

THE AIR OXIDATION OF 4,6-DI (2-PHENYL-2-PROPYL) PYROGALLOL. SPECTROSCOPIC AND KINETIC STUDIES OF THE INTERMEDIATES.

by

HENRY I. ABRASH

Department of Chemistry, Carlsberg Laboratory
Gamle Carlsbergvej 10 - DK-2500 Copenhagen, Valby¹

¹) Current address: Department of Chemistry, California State University at Northridge,
Northridge, California 91324, USA

Key words: 4,6-di (2-phenyl-2-propyl) pyrogallol,
consecutive reactions, oxidation, oxygen, pH, quinone, semiquinone, spectra

Two colored extinction bands, one with λ_{max} near 520 nm and the other near 770 nm, form and decay during air oxidations of 4,6-di(2-phenyl-2-propyl) pyrogallol in alkaline methanol. The 770 nm band appears to be due to the semiquinone monoanion while the extinction near 500 nm is thought to be due to both the semiquinone and 3-hydroxy-*o*-quinone. Although the rates of formation and decay of the two bands are indistinguishable in the presence of excess dissolved oxygen, the 770 nm band disappears slightly before the 500 nm extinction when the pyrogallol reactant is initially in excess of the dissolved oxygen. Except at high methoxide concentrations, the kinetics indicate a system of two consecutive reactions with pseudo first-order rate constants k_1 and k_2 . The pH' dependence of k_1 indicates that the neutral pyrogallol, its monoanion and dianion all react, the rate increasing with the negative charge of the species. The k_2/k_1 ratio is constant at 5 from pH' 11 to 16. Extinction coefficients at both wavelengths increase with pH'. The 770 nm extinction disappears immediately after acidification while the 500 nm extinction decays at a rate consistent with oxidation. The rate constants k_1 and k_2 are insensitive to changes in pyrogallol concentrations, indicating an absence of irreversible semiquinone disproportionations. Increased oxygen concentration raises k_1 and k_2 to the same extent.

1. INTRODUCTION

There are many reports of colored intermediates of pyrogallol oxidations. Pyrogallol forms a green intermediate during air oxidation in alkaline solutions (17, 18), and peroxidase catalyzed oxidation of pyrogallol at neutral pH produces a transient extinction at 600 nm (20).

Air oxidation of methyl gallate in aqueous ammonia is accompanied by a transient rose color (13). Several authors (9, 24) have described a violet color during air oxidation of 4,6-di-*tert*-butylpyrogallol and 4,6-di(2-phenyl-2-propyl)pyrogallol (2) (Fig. 1, I). SALFELD (23) has recorded the spectrum of a violet in-

Molecular Structures

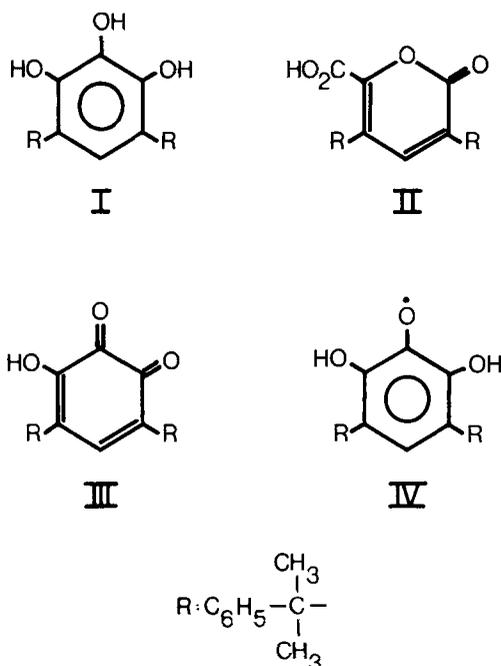


Figure 1. Structures of molecules involved in this study.

- I. 4,6-di(2-phenyl-2-propyl)pyrogallol; II. 3,5-di(2-phenyl-2-propyl)-2-pyrone-6-carboxylic acid; III. quinone derived from 4,6-di(2-phenyl-2-propyl)pyrogallol; IV. semiquinone derived from 4,6-di(2-phenyl-2-propyl)pyrogallol.

intermediate, presumably a 3-hydroxy-*o*-quinone, formed by silver oxide oxidation of 4,6-di-*tert*-butylpyrogallol in carbon tetrachloride.

