term (2.45×10^8). At room temperature these two differences cancel, and the actual rates are quite comparable as indicated above.

Although Sangster and Thynne find that in their studies trifluoropropyl radicals add to the ethylene to some extent, the scavenger used by them (H_2S) is considerably less efficient than iodine, and the overall chemistry appears to be somewhat more complex. In the present study such addition would be manifest as a decrease in the apparent value of k_2/k_1 with increased ethylene concentration or an increase with increased iodine concentration. It is seen in Table I that at both 25 and $-45°$ a tenfold increase in either ethylene or iodine has little, if any, effect on the value of k_2/k_1. There is therefore no evidence in the present study that any significant addition of these radicals to ethylene occurs in competition with the very rapid scavenging by iodine.

In addition to the factual results reported above, the present work demonstrates the ease with which kinetic investigations of this type can be carried out using γ-ray initiation as the source of radicals. In particular, studies at low temperatures are readily carried out. The high reproducibility and freedom from trivial experimental problems makes accurate determinations of activation energies possible.

Kinetic Studies on the Autoxidation of 3,5-Di-*t*-butylpyrocatechol[1,2]

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The use of 3,5-di-*t*-butylpyrocatechol in 50% methanol as a model for the autoxidation of pyrocatechol to *o*-quinone is explored. Manometric studies indicate a first-order dependence on substrate under conditions where O_2 concentration is held constant by recycling. Rate constants for the disappearance of H_2L, HL^-, and L^{2-} forms of the substrate are calculated. The rate of oxygen uptake is found to follow combined first- and second-order kinetics, and possible mechanistic interpretations of these results are discussed. Equilibrium constants for the *o*-semiquinone anion radical dismutation are found by combined esr and potentiometric measurements, and the rate constants are estimated from rapid-flow esr experiments. A novel apparatus for simultaneous measurements by manometry, spectroscopy, and titrimetry and for manometric experiments in buffer-free systems is described. Kinetic studies by esr provide information on possible autoxidation mechanisms.

A kinetic investigation of the autoxidation of pyrocatechols to *o*-quinone is necessary to provide the basis for a similar study of the metal-catalyzed oxidation. Because of the complex nature of pyrocatechol autoxidation,[4-7] 3,5-di-*t*-butylpyrocatechol (35DTBP) was chosen as an alternate substrate. Autoxidation of this derivative yields the *o*-quinone (35DTBQ), which is stable and easily characterized.[5,8] Previous esr studies on 3,5-di-*t*-butyl-*o*-benzosemiquinone (35DTBSQ) indicate that this species is also relatively stable in solution.[9,10] Blocking the 3 and 5 positions appears to reduce the rate of solvolytic attack on the quinonoid nucleus, which complicates the autoxidation of pyrocatechol.[11,12] Peroxy adducts in the *para* positions, characteristic of 2,4,6-tri-*t*-butylpyrocatechol autoxidation,[13,14] were not observed in high resolution esr work.[15] Degradation products are colorless[5] and do not interfere with spectral product analysis or kinetic investigations.

In this work the 3,5-di-*t*-butylpyrocatechol–O_2 system is studied by manometric, esr, and spectrophotometric

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methods in 50% methanol containing 0.10 M KNO_3 with several objectives in mind. First, the rate law for autoxidation is to be determined and compared insofar as possible with that reported for pyrocatechol.[16] Second, reasons for the lower reported yields of 35DTBQ in the absence of metal ions are needed as an aid in understanding why Mn(II) and Co(II) catalysts are so efficient. Third, the kinetics in the absence of metal ions is needed for comparison with the metal-catalyzed oxidation. Fourth, an interpretation of the kinetics in terms of probable autoxidation mechanisms was considered possible and useful.

In regard to the last objective, the difficulty in quantitatively resolving whether one- or two-electron transfer to oxygen is involved in the rate-determining step has long puzzled organic chemists.[17] Since 60–65% of the electron density in *o*-benzosemiquinones is concentrated at the oxygen atoms a second electron could easily be transferred before the reactants escape into the bulk of the solution.[15,17] Rapid dismutation between pyrocatechols and their quinones (and the high reactivity of these quinones) has so far made this problem impossible to solve kinetically. Nonetheless, it is worthwhile to determine forward and back dismutation constants in the event that these might be low enough due to steric interference of the *t*-butyl groups to use rapid techniques to resolve the one-electron, two-electron problem.

Experimental Section

Reagents. 3,5-Di-*t*-butyl-*o*-benzoquinone was prepared from a concentrated solution of the pyrocatechol *via* Mn(II)-catalyzed oxidation in 50% methanol and recrystallized once from isooctane (mp 113.2–113.8°; lit.[8] mp 113°). The electronic and ir spectra corresponded to those published.[18,19] Oxygen gas mixtures were analyzed (to 1 part per 10,000) and supplied by Matheson Co. The oxygen atmosphere referred to as 100% oxygen was 99.4% oxygen by analysis. All other materials are as described earlier.[20]

Instruments. Standard analytical instruments used in the experimental work are an automatic di-functional recording titrator[21] (International Instrument Co., Canyon, Calif.), Beckman DK-2 recording spectrophotometer, and a Varian V-4502-12 electron paramagnetic resonance spectrometer. A Beckman Research pH meter was used to check pH meter readings of the titrator.

Description of Apparatus. The apparatus used in the kinetic studies was of the "bubble-type," constant volume variety, designed to made simultaneous measurements by the techniques of manometry, titrimetry, and spectroscopy and to operate in buffer-free solutions. The latter two techniques include automatic recording instruments and full automation is potentially possible.

Two flow systems are involved. The reaction solution is saturated with the desired atmosphere by using a small bellows pump which cycles the gas through a glass frit beneath the surface of the solution and through the manometric device. A second flow system involves peristaltic pumping of the reaction solution from the reaction cell through flexible tubing to a suitable detection unit (esr, ultraviolet, or visible spectroscopy) and back to the cell. Only one previous instance of a gas cycle system having been used in manometric studies was found.[22] In the apparatus employed, provision apparently was not made for either simultaneous kinetic measurements of more than one variable, or automatic pH control.

A sketch of the reaction cell and cover appears in Figure 1. A greased rubber O-ring sits in a groove inside the Teflon cover and provides an air-tight seal with the glass wall. Six holes in the cover (top insert, Figure 1) accommodate a glass and calomel electrode pair set in O-ring sockets, two hypodermic needles for separate addition of acid and base, a $^1/_4$-in. brass swage lock with Teflon pressure fitting to hold the glass frit, and a $^3/_8$-in. brass swage lock with similar fitting for the gas exit tube. The reaction solution return line is sealed into the elbow of the glass exit tube with epoxy resin.

