Metal-Catalyzed Hydroperoxide Reactions. I.
Substituent Effects in the Oxidation of Aniline[1]

G. R. HOWE* AND R. R. HIATT

Department of Chemistry, Brock University, St. Catharines, Ontario

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Aniline is readily oxidized by *tert*-butyl hydroperoxide in the presence of catalytic quantities of certain molybdenum and vanadium compounds, the only detected product being nitrobenzene. Corresponding compounds of tungsten and cobalt do not catalyze the oxidation. The rates of oxidation of six ring monosubstituted anilines relative to aniline in the presence of vanadium oxyacetylacetonate have been determined by a competitive method, and these correlate reasonably well with both Hammett σ constants and Brown–Okamoto σ^+ constants giving ρ values -1.63 and -1.42, respectively. The separation of substituent effects into polar and resonance contributions by various semiempirical relationships is reasonably successful; the form of these relationships indicates the importance of a substituent direct field effect in this reaction. The kinetics of the aniline oxidation itself could not be followed accurately due to autoinhibition of the reaction by *tert*-butyl alcohol, and to catalyst degradation, but the reaction is first order in aniline. The observations are consistent with previously suggested mechanisms for this type of reaction, involving a rapid reversible complex formation between peroxide and catalyst, preceding a rate-determining heterolysis of the O–O bond of this complex.

Organic hydroperoxides in the presence of catalytic amounts of chromium, molybdenum, or vanadium compounds have been shown to perform many of the same heterolytic oxidations as organic peracids, e.g., epoxidation of alkenes,[2-4] oxidation of tertiary amines to N-oxides,[5] and of sulfoxides to sulfones.[6] The heterolytic nature of this type of reaction has been demonstrated by the fact that (a) iron or cobalt compounds, known to promote homolytic reactions of peroxides, do not catalyze it, and (b) there is a qualitative similarity between the reactivities of different alkenes with peracids and with the hydroperoxide–metal ion combination.[3] The proposed mechanism for epoxidation,[3,4] supported by kinetic evidence, involves a rapid reversible complex formation between peroxide and catalyst, followed by a rate-determining heterolysis of the O–O bond of this complex.

The present report describes an investigation of the oxidation of aniline to nitrobenzene in the presence of catalytic amounts of vanadium and molybdenum compounds, together with a comparative study of the rates of oxidation of aniline and six ring monosubstituted anilines in the presence of vanadium oxyacetylacetonate. The results are consistent with the type of mechanism proposed for epoxidation and indicate an electron-deficient transition state in the rate-determining step of the reaction.

Results and Discussion

In general oxidations were carried out at 60–70°, with *tert*-butyl hydroperoxide (2–4 M),[7] amine (1–2 M), and catalyst (0.002–0.006 M) in benzene–chlorobenzene (6:1, v/v). Under these conditions no reaction occurred in the absence of either catalyst or amine. The sole product from aniline was nitrobenzene, identified from its vpc retention volume and by the pmr spectrum of a trapped sample. Loss of aniline and formation of nitrobenzene showed a 1:1 stochiometic relationship. No traces of the presumed intermediates,[8] phenylhydroxylamine and nitrosobenzene, were found either by vpc or by pmr analysis of partly or completely reacted solutions. Oxidation of the substituted anilines in each case gave only one vpc detectable product, presumed to be the corresponding substituted nitrobenzene by analogy with the aniline results. The pmr spectrum of the reacting solutions further supported this conclusion.

The extent of the reaction was followed by loss of

(2) (a) J. Kollar, Belgium Patent 641,452 (1964); (b) N. Indictor and W. F. Brill, *J. Org. Chem.*, **30**, 2074 (1965).

(3) N. M. Sheng and J. G. Zajacek, International Oxidation Symposium, San Francisco, Calif., Aug 1967; Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968.

(4) E. S. Gould, R. R. Hiatt, and K. C. Irwin, *J. Amer. Chem. Soc.*, **90**, 4573 (1968).

(5) M. N. Sheng and J. G. Zajacek, *J. Org. Chem.*, **33**, 588 (1968).

(6) Von F. List and L. Kuhnen, *Erdoel Kohle, Erdgas, Petrochem.*, 192 (1967).

(7) *tert*-Butyl hydroperoxide is subsequently referred to simply as "peroxide."