Spectroscopic studies of these intermediates and measurement of their rates of formation and decay can yield important information concerning the mechanism of pyrogallol oxidations. The current work describes the kinetics of the spectroscopic changes accompanying the air oxidation of 4,6-di(2-phenyl-2-propyl)pyrogallol in alkaline methanol and the effects of pH and reactant concentrations on the reaction rates and intermediate spectra.

2. MATERIALS AND METHODS

2.1. Reagents and solvents.

4,6-Di(2-phenyl-2-propyl)pyrogallol, m.p. 119.5-120°C, was prepared from pyrogallol and 2-phenylpropene by the method of JÖNSSON (16).

The following reagents were used in kinetic studies: analytic grade methanol and analytic grade 5,5-diethylbarbituric acid, E. Merck, Darmstadt; analytic grade phthalic acid and practical grade sodium methoxide, Fluka AB, Switzerland; oxygen and nitrogen, Dansk Ilt og Brint Fabrik A/S, Copenhagen.

2.2. Methanolic buffers and pH' measurement.

The alkalinity of all methanolic solutions, both sodium methoxide and buffer solutions, is reported as pH' values – the negative logarithm of the activity of protonated solvent (lyonium ion) compared to unit activity of an ideal lyonium ion in the same solvent (5).

The molarity of a 0.195 M-sodium methoxide stock solutions in methanol was determined by adding 50 μ l of this solution to an aqueous solution containing 50 μ l of 0.196 M-phthalic acid in methanol and titrating to the second inflection point of phthalic acid. The titrations were performed by the stepped titration method with 0.1030M-aqueous NaOH. The automatic titrator (Radiometer, Copenhagen) consisted of a PHM 64 research pH meter with a G 2222C glass electrode and a K 130 calomel electrode, a TTT 60 titrator, a ABU 13 autoburet and a REC 61 Servograph recorder equipped with a REA 160 Titrigraph module and REA 300 Titrigraph pen drive. The pH meter was standardized at pH 7.00.

This stock sodium methoxide solution was used to prepare a series of more dilute methoxide solutions ranging down to 0.0049 M. The pH' values of the sodium methoxide solutions in the kinetic runs were estimated assuming ideal solutions and a $pK_{\text{autoprotolysis}}$ value of 16.7 for methanol (6). Corrections were made for dilution by the reactant stock solutions and for neutralization by the pyrogallol reactant, assuming that this compound acts as a monoprotic acid in the more dilute sodium methoxide solutions.

Methanolic phthalate buffers covering the pH' range 11-12.1 were prepared according to the data of BROSER and FLEISCHAUER (8). The appropriate amount of 0.195 M-phthalic acid stock solution was mixed with 2.50 ml 0.196 M-sodium methoxide and the solution diluted to 25.0 ml.

Methanolic veronal buffers covering the pH' range 12-13.5 were prepared by dissolving various amounts of 5,5-diethylbarbituric acid in 22.5 ml methanol and adding 2.50 ml 0.195 M-sodium methoxide. Although this procedure probably forms sodium 5,5-diethylbarbiturate in excess of its solubility in methanol, the solutions were stable for several days without precipitation or pH' change. The pH' values of the veronal buffers were determined by adding small amounts of bromthymol blue solution and recording the ratio of the extinction at 617 nm (the λ_{\max} of the conjugate base of bromthymol blue) and 493 nm (the isosbestic point for the acid-base reaction). Experiments with phthalate buffers showed the validity of the equation:

$$a'_H = 1.67 \times 10^{-12} \left[\frac{6.77}{r - 0.22} - 1 \right]$$

where a'_H is the lyonium ion activity defined in terms of an ideal methanolic solution and r the ratio of the extinctions at 617 and 493 nm. This equation was used to calculate the pH' values of veronal buffers in the 12-12.6 range. From these pH' values, we calculate a K'_a value of 2.5×10^{-13} for 5,5-diethylbarbituric acid in methanol and use this value to compute the pH' values of more alkaline veronal buffers. The K'_a value agrees closely with that reported by TABAGUA (25). The use of this somewhat imprecise method to estimate pH' values of veronal buffers in the 12.6-13.5 range is justified by the relative insensitivity of the reaction rates to pH' in this range. (See section 3).

