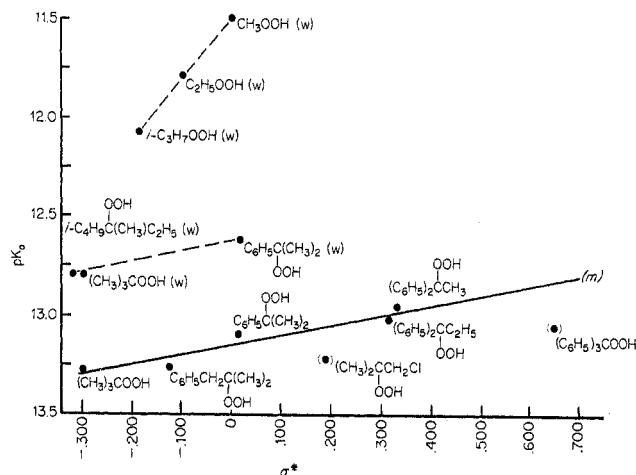
Figure 1.—An Ingold-Taft correlation of the pK_a values of hydroperoxides in water (w) and 40% aqueous methanol (m).

Prediction of absolute pK_a values of tertiary hydroperoxides from the correlation equation is quite good. With σ^* values of 0 and 1.0, pK_a values are calculated to within ±0.02 and ±0.09 unit (probable error), respectively. This is within the range of error for actual measurements between various workers. Chloro-*tert*-butyl and trityl hydroperoxide each deviate from the least squares line by about 0.2 of a pK_a unit, which is not particularly large in absolute terms. Deviation by this amount for the former hydroperoxide is not surprising, considering that the pK_a is obtained by an indirect kinetic method and that the ionic strength differs. A possible explanation for the deviation of trityl hydroperoxide is that it may be due to steric inhibition of solvation by the bulky substituent group.

Although the correlation line for tertiary hydroperoxides in water is tenuous, there is some support for the legitimacy of the ρ^* value (0.59 ± 0.06, $r = 0.991$), since it approximately parallels the correlation line for tertiary hydroperoxides in 40% aqueous methanol. The approximately constant difference between the two lines is reasonably due to a solvent effect. Hydrogen peroxide shows a similar change in pK_a upon changing the solvent from water to 40% aqueous methanol. The trend to higher pK_a values for acids in aqueous alcoholic solvents compared to water is well known.[14] It is evident from Figure 1 that the primary and secondary hydroperoxides are not correlated with the tertiary hydroperoxides. Although a correlation line may be placed through the primary–secondary hydroperoxides, the correlation ($r = 0.999$) may be fortuitous since an unusually large ρ^* value of 3.16 ± 0.10 results. We have attempted to measure the pK_a of a secondary hydroperoxide (benzhydryl hydroperoxide), which would increase the spread of σ^* values in this series. Unfortunately, benzhydryl hydroperoxide undergoes rapid decomposition under the strongly basic conditions of the measurement, presumably to benzophenone, and a pK_a value could not be obtained.

Spectral Correlations with pK_a.—A correlation between pK_a and a spectral property of hydroperoxides would be attractive as an aid to predicting pK_a valued where σ^* values are unknown or not easily calculated.

(14) References 9, p 66; ref 11, p 222.

Also the possibility exists for a more accurate prediction of the pK_a by a spectral correlation. Ease of obtaining the spectral data is of importance and for this reason nmr chemical shift data are an attractive possibility. A linear free energy relationship has been established between σ^- and the chemical shift, which results from hydrogen bonding with dimethyl sulfoxide (DMSO) solvent, in a series of substituted phenols.[15] The chemical shift data for tertiary hydroperoxides in DMSO are given in Table III. No change in the chem-

TABLE III

CHEMICAL SHIFTS OF TERTIARY HYDROPEROXIDES IN DMSO

Hydroperoxide	δ (ppm)^a
$(CH_3)_3COOH$	10.72
$C_6H_5CH_2C(CH_3)_2OOH$	10.76
$C_6H_5C(CH_3)_2OOH$	11.02
$(CH_3)_2C(CH_2Cl)OOH$	10.96
$(C_6H_5)_2C(C_2H_5)OOH$	10.89
$(C_6H_5)_2C(CH_3)OOH$	11.34
$(C_6H_5)_3COOH$	11.34

^{a} Relative to TMS internal standard.

ical shift was observed when the hydroperoxide concentration was varied from 2.5 to 10% (wt/vol.). Unfortunately, a least squares fit of all of the data in Table III with corresponding pK_a values is very poor ($r = 0.754$). However, if 1,1-diphenyl-1-propyl hydroperoxide is excluded, the correlation is fair[2b,13] ($r = 0.909$) and the correlation equation is $pK_a = (-0.43 \pm 0.07)\delta$ (ppm) $+ 17.88 \pm 0.81$. The low correlation coefficient is due, at least in part, to the small spread in both δ and pK_a. Considering the error in this correlation, the use of the σ^* correlation is preferred, except possibly in those instances where a qualitative prediction of pK_a is required and the σ^* values are unattainable.