At the bottom of the reaction cell is a solution outlet. A Teflon disk, high enough to minimize bubbles from entering the liquid line, rests on the bottom of the cell when spectral measurements are being made. A Teflon-coated magnetic stirrer rests on top of the disk and its rotating action pulls gas bubbles down and away from the glass frit, effectively saturating the solution with them. Oxygen depletion in the liquid lines can be minimized by maintaining a high pump rate and short flow lines. A three-way Teflon stopcock in the solution exit line just after the O-ring allows the removal of aliquot samples during the course of a reaction.

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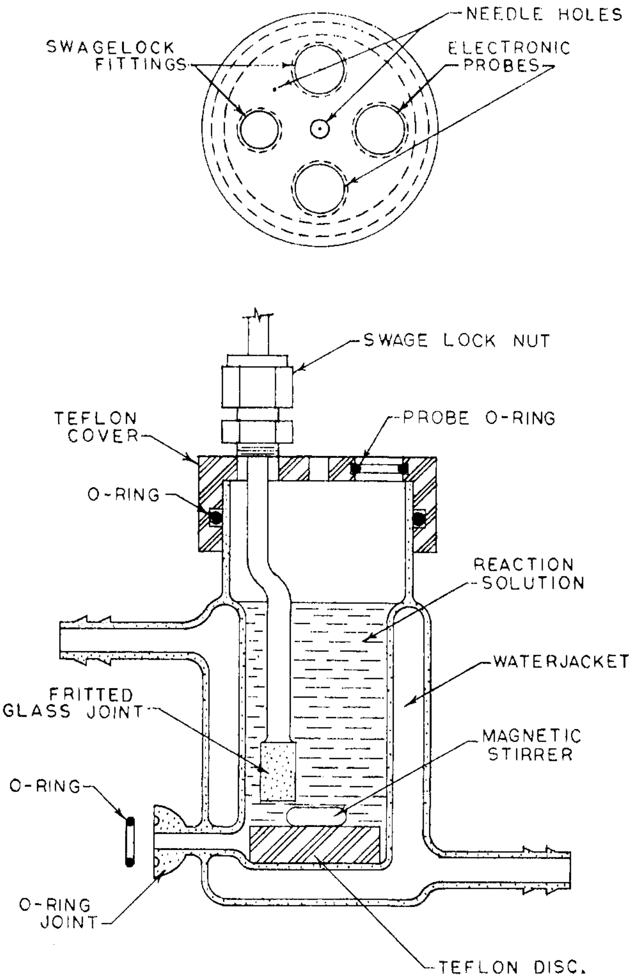

Figure 1. Reaction cell, top insert: top section of Teflon cover. Bottom insert: cross section of Pyrex reaction cell with cover in position.

An automatic titrator with syringe device for addition of acid or base for pH control was used to eliminate the need for buffer. Provision for other reagents was made possible by means of a hypodermic needle inserted through a narrow hole drilled in the Teflon cover. With this experimental arrangement pH control to ±0.03 units or better was achieved in systems with 1.0×10^{-2} *M* substrate and to ±0.05 units with less than 2.0×10^{-3} *M* substrate present. Automatic control could usually be established within 15 sec of the start of the reaction.

The gas pump is placed near the reaction vessel in a separate chamber constructed of a brass inner wall and masonite outer wall. Metal screws bolt a plexiglass cover tightly against a rectangular rubber washer which sets on top of the walls and houses swage locks for intake and outlet gas lines. The gas pump is of the aquarium variety with negligible temperature buildup from the electromagnet. Temperature control to ±0.1° is maintained by circulating bath water through copper coils circling the brass inner wall.

In the manometric studies water-jacketed reference fuel type burets and Krebs solution were used. Fluid level displacement of the gas pump is of the order of 5 mm. Most reproducible results were obtained with the present design for reactions with half-lives between 0.5 and 30 min.

Experimental Techniques. For manometric reactions alone a Teflon plug was inserted in the solution outlet of the reaction cell, and the liquid return line was closed. Substrate was weighed in and 60 ml of slightly acidified stock solution (pH 3.50) was added. With cover and connections in place the reaction atmosphere was bubbled through for 0.5 to 1 hr. After closing off the system to the external atmosphere, the bubbler was started. When the fluid level in the open arm stabilized, a "shot" of NaOH, estimated in advance to be sufficient to bring the system to reaction pH, was added manually with the syringe. The syringe was then clamped on the autotitrator drive unit and the pH control switched on. Fluid level readings were taken at 15- or 30-sec intervals initially and converted into standard conditions using an external barometer.

Analytical Procedure for 3,5-Di-t-butyl-o-benzoquinone. 3,5-Di-*t*-butyl-*o*-benzoquinone absorbs strongly between 390 and 420 mμ and under the experimental conditions (pH <11.0) the hydroxy adduct[23] and the semiquinone do not interfere. The value of ϵ_M for the *o*-quinone at 404 mμ is 1.58×10^3 M^{-1} cm^{-1} in 0.10 *M* KNO_3, 50% methanol, and the Beer's law plot of absorbance *vs.* concentration is linear through 1.22×10^{-3} *M* *o*-quinone.

Analytical Procedure for Hydrogen Peroxide. Aliquots of 25 ml of the reaction mixture were taken after quenching the solution with acid to stop the autoxidation and were extracted twice with equal volumes of dichloromethane. The acidified methanol-water layer showed no appreciable visible or uv absorption to 220 mμ. The extracted aqueous layer was titrated with 0.974 *N* Ce(IV) with ferroin as an indicator.[24] A small correction (<1.5%) was applied for the peroxide lost to the organic layer by assuming the solubility of hydrogen peroxide and water were the same in the organic component.[25] Reproducibility with Ce(IV) was ±1%.

Analytical Procedure for 3,5-Di-t-butyl-o-benzosemiquinone. Free-radical species were observed in kinetic runs on the autoxidation using esr spectroscopy. When the spectrum was magnified, it was identified positively to be that of 3,5-di-*t*-butyl-*o*-benzosemiquinone radical ion.[15] No other radicals were observed.