(8) See, e.g., A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans Ltd., London, 1956, p 628.

amine and formation of the nitrobenzene by either vpc or pmr. Monitoring by peroxide loss using iodometric techniques was very much less accurate due to the high degree of coloration developed in the reacting solutions, presumably from very small amounts of further aniline oxidation products. The reaction requires 3 mol of peroxide to be reduced for each mole of aniline oxidized. While this stoichiometry was not directly verified owing to the difficulty of titrating *tert*-BuO$_2$H, it could be assumed with some confidence since (a) no other oxidation products were formed in significant quantity, (b) peroxide did not decompose in the absence of aniline, and (c) atmospheric oxygen was not absorbed.

Catalyst Effectiveness.—Table I lists the percentage

TABLE I

OXIDATION OF ANILINE TO NITROBENZENE BY
tert-BUTYL HYDROPEROXIDE WITH VARIOUS CATALYSTS AT 66.1°[a]

Catalyst[b]	% conversion[c]
None	0
Mo(CO)$_6$	9
Mo(nap)[d]	15
[Mo(cp)(CO)$_3$]$_2$[e]	8
VO(acac)$_2$[f]	39
V(nap)	25
W(CO)$_6$	0
Co(nap)	0
Co(acac)$_2$	0

[a] Reaction conditions: *tert*-butyl hydroperoxide (4.35 mmol), aniline (2.31 mmol), benzene (1.09 ml), chlorobenzene (0.21 ml), and water (0.05 ml). [b] Catalyst concentration, 0.001 g. [c] Based on aniline conversion to nitrobenzene at 40 min. [d] nap = naphthenate. [e] cp = cyclopentadienyl. [f] acac = acetylacetonate.

conversion of aniline after 40 min in the presence of 0.001 g of the catalysts investigated. A more accurate quantitative comparison is unwarranted in view of several differential factors, namely induction periods, catalyst degradation, uncertain catalyst composition, and autoinhibition by *tert*-butyl alcohol. There is, however, sufficient difference in behavior between the catalysts to make some quantitative comparison viable.

The reaction is catalyzed by molybdenum and vanadium compounds but not by cobalt compounds or by tungsten hexacarbonyl. Vanadium appears more effective than molybdenum (*subject, of course, to the above qualifications*), the oxyacetylacetonate giving almost 40% conversion after 40 min. The order is in reasonable agreement with that found for the oxidation of tertiary amines[5] and again offers strong support for a heterolytic rather than free-radical mechanism. Molybdenum hexacarbonyl required 5–10 min to become a fully active catalyst; similar effects have been noted in its use to catalyze expoxidation[3,9] and attributed to a need to lose one CO ligand prior to reaction.[3] The cyclopentadienylmolybdenum tricarbonyl dimer appears to be a very effective catalyst for the reaction but rapidly decomposes in the reaction conditions used and ceases to have any further activity, this behavior again being apparent in the case of epoxidation reactions of this compound.[9]

Substituent Effects.—Individual reaction rates for aniline and the substituted anilines could not be determined due to experimental difficulties (*vide infra*). The relative rates for the substituted compounds, however,

(9) R. R. Hiatt and G. R. Howe, unpublished observations.

may be determined by a competitive method, if the rate equations for the two competing reactions are of the same form. In particular, if the reaction is first order in amine (A) then the rate equation may be written (using the usual symbolism) (eq 1) where f(P_i) is some

$$\frac{dA}{dt} = k_a A \, f(P_i) \qquad (1)$$

function of all the other variables in the system. At anytime t

$$\ln \frac{A}{A_0} = k_a \int_0^t f(P_i) \, dt \qquad (2)$$

For two competing substrates A and B, in the same reaction, if f(P_i) is the same for both, then

$$\int_0^t f(P_i)$$

is also identical as both are in the same concentration of reactants. Therefore, from eq 2 we may write eq 3.

$$\ln B = \frac{k_b}{k_a} \ln A + \ln \frac{B_0}{A_0} \qquad (3)$$

For the six ring monosubstituted anilines studied at 66.1° using vanadium oxyacetylacetonate as catalyst, plots of ln (substituted compound) *vs.* ln (aniline) were found to be linear in the range studied (up to 80% of the reaction in the most reactive component). Table II

TABLE II

VALUES OF k_B/k_A[a] AND STANDARD DEVIATIONS
FOR SOME SUBSTITUTED ANILINES

Substituent	k_B/k_A	SD[b]
m-Cl	0.247	0.006
p-Cl	0.509	0.016
m-Br	0.093	0.008
p-Br	0.396	0.004
m-Me	1.159	0.032
p-Me	2.134	0.006

[a] k_B = rate constant for substituted aniline, k_A for aniline, as given by eq 3. [b] Standard deviations.

lists the least mean squares value for k_b/k_a as given by eq 3, together with their standard deviations. The fit of eq 3 is good evidence both for the reaction being first order in amine, and for the rate equation for the substituted compounds being of the same form as for aniline itself.