Linear relationships between pK_a and hydrogen bonded OO–H stretching frequencies are proposed.[4,5] The original basis for this correlation rests on a plot of pK_a vs. $\log K$, where K is the equilibrium constant for hydrogen bonding to cyclohexyl methyl sulfoxide. Three hydrogen donors were used for the plot: *tert*-butyl hydroperoxide, thymol, and phenol.[4] Subsequently, a two-point correlation was formulated with data from phenol and *tert*-butyl hydroperoxide.[16] Considering the ease of measurement (concentration variation studies must be made), the problems in separating intra- and intermolecular hydrogen bonding,[4] and the error[16] in the infrared spectral correlation, it does not appear to be an attractive method for predicting pK_a values of hydroperoxides. Providing that σ^* values are tabulated or can be calculated, the prediction of pK_a values from the pK_a vs. σ^* is not only easier but it offers the best values at present.

Transmission Effects.—A comparison of the effect of substituents (R) on the pK_a of hydroperoxides (ROOH) and alcohols (RCH$_2$OH) will provide a measure of the ability of R to relay polar effects through oxygen vs. carbon (CH$_2$) to the reaction site. The transmission

(15) R. J. Quellette, *Can. J. Chem.*, **43**, 707 (1965).

(16) A least squares treatment of the data used in the three-point correlation[4] gave $pK_a = (-3.06 \pm 0.77) \log K + 17.3 \pm 1.6$, with probable error. The reported[4] equation is $pK_a = -3.89 \log K + 19.2$. The two-point equation is reported as[5] $pK_a = -3.07 \log K + 17.1$.

factor for carbon has received considerable attention,[17] but such is not the case for oxygen.[17,18]

The relative transmission factor $(\phi)^{17h}$ is given by $\phi_{O,C} = \rho^*_O/\rho^*_C$, which is approximately[19] equal to 0.36 (= 0.51/1.42) for tertiary hydroperoxides (ROOH) compared to alcohols (RCH$_2$OH).[3a] A possible reason for the poorer relay of polar effects through oxygen compared to carbon can be seen by considering the field effect model for transmission of polar effects.[20] The Kirkwood–Westheimer equation (5) may be used to

$$\log K_a/K'_a = \frac{e\mu\cos\theta}{2.303\ kTD_e r^2} \quad (5)$$

calculate the direct field effect of a substituent group on the ionization constant, where K_a and K'_a are the ionization constants with a given substituent and the reference substituent, e is the electronic charge, μ is the dipole moment of the substituent, θ is the angle between the dipole axis and a line joining the center of the dipole to the reaction center, r is the length of the latter line, D_e is the effective dielectric constant, k is the Boltzmann constant, and T is the absolute temperature.[21] The terms in eq 5 that determine the transmission of substituent effects are $\cos\theta/r^2D_e$.[17] The relative transmission factor ϕ is then given by eq 6.[17]

$$\phi_{O,C} = \rho^*_O/\rho^*_C = \frac{D_{eC}r_C^2\cos\theta_O}{D_{eO}r_O^2\cos\theta_C} \quad (6)$$

Typically molecules are considered to be cavities of low dielectric constant and the bulk dielectric constant of saturated hydrocarbons ($D = 2.0$) is used as the first approximation for the effective dielectric constant. Thus, the effective dielectric constant for the alcohols (RCH$_2$OH), with a methylene group interdisposed between the reaction site and the substituent (R), may be given by $D_{eC} = 2.0$. The value of D_{eO} is now calculated from eq 6 to be 5.2 with $D_{eC} = 2.0$, $r_C = 1.84$ Å, $r_O = 1.81$ Å, $\theta_O = 52.4°$, $\theta_C = 47.3°$, and $\phi_{O,C} = 0.36$ (see above).[22] Thus, according to the field effect model, the poorer response of pK_a values to substituents in hydroperoxides compared to alcohols (RCH$_2$OH) is due to an increase in the effective dielectric constant which results from replacing the CH$_2$ unit with an oxygen atom.