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Table I: Dependence of k_{obsd} on $[\mathrm{H}^+]^a$

$-\log [\mathrm{H}^+]^b$	Mol of O_2 uptake $\times 10^3$	Mol of 35DTBQ^c $\times 10^3$	Mol of H_2O_2^{c} $\times 10^3$	Reaction time, min	$10^2\alpha_1{}^d$	$10^7\alpha_2{}^d$	10^1k_{obsd},^{e} min^{-1}
8.00	4.00	3.98	3.48	14	0.440	0.0088	0.717
8.10	5.26	5.03	4.08	14	0.566	0.0126	0.931
8.22	4.92	4.84	4.34	14	0.733	0.0243	1.002
8.35	6.22	5.94	5.16	14	0.990	0.0442	1.359
8.36	6.28	5.75	4.62	14	0.996	0.0456	1.410
8.38	7.25	7.15	5.46	14	1.05	0.0504	1.450
8.49	6.60	6.24	5.34	12	1.36	0.0839	1.555
8.64	6.02	5.81	5.02	9	1.79	0.1555	1.73
8.87	7.64	7.15	5.90	16	3.17	0.468	2.04
8.93	7.80	6.00	5.48	14	3.96	0.736	2.80
9.19	7.82	5.06	4.25	16	6.81	2.25	3.71
9.24	7.52	5.92	4.75	12	6.95	2.83	3.97
9.34	10.15	8.54	4.26	12	8.79	3.84	4.10
9.46	10.02	6.89	1.56	12	11.3	6.50	5.34
9.56	7.20	4.41	0.78	16	13.8	10.0	5.61
9.67	8.41	3.86	1.43	9	17.1	15.9	6.40
9.70	9.79	3.33	1.10	7	18.1	18.1	6.95
9.83	8.83	3.18	1.40	5	23.1	31.2	7.46
10.10	8.87	3.07	0.49	12	35.4	88.8	10.1
10.25	9.80	3.21	0.70	7.5	44.0	156.0	13.5
10.6	8.87	2.33	0.24	2.5	63.8	506.0	22.1

[a] Experimental conditions: 35DTBP concentration adjusted to 1.00×10^{-2} *M;* 0.10 *M* KNO_3 50 wt % methanol, 25°, 100% O_2 atmosphere. [b] Solvent ion product is 1.34×10^{-14} M^2. [c] Average of two determinations. [d] $\alpha_1 = [\mathrm{HL}^-]/[\mathrm{S}]$; $\alpha_2 = [\mathrm{L}^{2-}]/[\mathrm{S}]$. [e] Corrected for solvent partial pressure. Reference to 760 mm, 25°.

In the kinetic runs thin-bore (1.5 mm i.d.) Pyrex glass tubing passing completely through the esr spectrometer cavity was used as a sample cell. The 10-G range from 3386 to 3396 was swept every 0.5 min from the time the solution was brought to reaction pH with base. The free-radical concentration was determined by integrating the area under the absorption peak at moderate signal strength and low to moderate modulation amplitude and comparing it with an area *vs.* concentration plot for 4-carbamido-2,2,5,5-tetramethyl-Δ^3-pyrroline-1-oxyl, a stable free radical, under identical experimental conditions.

Results

Stoichiometry. The stoichiometry of the reaction was determined in two ways. The yield of *o*-quinone product was first studied as a function of experimental pH, where pH is $-\log [\mathrm{H}^+]$ in 50% methanol, 0.10 *M* KNO_3.[20] It was observed that in reactions at high alkalinity, the absorbance at 404 mμ reached a maximum height rapidly, and thereafter decreased to a value intermittent between zero and the maximum. The per cent yield of *o*-quinone could then be estimated from 100 times the maximum absorbance divided by the theoretical absorbance which should have been observed for complete consumption of starting material. The results of several runs in the presence and in the absence of 1:100 Mn (II)–35DTBP are shown in Figure 2. Reaction times were >1 hr for low pH runs and this ratio of Mn(II) to 35DTBP had no appreciable catalytic effect.

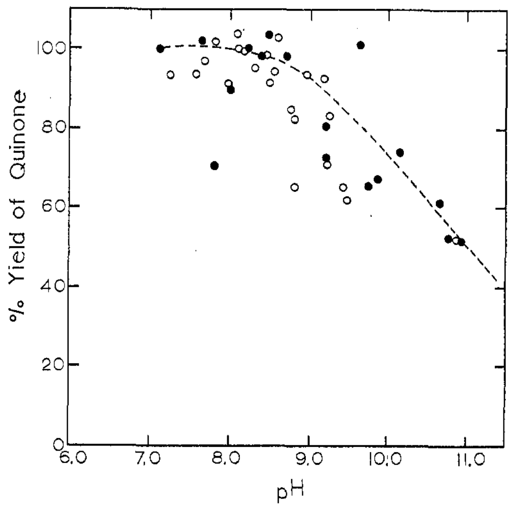

Figure 2. Per cent yield of 3,5-di-*t*-butyl-*o*-benzoquinone *vs.* reaction pH. Spectrophotometric measurements in which $A_{\max}$ compared with A_∞ expected, based on $[\mathrm{S}]_0$. $[\mathrm{S}]_0$ varied from 6.5×10^{-4} to 1.40×10^{-3} *M.* ○, 1:100 Mn(II)-35DTBP; ●, 35DTBP alone. 50% methanol, 0.10 *M* KNO_3, 25°.

In a second series of experiments O_2 consumed, and *o*-quinone and H_2O_2 formed, were simultaneously determined at different times during reaction. At pH <8.7 and low reaction time the quantity of hydrogen peroxide titrated was within 10% of stoichiometric (Table I) and can be expressed by the equation

$$35DTBP + O_2 \xrightarrow{k_{obsd}} 35DTBQ + H_2O_2 \qquad (1)$$

As reaction pH and time are increased the yield of hydrogen peroxide decreases to a greater extent than that of *o*-quinone.

Explanations for these lower yields were sought in terms of a reaction between hydrogen peroxide and the organic components in the system. *o*-Quinone autoxidation does not occur in neutral solution and oxygen uptake ceases coincident with attainment of A_{max} at 404 mμ. Hydrogen peroxide, however, does react with 35DTBQ in mildly alkaline solutions, confirming earlier observations in 75% methanol–water,[5] at rates increasing with alkalinity, but not in neutral solution. In the latter case 50 ml of 1.0×10^{-3} *M* 35DTBQ in 50% methanol, 0.10 *M* KNO_3, under air, to which 0.14 ml of 30% H_2O_2 was added, showed no change at 404 mμ after 1 hr but the yellow quinone color was completely discharged within 30 sec when the solution was made strongly alkaline. Control experiments in mildly alkaline solutions using chromotropic acid impregnated filter paper[26] showed negligible formaldehyde present from solvent oxidation. Highly reproducible results in the analytical determination of H_2O_2, which forms a nontitratable complex with formaldehyde,[27] is further evidence of minimal solvent oxidation.