It is obvious from the results in Table II that the effect of substituents upon the reaction rate is what one would expect from a reaction involving an electron-deficient transition state, in that electron-withdrawing groups decrease the rate, and *vice versa*. Furthermore, the relative order, *viz., p*-Me > *m*-Me > aniline > *p*-Cl > *p*-Br > *m*-Cl > *m*-Br, is the same as observed in electrophilic aromatic substitution. Consequently linear regression analyses were carried out using the log of the relative rates and both Hammett σ constants and Brown–Okomoto σ^+ constants. The fit of any of these functions may be judged by the ratio of the standard error of estimate to the root mean square value of the independent variable[10] called for convenience the normalized standard error (NSE).[11] The smaller the NSE,

(10) P. R. Wells, S. Ehrenson, and R. W. Taft, in "Progress in Physical Organic Chemistry," Vol. 6, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience, 1968, p 147.

(11) G. R. Howe, Ph.D. Thesis, University of Leicester, 1969.

the better the fit. The results of these analyses are given in Table III, together with the results of an anal-

Figure 1.

TABLE III

CORRELATION[a] OF LOG (RELATIVE RATES FOR SUBSTITUTED ANILINES) WITH σ AND σ^+ CONSTANTS[b]

Experi-mental data used	Type of con-stant used	ρ	SD	C[c]	SDc[d]	NSE[e]
All	σ	-1.97	0.28	0.00	0.07	0.30
	σ^+	-1.71	0.24	-0.11	0.06	0.30
All except	σ	-1.63	0.11	0.01	0.02	0.15
m-bromo	σ^+	-1.42	0.15	-0.08	0.03	0.23

[a] Values of ρ, C, standard deviations, and NSE for $\log \dfrac{k}{k_0} = \rho\sigma + $ C. [b] Values from ref 12. [c] C = constant. [d] SDc = standard deviation of C. [e] See text for definition.

ysis omitting m-bromoaniline, which shows the largest deviation from the least mean squares line, and whose standard deviation (Table II) is of a higher order than any of the other compounds studied. (Figure 1 shows the plot for σ^+.)

The correlation with σ and σ^+ constants is quite good; this and the values for ρ obtained (-1.42 to -1.97) indicate an electron-deficient transition state in the rate-determining step, but apparently without a significant differential π electron delocalization as compared to the ground state.[12] The ρ values are of the same order as found by Ibne-Rasa and Edwards[13] for the oxidation of aniline by peroxyacetic acid in ethanol at 30°[14] ($\rho = -1.86$).

Dual Effect Correlations of Substituent Effects.—The qualitative ideas developed so successfully by Ingold[15] of separable substituent effects upon aromatic reactivity have found quantitative expression in many empirical and semiempirical relationships. Most of these may be expressed in the form[11,16] (eq 4) where the sum-

$$\log \frac{k}{k_0} = \Sigma_i \pi_j{}^i A_i \qquad (4)$$

mation runs over all the proposed separable effects (*e.g.*, $i = 1$ polar effect, $i = 2$ π electron delocalization effect, etc.) and the product over all the parameters of the reaction (*e.g.*, $j = 1$, ^1A is characteristic of the aromatic system, etc.).

Two equations of this form are the Yukawa–Tsuno equation (eq 5)[17] and the generalized Taft equation (eq 6).[10] They differ in that in eq 5 the positional de-

$$\log \frac{k}{k_0} = \rho\sigma + \gamma\rho(\sigma^+ - \sigma) \qquad (5)$$

$$\log \frac{k}{k_0} = \rho_I\sigma_I + \rho_R\sigma_R \qquad (6)$$

pendence of the reaction is factored into the σ values so that one requires separate σ_{meta} and σ_{para} values for each substituent, and in eq 6 the positional dependence is factored into the ρ values so that separate ρ_{meta} and ρ_{para} values are required for each reaction.