Experimental Section[23]

Materials.—Hydrogen peroxide of 30% (Matheson, Coleman and Bell) and 98% (FMC) strength were used as received.

(17) (a) C. K. Ingold, *Chem. Rev.*, **15**, 225 (1934); (b) H. H. Jaffé, *ibid.*, **53**, 191 (1953); (c) O. Exner and J. Jonáš, *Collect. Czech. Chem. Commun.*, **27**, 2296 (1962); (d) J. C. McGowan, *J. Appl. Chem.*, **10**, 312 (1960); (e) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963); (f) K. Bowden, *Can. J. Chem.*, **41**, 2781 (1963); (g) S. H. Marcus, W. F. Reynolds, and S. I. Miller, *J. Org. Chem.*, **31**, 1872 (1966); (h) K. Bowden, *Can. J. Chem.*, **43**, 3354 (1965); (i) K. Bowden, *ibid.*, **44**, 661 (1966); (j) K. Bowden and D. C. Parkin, *ibid.*, **47**, 177 (1969).

(18) K. Bowden and D. C. Parkin, *ibid.*, **44**, 1493 (1966).

(19) Precisely, $\phi_{O,C}$ should be calculated from data in the same solvent; however, the ρ^* values are not expected to change greatly between 40% aqueous methanol and water. For alcohols, $\rho^* = 1.42$ in water[3a] and 1.36 in 2-propanol.[2c] Our data suggest that there is only a small change in ρ^* for tertiary hydroperoxides in 40% aqueous methanol and water.

(20) For a review of field effects compared to inductive effects, see S. Ehrenson, "Progress in Physical Organic Chemistry," Vol. 2, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience, New York, N. Y., 1964, p 195.

(21) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938).

(22) Bond distances and angles required for the calculation are obtained from "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1958, Special Publication No. 11.

Ninety per cent *tert*-butyl hydroperoxide (Lucidol Division, Wallace and Tiernan, Inc.) was purified by azeotropic distillation.[24] The purified hydroperoxide was shown to be 99% pure by iodometric titration.[25] Cumyl hydroperoxide[25] (Matheson, Coleman and Bell), 82.5% pure by iodometric titration,[25] was purified by the sodium salt method.[26] After two purification cycles through the salt, cumyl hydroperoxide was obtained as a clear colorless oil, 99.5% pure by iodometric titration,[25] n^{20}D 1.5245 (lit.[26] 1.5242). The 40% aqueous methanol solvent was prepared by volume at 25° from 40 parts methanol (Baker, reagent) and 60 parts doubly distilled water.

1,1-Diphenylethyl Hydroperoxide.—To 10 ml (0.18 mol) of 50% hydrogen peroxide (Fisher Scientific Co.), 1 ml of concentrated sulfuric acid was added dropwise with stirring at room temperature. This was followed by the addition of 10 ml of acetic acid and then 1.0 g (5.0 × 10^{-3} mol) of methylbenzhydrol (Eastman Organic Chemicals) in 10 ml of chloroform. The reaction flask was immersed into a 45° water bath and the bath temperature was increased to 55° over a 15-min period. The reaction mixture was then poured onto 50 ml of water. The chloroform phase was separated, washed with water and saturated sodium bicarbonate solution, and dried. Evaporation of the solvent gave an oily solid which was repeatedly recrystallized from chloroform–pentane solvent to give a 62.5% yield of 1,1-diphenylethyl hydroperoxide, mp 83–84° (lit.[27] 86°). The structure was confirmed by the nmr spectrum in dimethyl sulfoxide (Matheson, Coleman and Bell, Spectroquality): 11.34 (OOH, singlet, area = 1.0), 2.0 (CH$_3$, singlet, area = 3.2), and 7.36 ppm (aromatic protons, single absorption, area = 10.3). The hydroperoxide was 100% pure by iodometric titration.[25]

1,1-Diphenyl-1-propyl hydroperoxide.—This hydroperoxide was prepared from diphenylethylcarbinol[28] by the above method in 86% yield (98.4% pure).[25] Recrystallization from chloroform-pentane gave white crystals (100% pure),[25] mp 79.0–79.5° (lit.[28] 79.0–79.5°). The nmr spectrum in carbon tetrachloride showed the following absorptions: 6.82 (OOH, singlet, area = 1.00), 7.22 (aromatic, singlet, area = 10.3), 2.40 (CH$_2$, quartet, area = 1.93), and 0.88 ppm, (CH$_3$, triplet, area = 3.06).