Hydrogen peroxide may also decompose, either restoring oxygen to the atmosphere or reacting with substrate. In the absence of oxygen no reaction was observed spectrophotometrically between H_2O_2 (tenfold excess) and 35DTBP. Also, only an 8% loss titer over a 10-day period occurred for a peroxide solution in this 0.10 *M* KNO_3 medium with no pyrocatechol present. When 0.10 *M* $KHCO_3$ was added to this solution over half the titer was lost in 5 min. The reactivity of 35DTBP toward H_2O_2 is the same as that reported for 3,5-dimethyl-2-hydroxy-1,4-hydroquinone.[28]

On the basis of these experiments, the data in Table I was tested for the overall stoichiometry expressed by eq 1 together with 2–4, where P is equal to degradation

$$H_2O_2 + 35DTBQ \longrightarrow P \qquad (2)$$

$$\begin{cases} 2H_2O_2 \longrightarrow 2H_2O + O_2 & (3) \\ H_2O_2 + 35DTBP \longrightarrow 35DTBQ + 2H_2O & (4) \end{cases}$$

products. In runs above pH 9.6 this overall stoichiometry satisfies the results exactly.

Dismutation Equilibria. The equilibrium constant (eq 5) for the dismutation reaction was determined

$$2SQ\cdot^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Q + L^{2-} \qquad K_{SQ}{}^{QL} = \frac{[Q][L^{2-}]}{[SQ\cdot^-]^2} \qquad (5)$$

from direct potentiometric and esr measurements in the first p*K* region for 35DTBP ($SQ\cdot^-$ is semiquinone anion, Q is quinone, and L^{2-} is pyrocatechol dianion). Spectrophotometric methods, used frequently in the past,[29–32] were precluded because of the high pK_2 for 3,5-di-*t*-butylpyrocatechol[20] and complications from hydroxide adduct formation[23,29] and/or degradation.[32] The method here also differs from that of Yamazaki and Ohnishi,[33] who determined the rate constant for forward and back dismutation reaction of *p*-benzosemiquinone by esr, and that of Smith and Carrington,[34] who studied dismutation of the pyrocatechol radical in a similar way.

The appropriate material balance equations were combined to give

$$K_{SQ}{}^{QHL} = \frac{\left(T_Q - \frac{[SQ\cdot^-]}{2}\right)\left(T_L - \frac{[SQ\cdot^-]}{2}\right)}{[SQ\cdot^-]^2[H^+](K_2{}^H[H^+] + 1)} \qquad (6)$$

where $K_{SQ}{}^{QHL}$ is a constant for the overall reaction

$$H^+ + 2SQ\cdot^- \rightleftharpoons HL^- + Q \qquad (7)$$

A value of 3.75×10^{13} M^{-1} was determined for $K_{SQ}{}^{QHL}$ from two runs of 3.42×10^{-3} *M* *o*-quinone and two different substrate concentrations. Using 14.7 for log $K_1{}^H$,[4] $K_{SQ}{}^{QL}$ for eq 5 is 7.5×10^{-2}, of the same order of magnitude as for the more stable *p*-benzosemiquinones.[29] By combination with log $K_2{}^H$ the equilibrium constant $K_{SQ}{}^{QH_2L}$ for the process

$$2H^+ + 2SQ\cdot^- \overset{K_{SQ}{}^{QH_2L}}{\rightleftharpoons} H_2L + Q \qquad (8)$$

is found to be 8.48×10^{23} M^{-2}. These are the first reported dismutation constants involving an *o*-quinone radical anion.

Rapid-flow esr experiments at pH 7.6 and 8.6 in 0.1 *M* KHP buffers were used to obtain estimates of k_r and k_f, respectively. These were found to be

$$k_r = 4 \times 10^7\ M^{-1}\ sec^{-1} \text{ and } k_f = 1.0 \times 10^9\ M^{-1}\ sec^{-1}$$

Manometric Runs. Tabulations of initial rate constants, corrected for external atmospheric pressure and solvent partial pressure, as a function of pH and substrate concentration appear in Tables I and II. Reported rate constants have been corrected for solvent partial pressure, about 10 ± 1% of atmospheric for 50% methanol, by division by $(P_{atm} - p_{solv})/(P_{atm})$ where $p_{solv} = 0.485 \times p_{me} + 0.60 \times p_{H_2O}$ at reaction temperature. These factors are derived from known partial pressure data at two temperatures spanning

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Table II: Dependence of k_{obsd} on [35DTBP][a]

Mol of 35DTBP × 10^3	Mol of O_2 uptake × 10^3	Mol of 35DTBQ[b] × 10^3	Mol of H_2O_2[b] × 10^3	Reaction time, min	$10^1 k_{obsd}$,[c] min^{-1}
2.41	1.81	1.85	1.70	7	2.19
3.48	1.84	1.64	1.64	5	1.79
4.26	2.74	2.77	2.65	12	1.98
4.59	2.58	2.69	3.09	12	2.20
4.78	2.72	2.62	2.60	5	2.10
6.57	4.55	4.43	4.30	7	1.72
6.95	5.50	5.44	4.85	12	2.15
10.48	5.45	. . .	4.89	10	2.25
14.2	5.33	5.86	5.10	12	1.03
19.1	9.68	9.52	6.50	12	2.23
25.0	8.43	6.04[d]	7.61	12	1.30
39.8	15.6	5.25[d]	13.3	12	1.59
				Av	1.88

[a] Experimental conditions: pH 8.55, 0.10 *M* KNO_3, 50% methanol, 25°, 100% O_2 atm. [b] Average of two readings. [c] Corrected for solvent partial pressure by division of k_{obsd} by $(P_{atm} - p_{solv})/P_{atm}$. [d] Precipitate present.

25°.[35] Rate constants are reported for reactions at 25°, 760 mm.

Rate constants for disappearance of H_2L, HL^-, and L^{2-} forms may be calculated from the pH dependence of the reaction. If the concentrations of HL^- and L^{2-} are insignificant with respect to that of H_2L, we have

$$k_{obsd} = k_0 + (k_1 - k_0)\alpha_1 + (k_2 - k_0)\alpha_2 \qquad (9)$$

where k_0, k_1, and k_2 are the respective first-order rate constants and α_1 and α_2 are molar fractions of substrate present as monoanion and dianion. A plot of k_{obsd} (Table I) *vs.* α_1 is linear up to $\alpha_1 = 0.14$. The direct determination of k_2 is impossible with the present experimental arrangement even at lower [35DTBP], because this rate constant is too high. Consequently, k_0 and k_1 were determined graphically to be 5.6×10^{-2} and 4.2×10^0 min^{-1}, respectively, and k_2 was estimated to be 7×10^3 min^{-1} from a least-squares fit of the data in Table I to eq 9. This value for k_2 is only an estimate.