In general it may be shown[11,16] that one needs the minimum number of parameters to describe the maximum amount of data by a maximum number of j and a minimum number of i in eq 4. In particular, if one can factorize out the positional dependence of a reaction and derive parameters characteristic of meta and para orientations, the number of parameters may be reduced considerably.[18] In addition, one may make useful deductions as to the origin of substituent effects. The disadvantage of factorizing out the positional dependence, or more generally increasing the number of i of eq 4, is that it may lead to a decrease in the accuracy with which the derived function fits the data.

With these considerations in mind, a three variable, two effect eq 7 has been proposed.[11,16] F and M are pa-

$$\log \frac{k}{k_0} = A + BFX_{\text{sr}} + CMY_{\text{sr}} \qquad (7)$$

rameters characteristic of the polar and resonance effect of a substituent, respectively, and are taken from the compilation by Gardner Swain and Lupton.[19] X and Y are characteristic of the orientation of substituent (s) and reaction center (r) and describe the transmission of the polar and resonance effect, respectively. Y_{sr} may be approximated to by π_{sr}, the atom–atom polarizability of atoms R and S as given by simple Hückel MO theory.[20]

The form of X_{sr} depends on the type of polar effect involved; it appears that the direct field effect model of Kirkwood and Westheimer[21] may successfully account for the major part of this type of interaction.[20,22] Specific functional forms proposed for X include[20,22,23] $1/d$, $1/d^2$, $\cos \theta/d$, $\cos \theta/d^2$, where d is the distance between

(12) L. M. Stock and H. C. Brown in "Advances in Physical Organic Chemistry," Vol. 1, V. Gold, Ed., Academic Press, New York, N. Y., 1963, p 35.

(13) K. M. Ibne-Rasa and J. O. Edwards, *J. Amer. Chem. Soc.*, **84**, 763 (1962).

(14) A referee has suggested that the agreement with peracid oxidations may be fortuitous on the grounds that amine–vanadyl complexes may be involved in the rate-determining step, their relative stabilities contributing to a composite ρ value. We are inclined to think such contribution would be slight on mechanistic grounds (*vide infra*). Moreover, the *qualitative* similarity of substituent effects on peracid *vs.* peroxide–metal ion reactivity in at least one other reaction, *i.e.*, epoxidation of olefins, is well established.[2b,3]

(15) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., London, 1953.

(16) K. C. C. Bancroft and G. R. Howe, unpublished work.

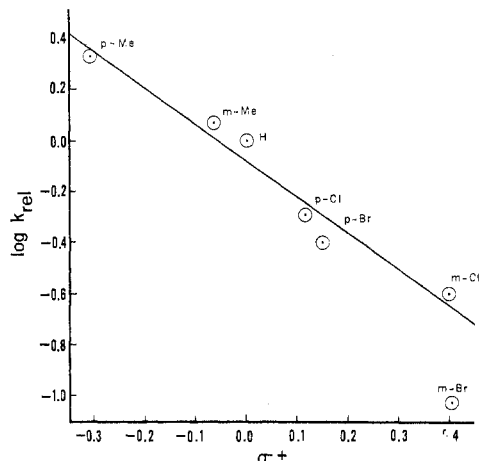(17) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jap.*, **32**, 971 (1959), and preceding papers.

(18) This argument applies to an even greater extent in polycyclic systems, *e.g.*, in naphthalene there are 14 possible different orientations between substituent and reaction center.

(19) C. Gardner Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

(20) M. J. S. Dewar and P. J. Grisdale, *ibid.*, **84**, 3539, 3541, 3546, 3548 (1962) and references therein.

(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) P. R. Wells and W. Adcock, *Aust. J. Chem.*, **18**, 1365 (1965).