1-Phenyl-2-methyl-2-propyl Hydroperoxide.—The hydroperoxide was prepared by addition of α,α-dimethylphenethyl alcohol (Eastman Organic Chemicals) to 98% hydrogen peroxide, which was prepared acidified with sulfuric acid. The general method was previously reported,[29] *but the order of addition is critical to avoid explosions*[30] The hydroperoxide was obtained in 76% yield, mp 43.9–44.9°. Recrystallization from *n*-pentane gave white crystals, mp 44.2–45.2° (lit.[29a] 44.0–44.6°), which were 99.9% pure.[25] The nmr spectra were in agreement with the structure. All of the absorptions were singlets and the δ values and areas in carbon tetrachloride and perdeuterio-DMSO, respectively, are 7.78 (OOH, 1.00), 10.76 (OOH, 1.00), 7.18 (aromatic, 4.95), 7.14 (aromatic, 5.18), 2.87 (CH$_2$, 2.00), 2.76 (CH$_2$, 2.15), 1.19 (CH$_3$, 6.00), 1.04 ppm (CH$_3$, 6.05).

Trityl Hydroperoxide.—This hydroperoxide was prepared by the method of Bissing, Matsuzak, and McEwen[31] in 55% yield. Recrystallization from ether-pentane and then from chloroform-pentane gave white crystals, mp 87.5–88.5° (lit.[31] 84–86°). The nmr spectrum was measured in dimethyl sulfoxide: 11.34 (OOH, singlet, area = 1.0) and 7.36 ppm (aromatic protons, single absorption, area = 15.0). The hydroperoxide was 99.4% pure by iodometric titration.[25]

pK_a and pK_h Determinations.—The pH measurements were obtained with a Beckman Research pH meter using a Corning glass electrode and a Thomas calomel reference electrode. The pH meter was standardized with a freshly prepared aqueous saturated calcium hydroxide solution, pH 12.45 at 25°. The

(23) All melting points are corrected and were determined with a Hoover–Thomas capillary melting point apparatus. Nuclear magnetic resonance spectra were obtained with a Varian Model A-60 spectrometer. Chemical shifts are expressed in parts per million (ppm) relative to internal tetramethylsilane as 0 ppm (δ scale).

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temperature for the pH readings was maintained at 25.0 ± 0.2° by the use of water-jacketed beakers. The basic solutions were protected from atmospheric carbon dioxide with an Ascarite tube. To ensure good pH response by the glass electrode, the immersion time of the electrodes in the solutions was kept to a minimum and the electrodes were allowed to stand in distilled water before each measurement.[32] Sodium ion corrections, when needed, were taken from the nomograph for aqueous solutions which was supplied with the electrode. The actual pH values were measured at the same time as the spectral measurements were recorded.

All absorbencies were measured with a Beckman DU Model 2400 spectrophotometer using the hydrogen lamp. The cell compartment temperature was maintained at 25.0 ± 0.2°. The pK_a measurements were made at several different wavelengths, which covered a range of 240–296 mμ. The value of A^0 was obtained in pure solvent and A^{eq} was determined in a series of solutions with accurately known sodium hydroxide concentrations and pH values that spanned both sides of the pK_a value. All solutions were maintained at constant ionic strength of 0.600

by adding the appropriate volume of a stock potassium chloride solution. All of the tertiary hydroperoxides were stable under the basic conditions, with the exception of 1,1-diphenylethyl and trityl hydroperoxide. For the latter hydroperoxides, A^{eq} slowly increased with time if the pH of the solution was near the pK_a. In neutral or strongly basic solutions (pH *ca.* 13.7), the absorbencies were constant. Hydrogen peroxide was stable in neutral solutions, but displayed a marked decrease in A^{eq} with time as the pH increased. Therefore, the sample of hydroperoxide or hydrogen peroxide was added just prior to absorbance and pH measurements. In the event that A^{eq} did change with time, it was graphically extrapolated back to the time of mixing. Since no isosbestic points were observed, constancy of pK_a with wavelength was taken as evidence for the absence of absorbing impurities.

(32) Reference 11, p 324.