The results in Table II indicate that 35DTBP disappearance is first order over the concentration range 2.4×10^{-3} to 4.0×10^{-2} *M*. Above $[35DTBP]_0 = 2.0 \times 10^{-2}$ *M* and at pH 8.55 *o*-quinone is salted out of solution.

Reactions at different oxygen pressures were run at different alkalinities between pH 8.25 and 9.75. The initial rate constants k_0' were divided by those obtained from runs under 100% pressure (Table I) at the same pH and the average results at each oxygen pressure appears in Table III. The constant k_{obsd} can be seen to be a linear function of oxygen pressure from 1 atm to considerably below 0.60 atm.

Combined First- and Second-Order Kinetics. Manometric runs showed pronounced deviation from the expected first-order kinetics with time. The effect is shown clearly in typical runs in Figure 3. Here n_{O_2} represents the mole fraction of 35DTBP unreacted, based on the assumption that the ratio of 1 mol of O_2/mol 35DTBP reacting (eq 1) holds. For all runs at high alkalinities good linear plots were obtained for more than one half-life. At alkalinities below pH 9.5 the plots show curvature indicating a decrease in the net rate of oxygen uptake relative to first-order kinetics with time. 35DTBQ did not inhibit the reaction, based on spectrophotometric experiments. Going to 68% (wt/wt) CH_3OH, changing ionic strength and 35DTBP concentration, did not remove the curvature effect.

Table III: Dependence of k_{obsd} on Oxygen Pressure[a]

% Oxygen in atmosphere[b]	Ratio k_0'/k_{obsd}[c]
100.0	. . .
80.1	0.820
59.8	0.586
20.9	0.309

[a] Experimental conditions: manometric technique, 1.0×10^{-2} *M* 35DTBP, 0.10 *M* KNO_3, 50% methanol, 25°. [b] Corrected for solvent partial pressure. [c] k_0' is the initial first-order rate constant from runs in less than 100% oxygen atmosphere; k_{obsd} is the initial first-order rate constant from runs at same pH in 100% oxygen atmosphere (data in Table I), average of five runs each atmosphere.

Replots of the experimental points as dx/xdt *vs.* x, where x is the concentration of unreacted substrate, were linear (examples, inset in Figure 4) in all cases. This suggested the following rate law

$$-\frac{dx}{dt} = (k' - k''x)x \qquad (10)$$

Two general schemes could be used to explain these kinetics. For some reason preequilibrium conditions may not be maintained during the reaction and α_1 and α_2 decrease with time. For the region below pH 8.7 (eq 11) where $(k_2 - k_0)\alpha_2$ does not contribute significantly

$$-\frac{dx}{dt} = [k_1 + (k_1 - k_0)\alpha_1]x \qquad (11)$$

to the kinetics based on known K_n^H for 35DTBP[4] and values for the rate constants determined above. Assume $\alpha_1 = f(x)$, and since $\alpha_1 \rightarrow 0$ before $x \rightarrow 0$ (Figure 3), $\alpha_1 = \beta(x_0 - x_\infty)$ where $\beta = \alpha_{1,0}/(x_0 - x_\infty)$ and subscripts 0 and ∞ are for times $t = 0$ and t when $\alpha_1 = 0$, respectively. When $\alpha_1 = 0$, a limiting rate, $-dx/dt = k_0x$, should be observed, but experimental verification of this is complicated by a small amount of H_2O_2 decomposition which becomes relatively significant as the reaction progresses. Therefore the hypothesis must be tested in the region where k_{obsd} varies ($t = 0$ to 15 min)

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(35) "International Critical Tables," Vol. III, McGraw-Hill Publications, New York, N. Y., 1928, p 290.

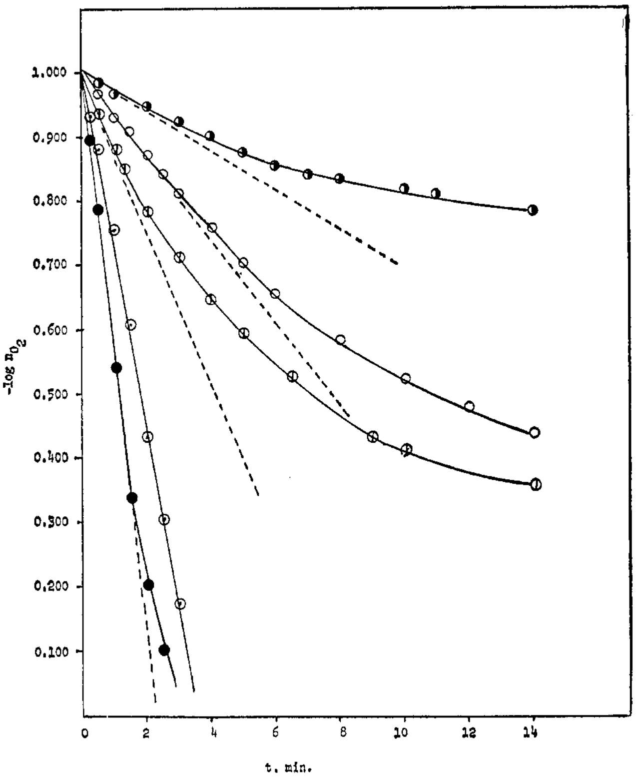

Figure 3. Manometric runs. $-\text{Log } n_{O_2}$ *vs.* reaction time, in min n_{O_2} based on theoretical consumption of O_2 assuming eq 1 holds exclusively. ◑, pH 8.00; ○, pH 8.38; ⦶, pH 8.87; ⊙, pH 9.67; ●, pH 10.1. 50% methanol, 0.10 *M* KNO_3, 25°.
---- Theoretical first-order plots.

as follows. Substituting α_1 in (10), letting $(k_1 - k_0) = \gamma k_0$, integrating, and rearranging, one obtains

$$\frac{1}{x} = \frac{Be^{k_0(1-\gamma\beta x_\infty)t} - \gamma\beta}{1 - \gamma\beta} \tag{12}$$

where B is the constant of integration. If now $(1/x)$ is differentiated at t and constant intervals, Δ, and the partials are obtained by division, then

$$\frac{\partial(1/x_{t+\Delta})}{\partial(1/x_t)} = e^{k_0(1-\gamma\beta x_\infty)\Delta} \tag{13}$$

Plotting $1/x_{t+\Delta}$ against $1/x_t$ at different Δ should yield a family of straight lines with slopes given by (14). In Figure 4 all runs below pH 8.5 are so treated for $\Delta = 1$ min, and the plots are linear with slopes between 0.92 and 1.03. No trends are observed and the average of the slopes is 0.96. The observed linearity is taken as a further test of the correctness of eq 10 in describing the kinetics. (Table IV lists the results expected from $1/x_{t+\Delta}$ *vs.* $1/x_t$ plots. Only combined first- and second-order kinetics satisfy the observed reaction rates.) The narrow range of slopes (within experimental error) reflects the relative insensitivity of β_{x_∞} over the narrow pH range studied.