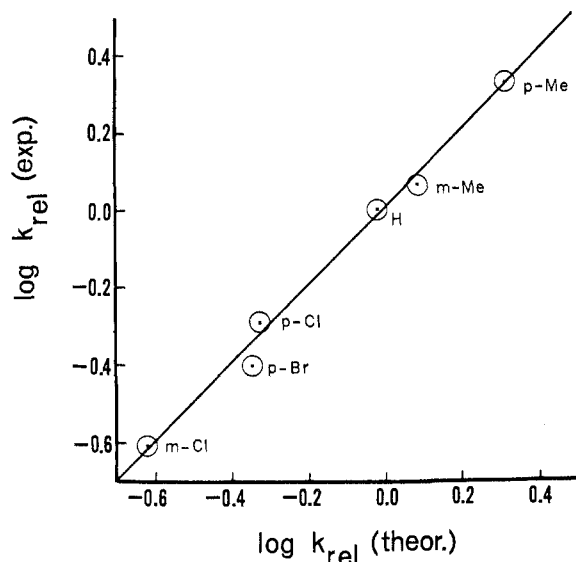(23) W. Adcock and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **89**, 379 (1967).

Figure 2.

the center of the dipole connecting substituent and reaction center, and θ is the angle between that dipole and the line along which d is measured.   Table IV shows the

TABLE IV

CORRELATION[a] OF LOG (RELATIVE RATES FOR SUBSTITUTED
AMINES[b]) WITH (1) YUKAWA–TSUNO EQUATION[c] AND (2)
EQUATION 7[d] OF THE TEXT

┌─────────────Results of correlation─────────────┐

Yukawa–Tsuno Equation

		B	SD_B	C	SD_C	NSE[e]
		−1.58	0.09	−0.50	0.28	0.12

Equation 7

Y	X	B	SD_B	C	SD_C	NSE[e]
π (benzene)	$1/d$	−2.95	0.24	13.18	3.13	0.18
π (benzene)	$1/d^2$	−9.40	1.06	10.36	4.13	0.24
π (benzene)	$\cos\theta/d$	−3.30	0.19	17.09	2.31	0.13
π (benzene)	$\cos\theta/d^2$	−10.68	0.78	14.30	2.79	0.16
π (aniline)	$1/d$	−3.11	0.25	−8.50	1.94	0.17
π (aniline)	$1/d^2$	−9.83	1.04	−6.81	2.47	0.23
π (aniline)	$\cos\theta/d$	−3.48	0.28	−10.84	2.02	0.17
π (aniline)	$\cos\theta/d^2$	−11.27	0.84	−9.20	1.84	0.16

[a] Values of B, C, standard deviations, and NSE; values of A are very small and do not significantly affect the correlation.
[b] Value for m-bromoaniline omitted as before. [c] $\log\dfrac{k}{k_0} = A + B\sigma + C\,(\sigma^+ - \sigma)$. [d] $\log\dfrac{k}{k_0} = A + BFX + CMY$. [e] See text for definition.

results of a linear regression analysis using the present substituent data in eq 7. Polarizabilities were calculated using (a) benzene as a model and (b) aniline with heteroatom parameters $h = 1.5$, $k = 0.8$.[24] All four functional forms of X were used. The results using the Yukawa–Tsuno equation (eq 5) are also presented.

The results in general are good, though the Yukawa–Tsuno equation gives a slightly better fit than the best given by eq 7; in view of the extra parameter factorized out of eq 7 and its theoretical incorporations as compared to the completely empirical Yukawa–Tsuno equation, this difference (0.01 NSE) is probably insignificantly small. What is certainly significant is the small values of the standard deviations of the polar coefficient B for functional forms of X: $1/d$, $\cos\theta/d$, and $\cos$
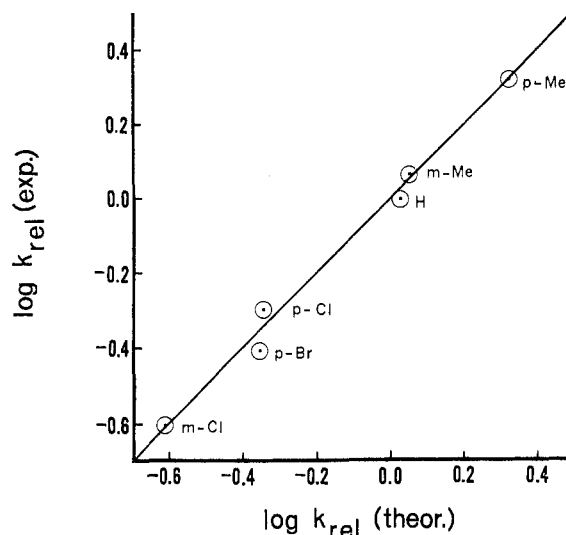
(24) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, Chapter 5.

Figure 3.