Reactions between Aliphatic Dihalides and Amines. I. Kinetic Study of the Reaction between 2-Phenyl-2-cyclohexyl-4,5-dibromovaleronitrile and Diethylamine

E. DE HOFFMANN,* J. P. SCHMIT, AND J. J. CHARETTE

Departments of Industrial Chemistry and Molecular Physics, Lovanium University of Kinshasa, Kinshasa, Democratic Republic of the Congo
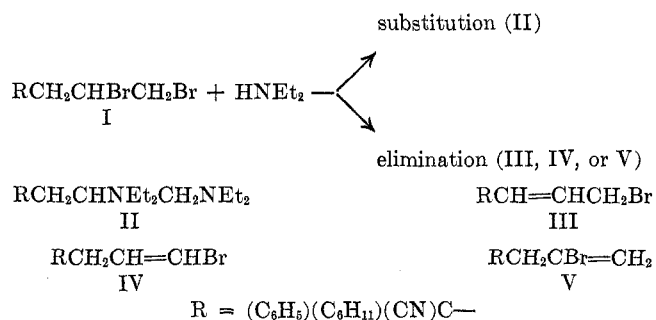
The kinetics of the action of diethylamine with 2-phenyl-2-cyclohexyl-4,5-dibromovaleronitrile in butyl alcohol as a solvent has been studied by use of conventional methods. This reaction gives two products whose structures are shown to be those of 1-bromo-4-cyclohexyl-4-phenyl-1-pentenenitrile (elimination) and ~2-cyclohexyl-2-phenyl-4,5-bis(diethylamino)valeronitrile (substitution). The ratio of the concentrations of elimination to substitution products is independent of the temperature, the time, and the initial concentrations of reactants. Hence, both reactions have the same rate-determining step with a rate equation (A). The mechanisms of these reactions are discussed.

$$V = e\frac{k}{h}Te^{-29.4/R}e^{-18.4\times10^3/RT}[\text{dibr}]\,[\text{amine}] \qquad (A)$$

The action of secondary amines on aliphatic dihalides may theoretically give competitive elimination and substitution reactions. Up to now, these reactions have received very little attention. In one instance, Attenburrow[1] has indeed treated the 2,2-diphenyl-4,5-dibromovaleronitrile with morpholine. He has mentioned only one diaminated substitution product with a yield of 70% and one elimination product of unknown structure.

In this work, we have investigated the action of diethylamine on 2-phenyl-2-cyclohexyl-4,5-dibromovaleronitrile (I). This reaction has a practical as well as

substitution (II)

RCH₂CHBrCH₂Br + HNEt₂ —<

I

elimination (III, IV, or V)

RCH₂CHNEt₂CH₂NEt₂   RCH=CHCH₂Br
II   III

RCH₂CH=CHBr   RCH₂CBr=CH₂
IV   V

R = (C₆H₅)(C₆H₁₁)(CN)C—

theoretical interest. By decyanation the aminated product gives the 1-phenyl-1-cyclohexyl-3,4-bis(diethyl-

amino)butane which is an antispasmodic drug. Hence, it may be inferred that the diaminated substitution product has the structure II.

We have determined the structure of the elimination product as well as the kinetic parameters of both reactions, in order to be able to propose a mechanism.

Experimental Section

A. Apparatus and Procedures.—Infrared spectra were recorded with Perkin-Elmer 137 and 237 spectrophotometers. The exact position of the bands was measured on the single-beam Perkin-Elmer 112G spectrophotometer. A grating with 75 grooves/mm and a blaze at 12 was used for the region 4000–600 cm⁻¹ and a grating with 47 grooves/mm and a blaze at 20 for the region 600–400 cm⁻¹. Nujol and hexachlorobutadiene mulls were used for the crystalline products.

Nuclear magnetic resonance spectra were obtained using a JEOL nmr measuring instrument, at 60 Mc at a temperature of 20°, with tetramethylsilane as reference. The range of frequencies was 0 (TMS) to 510 cps.

The hydrobromic acid concentrations were determined by Volhard procedure on 1-ml samples diluted in 8 ml of 3 *N* nitric acid.

B. Materials.—2-Phenyl-2-cyclohexyl-4,5-dibromovaleronitrile (I) was obtained by bromination of the ethylenic product in CHCl₃, according to the method described by Attenburrow, *et al.*,[1] for the corresponding 2,2-diphenyl derivative, and was purified by recrystallization from petroleum ether to a white crystalline powder, mp 73–75°.

α-Cyclohexylphenylacetonitrile was obtained by condensing benzylcyanide in boiling benzene with cyclohexyl bromide in the

* To whom correspondence should be addressed.

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