For systems which exhibit good kinetic reproducibility with time, suitable for computer analysis, the above approach has an advantage over logarithmic treatments.[36] because the iterative step, based on preliminary estimates of x_∞, is eliminated. Here, x_∞ can be determined directly from the relationship

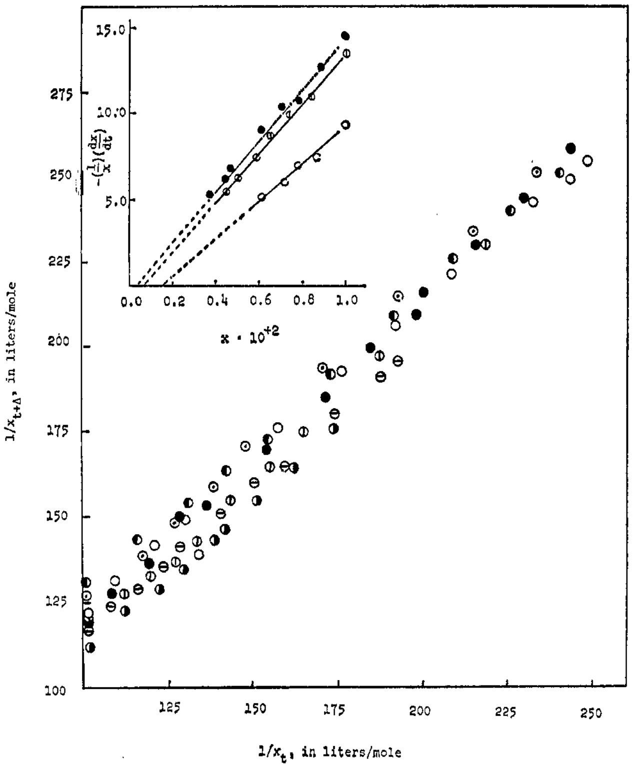

Figure 4. Manometric runs below pH 8.5 (Table I). $(1/x_{t+\Delta})$ *vs.* $(1/x_t)$, in M^{-1}. ◑, pH 8.00; ●, pH 8.10; ○, pH 8.22; ⦶, pH 8.35; ⊖, pH 8.36; ⊙, pH 8.38; ◐, pH 8.49. Δ = 1 min. Inset: $1/x(dx/dt)$ *vs.* x, x = unreacted [35DTBP]. Data from Table I. ○, pH 8.10; ⦶, pH 8.35, ●, pH 8.38.

Table IV: $1/x_{t+\Delta}$ *vs.* $1/x_t$ Plots for Various Rate Laws[a]

Order	Rate expression	$\partial(1/x_{t+\Delta})/\partial(1/x_t)$
0	$-\frac{dx}{dt} = k$	$\left\{\frac{x_0 - k(t+\Delta)}{x_0 - kt}\right\}^2$[b]
1	$-\frac{dx}{dt} = kx$	$e^{+k\Delta}$[c]
2	$-\frac{dx}{dt} = kx^2$	1.0
Combined 0 and 1	$-\frac{dx}{dt} = k_0 + k_1x$	$\frac{(Be^{-k_1t} - k_0)^2}{(Be^{-k_1(t+\Delta)} - k_0)^2}$[b]
Combined 1 and 2	$-\frac{dx}{dt} = (k_0 + k_1x)x$	$e^{k_0(1-\gamma\beta x_\infty)\Delta}$

[a] x is the mole fraction of the reactant. [b] Not constant; B is the constant of integration. [c] k may also equal $k_{obsd} - k_{inh}$, where k_{inh} is a first-order inhibition rate constant. [d] $\gamma = (k_1 - k_0)/k_0$; $\beta = \alpha_{1,0}/(x_0 - x_\infty)$ for the case where α_1 changes with time; or $k_i - k_sx_0$, where k_i = initial autoxidation rate constant and k_s = rate constant for side reaction, may also describe results.

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(36) K. J. Pedersen, *Acta Chem. Scand.*, 6, 285 (1952).

$$x_\infty = \{k_0 - 2.303 \log(\text{slope})\}x_0/\{k_{\text{obsd}} - 2.303 \log(\text{slope})\} \tag{14}$$

(slope from eq 13) and plots of k_{obsd} *vs.* $(x - x_\infty)$ should be linear with y intercept k_0. These plots were made for runs at low pH and, while there was some scatter in the results, the average intercept was 5.3×10^{-2} min^{-1}. Considering the lack of sensitivity under the experimental conditions, this agreement must be considered fortuitous.

One may equally well assume that a side reaction involving one of the products is occurring. Thus

$$-\frac{dx}{dt} = \{k_i - k_s(x_0 - x)\}x \tag{15}$$

where k_i = initial first-order rate constant for oxygen uptake, k_s = rate constant for the unknown reaction, and $(x_0 - x)$ is the product concentration. If k_s is pH independent, the ratio k_i/k_s increases with increasing alkalinity, and rate behavior approaches first-order kinetics throughout the entire run. This is qualitatively consistent with the results in Figure 3. Such a side reaction apparently does not come about by second-order decomposition of H_2O_2, restoring O_2 to the atmosphere, since this is inconsistent with linear k_{obsd} *vs.* x plots. Also, the rate of H_2O_2 decomposition was found to be too low to account for the observed curvature in Figure 3 under identical conditions. Similarly, 35-DTBP dimerization would show $-dx/xdt$ *vs.* x plots which intersect the origin, but this is clearly not the case (Figure 4, inset).

Table V: Semiquinone Yields in Kinetic Runs Compared with Predicted[a]

10^2[35DTBP]	pH	10^5[35DTBSQ] (max obsd)	10^5[35DTBSQ] (calcd)	% of calcd value
2.216[b]	9.10	2.48	1.462	170
2.487[b]	9.44	4.98	3.38	140
2.727[b]	10.00	13.73	12.40	110
2.988[b]	10.06	12.28	15.15	80
1.196	11.06	40.6	30.3	130
0.972	11.15	(36.1)[c]	28.2	130

[a] Experimental conditions: 0.10 *M* KNO_3, 50% methanol, 25°, 100% O_2 atmosphere. [b] Precipitate present. [c] Estimated value.