θ/d^2. This provides very good evidence for the approximations inherent in the functional form used, and for the importance of the direct field effect in this particular reaction.   The failure to significantly differentiate between the point dipole model and the vector dipole model (θ independent and θ dependent, respectively) is not unexpected; significant differences occur only when θ is fairly large.[11,16,20,22]

The comparatively much larger standard deviations in the resonance coefficient C indicate the failure of the index presently used; this may be due to either failure of π_{rs} itself or in the method of calculating π_{rs}.

Figures 2 and 3 show plots of $\log k/k_0$ (experimental) against $\log k/k_0$ (predicted), using the Yukawa–Tsuno equation and eq 7 [$X = \cos\theta/d$, $Y = \pi$ (benzene)], respectively.

Kinetics of the Aniline Oxidation. –Kinetic studies were carried out at 66.1° in benzene–chlorobenzene (6:1 v/v) using vanadium oxyacetylacetonate as catalyst.

The stochiometry of the reaction scheme may be symbolized as in eq 8 where A is the aniline concentration, P

$$A + P \longrightarrow B \tag{8a}$$

$$B + P \longrightarrow C \tag{8b}$$

$$C + P \longrightarrow D \tag{8c}$$

the peroxide, B and C the probable oxidation intermediates, phenylhydroxylamine and nitrosobenzene,[8] and D is nitrobenzene. If the initial concentration of A is A_0, and if $B_0 = C_0 = D_0 = 0$, then by material balance, at any time t

$$A_0 - A_t = B_t + C_t + D_t \tag{9}$$

The fact that a plot of $(A_0 - A_t)$ vs. D_t is a straight line of unit slope and zero intercept implies therefore that (a) aniline is being lost only through the reaction given by eq 8, and (b) B_t and C_t are effectively zero, thus confirming the previously mentioned analytical evidence. Since the rates of oxidation of B and C must be considerably greater than that of A, step 8a is rate determining (though, of course, the necessity for a catalyst implies greater complexity than indicated by the simple stochiometric equation).

The rate-determining step is first order in aniline in the range 0.4–2.1 M as shown by the studies on the substituted anilines. The order, with respect to catalyst and peroxide, could not be determined using an integrated form of the rate equation due to several of the previously mentioned factors. (a) Autoinhibition of the reaction by *tert*-butyl alcohol, also observed for epoxidation using vanadium oxyacetylacetonate,[4] was marked; initial addition of 0.1 mol of *tert*-BuOH/mol of peroxide slowed the initial rate by about 20%. (b) Catalyst degradation of the type previously observed in this type of reaction[3,4] was supplemented by the formation of insoluble catalyst complexes (also observed in the oxidation of tertiary amines, and ascribed to action of the amine oxide products).[5] Rates of reaction of anilines with electron-donating groups fell off noticeably faster than aniline itself.

Attempts to overcome these difficulties by measuring initial rates[4] were unsuccessful due to experimental difficulties of analysis.

A reaction, first order in all three components, and with zero concentration of the reaction intermediates, should follow a rate expression (assuming constant catalyst concentration and activity)

$$\frac{1}{P_0 - 3A_0} \ln \frac{P_0 A}{A_0 P} = kt \tag{10}$$

That such plots were in fact linear over some 50% of the reaction (*e.g.*, Figure 4) must be fortuitous, as eq 10 takes no account of catalyst degradation or autoinhibition. It does indicate, however, an order in peroxide varying between zero and one.

Mechanism of the Aniline Oxidation.—The mechanism proposed by Gould, *et al.*,[4] for the epoxidation of cyclohexene in the presence of vanadium acetylacetonate involves a rapid reversible complex formation between peroxide and catalyst, followed by heterolysis of the O–O peroxide bond, and leads to a rate equation (eq 11).

$$\text{rate} = \frac{k \text{ (catalyst)}}{1/(\text{peroxide}) K_p + 1} \tag{11}$$

In the case of the aniline oxidation, the kinetic evidence is not so conclusive, but the mechanism shown in Scheme I, analogous to the epoxidation mechanism, is in agreement with the experimental evidence, particularly the substituent effects, and it is difficult to conceive of another mechanism which fits the facts as well.

Despite a paucity of data, some speculation on the involvement of amine other than in step c (Scheme I) may be in order, particularly as it would influence ρ values. From published data on amine–vanadyl acetoacetonate complexes,[25] it can be estimated that (a) stability constants would vary by less than a factor of 4 from most basic (*p*-Me) to least basic (*m*-Cl) aniline, (b) under conditions here reported, a minimum of 0.3% of the VOacac would be uncomplexed, and (c) the percentage of uncomplexed acetylacetonate would vary by no more than a factor of 2 for the 1:1 aniline-substituted aniline mixtures subjected to competitive oxidation.[26] Since oxidation of complexed aniline seems un-
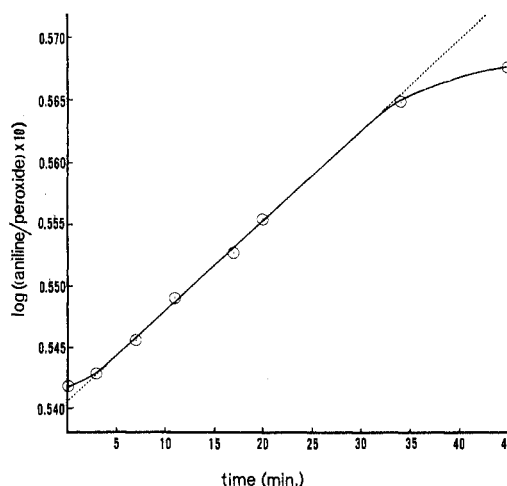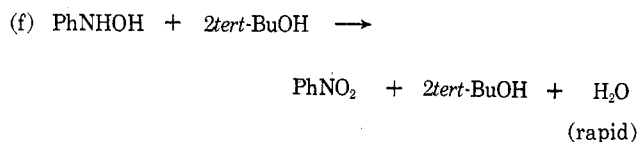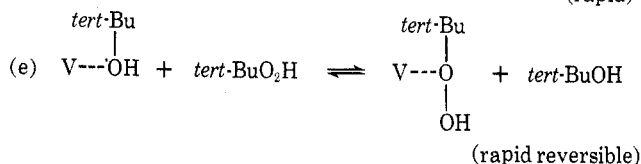
(25) R. L. Carlin and F. A. Walker, *J. Amer. Chem. Soc.*, **87**, 2128 (1965).
(26) While Corbin and Walker[25] did not investigate any anilines, they covered a sufficient range of amines to render the proportionality between pK_a and log (stability constant) reasonably precise, steric factors being equal. Estimation of the absolute stability constant for aniline is more difficult but, owing to the rather remarkable insensitivity of the stability to amine structure, a value of 100 seems a safe upper limit.
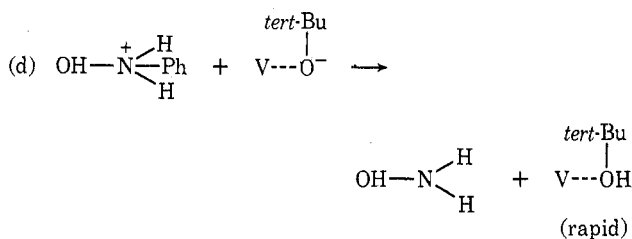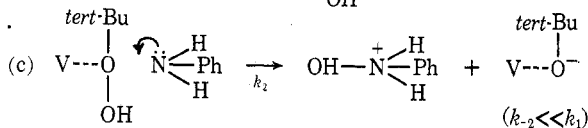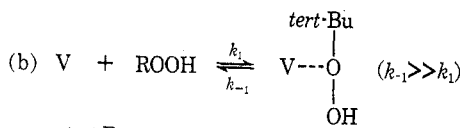

Figure 4.

SCHEME I

POSTULATED MECHANISM FOR THE ANILINE OXIDATION

(a) catalyst activation (rapid)

likely, the necessary electrons being otherwise occupied, the effect of amine–vanadyl complexation on the reaction might take either of two forms as extremes. (1) Formation of vanadium–peroxide complex from nonamine complexed VOacac₂. This would introduce a differential rate factor of 2 into the calculations and make the true ρ value for step c (Scheme I) 0.3 units higher than measured. (2) Formation of vanadium–peroxide complex *via* displacement on vanadyl–amine complex. Here the greater difficulty of displacement on a more stable complex is partially offset by the higher concentration of that complex; specifically, comparing a reaction with aniline alone *vs.* one with a 50:50 mixture of aniline and a substituted aniline for which the vanadyl

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.

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.

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