Electron Spin Resonance Runs. Semilogarithmic plots of [35DTBSQ] in the kinetic runs with those calculated from eq 16 is made in Table V on the assumption that dismutation is established faster than autoxidation proceeds. Maximum [35DTBSQ] should be observed at the halfway point of the autoxidation ($t_{1/2}$), *i.e.*

$$[\text{35DTBSQ}] = \left(\frac{(T_L/2)^2}{(1 + K_1^H[H^+] + K_1^H K_2^H[H^+]^2)7.5 \times 10^{-2}}\right)^{1/2} \tag{16}$$

when [35DTBP] = [35DTBQ]. There is fair agreement between calculated and observed values for $[\text{35DTBSQ}]_{\text{max}}$ at most alkalinities, but there is noticeable trend toward higher observed values as reaction pH decreases.

Spectrophotometric Runs. A limited number of kinetic runs were also made by following the increase in absorbance at 404 mμ as a measure of *o*-quinone formation. Slopes of tangents to the curves in the initial reaction stages gave first-order rate constants in good agreement with those derived from manometric runs, but the scatter was greater. No induction periods were observed in any runs. A least-squares curve-fitting program for consecutive first-order reactions was applied to data from spectrophotometric runs at high alkalinities without success because of failure to obtain convergence.

Discussion

Pyrocatechol and 35DTBP behave similarly in that all three forms are autoxidizable in solution and monoanion is the principal species undergoing autoxidation under mildly alkaline conditions (pK_1 region). A 125-ml aqueous solution of 0.1 *M* pyrocatechol monoanion has an initial absorption rate of 221 cm^3 of O_2 *M*/min compared with 2760 cm^3 *M*/min for 35DTBP monoanion in 0.10 *M* KNO_3, 50% methanol. No induction periods nor wall effects have been noticed in either study. The two media are sufficiently similar to suggest, in line with electrochemical studies,[37] that 35-DTBP is more readily autoxidizable, but that apart from the difference in rate coefficients, 35DTBP may in fact serve as a satisfactory model for the pyrocatechol to *o*-benzoquinone reaction.

The oxygen uptake kinetics of pyrocatechol and 35-DTBP do differ, however, in that with the latter the rate of oxygen uptake is found to exhibit a second-order decrease with time in moderately alkaline solutions. The effect is associated with the autoxidation system under study, because there was no appreciable difference in rates or time course plots with pyrocatechol using bubble-type and Warburg instruments and because the Mn(II)-catalyzed autoxidation does give the expected first-order oxygen uptake with time.[38]

Side reactions then appear to be responsible for the second-order effect. There is the possibility that at low alkalinities more autoxidizable species (the mono- and dianion) are not replenished fast enough to sustain the initial rate (eq 11–13). The overall autoxidation rate would than fall to that of the least reactive species. This explanation is unlikely because constant alkalinity is maintained, and the rate constant for neutral-

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[37] L. Horner and E. Geyer, *Chem. Ber.*, **98**, 2016 (1965); O. Ryba, J. Petranek, and J. Pospisil, *Collect. Czech. Chem. Commun.*, **30**, 2157 (1965); W. Flaig, H. Beutelspacher, H. Reimer, and E. Kalke, *Justus Liebigs Ann. Chem.*, **719**, 96 (1969).

[38] C. A. Tyson and A. E. Martell, manuscript in preparation.

ization and [OH^-] are both high (instant attainment of equilibrium in potentiometric studies).[20] It would appear also that 35DTBP dimerization and H_2O_2 decomposition are ruled out by the rate expression (eq 15). The second-order effect then apparently involves stoichiometric ratios of one of the products with 35DTBP, but the nature of this reaction remains obscure.

A side reaction involving product, particularly if reversible, could lead to low 35DTBQ yields and/or reduced rates at high [35DTBP] in the absence of metal ion catalysts. Positive factors contributing to low *o*-quinone yields are an H_2O_2 reaction with 35DTBQ at high alkalinities (Table I) and shifts in the acid–base buffer equilibrium, resulting in a decrease in [OH^-] with time (over one pH unit with $KHCO_3$). Under some conditions induced H_2O_2 decomposition can increase the rate of product formation and the yield, but reactions reported here (Figure 2) still require more than 1 hr for completion, which is not efficient compared with metal catalysis.[5]

Kinetic and other data were analyzed for the possibility of resolving the 35DTBP → 35DTBQ mechanism. Several reaction pathways are possible after initial electron transfer to oxygen and most of these have been summarized by LuValle and Weissberger.[39] Mechanisms involving semiquinone or *o*-quinone pyrocatechol dimers or reversible adducts cannot be ruled out entirely until the reason for the fall off in uptake rate is determined. Evidence from potentiometric, spectrophotometric, esr (both equilibrium and kinetic experiments), and inhibition (no effect with 35DTBQ added initially) studies is all negative with respect to detection of dimers. In any respect, if they exist, these are side reactions having little bearing on the one-electron, two-electron transfer problem.[17]

Autoxidation of 35DTBSQ does not compete with that of 35DTBP for several reasons. There was no induction period observed in any manometric or spectrophotometric run, a criterion for this reaction pathway to be dominant (*e.g.*, durosemiquinone).[40] The semiquinone concentration would not be greater than that determined by dismutation equilibria (Table V). The disappearance of semiquinone would be first order and pH independent in contrast to what is observed (Figure 5). If autoxidation of semiquinone is fast relative to that of substrate, a condition which must subtend from the availability of other reaction pathways with potentially high rate constants, it is hard to explain why the 35DTBSQ signal in kinetic and product identification studies lasts as long as it does.

The reaction mechanisms applicable are (1) semiquinone is first formed, followed by disproportionation to give 35DTBQ (eq 5, 7, and 8) and (2) the *o*-quinone is first formed in a two-electron transfer reaction, and semiquinone results from the reaction of 35DTBQ with starting material.

A central problem is the disposition of superoxide radicals, likely to be present in mildly alkaline solutions.[41–44] It is most probable that $O_2\cdot^-$ does not have a sufficiently long lifetime in the bulk of the solution to react with semiquinone radicals in subsequent steps, because secondary radical species were not detected in esr work and because $O_2\cdot^-$ disproportionation should be fast in 50% methanol, as it is in aqueous solution ($k = 10^7–10^9/M^{-1}$ min.[41,42] That is, for a reaction between 35DTBSQ and $O_2\cdot^-$ to be competitive it must have a rate constant comparable to or greater than that of $O_2\cdot^-$ disproportionation, which means that the former reaction would be indistinguishable kinetically from a two-electron transfer. It should also be noted from Table I that the maximum amount of $O_2\cdot^-$ disproportionation possible, as estimated from the difference in 35DTBQ and H_2O_2 yields for reactions in Table II, quenched at shorter times, is markedly lower. In the absence of quantitative data on the extent of H_2O_2 decomposition

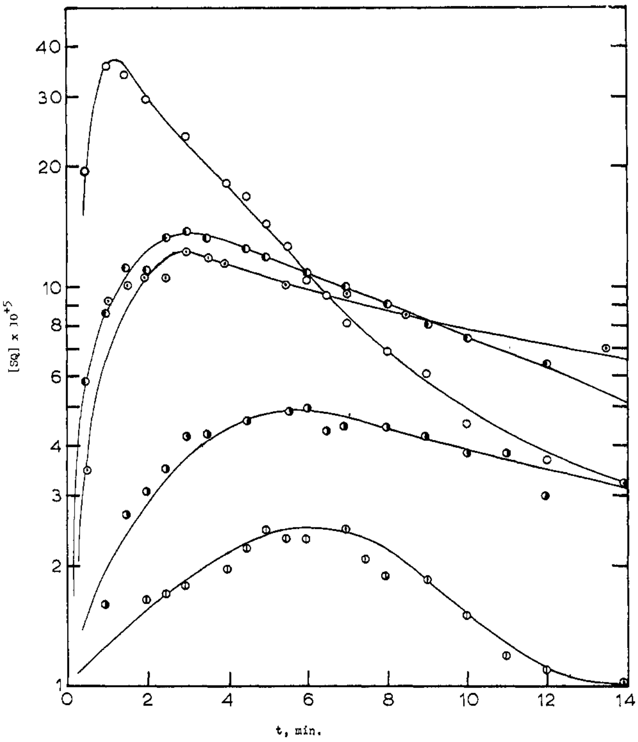

Figure 5. Esr runs. Molar concentration of 35DTBSQ ($\times 10^5$) *vs.* reaction time, in min: ⦶, pH 9.10; ◑, pH 9.44; ◐, pH 10.00; ⊙, pH 10.05; ○, pH 11.15. 50% methanol, 0.10 M KNO_3, 24–25°.

(39) J. E. LuValle and A. Weissberger, *J. Amer. Chem. Soc.*, **69**, 1567 (1947).

(40) T. H. James and A. Weissberger, *ibid.*, **60**, 98 (1938).

(41) J. Rabani, W. A. Mulac, and M. S. Matheson, *J. Phys. Chem.*, **69**, 53 (1965); J. Rabani and S. O. Nielson, *ibid.*, **73**, 3736 (1969).

(42) G. Czapski and L. M. Dorfman, *ibid.*, **68**, 1169 (1964).

(43) G. Czapski and B. H. J. Bielski, *ibid.*, **67**, 2180 (1963).

(44) J. H. Baxendale, W. G. Barb, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 462, 591 (1951).

with substrate not present, which should significantly lower the 15% maximum observed, we must conclude that disproportionation is a minor pathway for disposition of $O_2\cdot^-$ radicals.

Superoxide radicals then disappear either through a reaction with 35DTBP (termed hereafter, a free-radical mechanism)[45] or with 35DTBSQ (termed an ionic mechanism)[45] or both. It may be demonstrated, using steady-state approximations, that all three possibilities lead to essentially identical rate expressions and are consequently indistinguishable. Also, the high reactivity of 35DTBP toward free radicals was demonstrated by adding a stoichiometric amount of DPPH radicals to an acidified solution and observing the instantaneous bleaching of the purple hydrazyl color.

The esr data were analyzed for the possibility of resolving the mechanism. Several researchers[46] succeeded in doing this with enzyme reactions by showing that k_r' is too small relative to k_{obsd} in eq 17 to account for the observed semiquinone concentrations.

$$\frac{\mathrm{d}[\mathrm{SQ}\cdot^-]}{\mathrm{d}t} = k_{\text{obsd}}[\text{35DTBP}] + k_r'[\text{35DTBQ}][\text{35DTBP}] - k_f[\mathrm{SQ}\cdot^-]^2 \qquad (17)$$

where

$$k_r' = k_r/(1 + [\mathrm{H}^+]K_1^{\mathrm{H}} + [\mathrm{H}^+]^2K_1^{\mathrm{H}}K_2^{\mathrm{H}})$$

Comparison of k_r and k_f with k_{obsd} at neutral pH's for autoxidation of 10^{-3} to 10^{-2} M 35DTBP indicates that the mechanism could not be resolved ($k_r = 8.5$ M^{-1} min^{-1} at pH 7.6, [35DTBP] $= 4.0 \times 10^{-3}$ M, whereas $k_{\text{obsd}} = 6 \times 10^{-2}$ min^{-1} at the same pH). The atmospheric pressure would have to be increased several orders of magnitude to overcome the limited solubility of oxygen and to attain a high enough autoxidation rate to distinguish directly between pathways.

From time to time investigators have alluded to semiquinone as an intermediate in the autoxidation of pyrocatechol, implying that a free-radical mechanism occurs. No evidence for or against this point of view insofar as the *o*-quinone reaction is concerned has been found in the present work, and none has been found in the literature. The work here does not rule out the possibility that sensitive rapid-flow esr measurements in near neutral solutions may provide such evidence for the H_2L species. What is important to recognize in advance is that such kinetic evidence need not hold for the more autoxidizable HL^- or L^{2-} species.

Acknowledgment. The authors gratefully acknowledge the assistance of Dr. Helen Brooks in running the rapid-flow experiments.

[45] J. K. Kochi, *Science*, **155**, 415 (1967).

[46] T. Nakamura, "Free Radicals in Biological Systems," M. S. Blois, Jr., H. W. Brown, R. M. Lemmon, R. O. Lindblom, and M. Weissbluth, Ed., Academic Press, Inc., New York, N. Y., 1961, p 169 (laccase); I. Yamazaki and L. H. Piette, *Biochem. Biophys. Acta*, **50**, 62 (1961) (ascorbic acid oxidase); I. Yamazaki, H. S. Mason, and L. H. Piette, *Biochem. Biophys. Res. Commun.*, **1**, 336 (1959) (peroxidase).