2.3. Kinetics.

Spectroscopic changes occurring during the air oxidation of 4,6-di(2-phenyl-2-propyl)-pyrogallol were recorded on a Cary 118 UV-visible spectrophotometer (Varian Corp.,

Monrovia, Calif.). A rapid mixing device of the type described by AULD and FRENCH (4) was used to follow the fast reactions in more alkaline solutions. This apparatus, thermostatted at 25°C by Hetofrig Circulating Thermostat (Birkerød, Denmark), contained 1.0 ml of the appropriate methanolic solution, and this solution was stirred for several minutes before initiating the reaction to assure equilibration of temperature and gas solubility. The spectrophotometer was set to run at a constant wavelength with the pen scale chosen so that the expected extinction would rise above two tenths full-scale deflection but not reach full deflection. The chart speed was chosen to give a convenient display of the data, the most rapid speed being one inch per ten seconds. After the pen had been brought to zero with the zero suppression switch and balance adjust control, the extinction was recorded and a predetermined volume (usually 200 μ l) of an approximately 2.5 mM solution of 4,6-di(2-phenyl-2-propyl)pyrogallol in nitrogen purged methanol was injected into the reaction cell from a Hamilton 1001 Microlyter syringe (Whittier, Calif.) through a teflon tube. Extinction was recorded until it had fallen to less than one tenth full scale. In experiments in which the extinction did not rise above 0.3 full scale, extinction was recorded until it decreased to 0.05 full scale. Between experiments, the Microlyter syringe was refilled from a reservoir consisting of a 10 ml syringe via a Hamilton 4LLLF4 four-way valve. The solution from the previous experiment was removed from the reaction cell by means of a syringe connected to the lower part of the cell, and the cell was washed with one ml of the solution to be used in the next experiment.

Slower reactions at lower pH' values were measured in a thermostatted silica cell against a reference cell containing methanol. With 3.0 ml of the methanolic buffer in the sample cell, the pen was brought to zero with the balance control. The cell compartment cover was then removed, the desired volume (usually 50 μ l) of *ca* 25 mM reactant stock solution added from a Levy-Lang micro pipet, the solution stirred with a teflon rod, and the cell compartment cover quickly replaced. Extinction was

recorded within ten seconds of the start of the reaction.

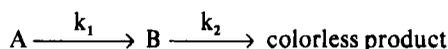
Experiments were performed with air-saturated or oxygen-saturated solutions. Oxygen-saturated solutions were prepared by bubbling oxygen through the sodium methoxide or buffer solution for at least ten minutes just before the experiment, and the spectrophotometer cell compartment was flushed with oxygen during the experiment. Estimates of oxygen concentrations are based on data in the International Critical Tables (15). In all cases, the initial concentration of dissolved oxygen was at least three times that of the pyrogallol reactant.

In spite of efforts to prevent exposure of the pyrogallol reactant stock solutions to air, these solutions darkened in the course of several hours due to exposure during transfer or air leaks in the reservoir syringe. In later experiments, stock solutions were discarded when they darkened enough to produce high initial extinction values. We have reported data from earlier runs with partially oxidized stock solutions after correcting for this oxidation. (See section 2.4.)

Some experiments involve rapid acidification of the solution after the colored intermediates had accumulated at high pH'. In the experiment shown in Fig. 4, 200 μ l of reactant stock solution was added to 1.0 ml of 0.0023 M-sodium methoxide. After about 30 seconds, 25 μ l of 28 mg/ml. phthalic acid in methanol was added through a hole in the top of the fast mixing apparatus, the hole quickly closed with a rubber stopper and the extinction recorded. For comparison, the phthalic acid was first mixed with the sodium methoxide and the rate of reaction in the resulting buffer measured by the fast reaction method.

2.4. Data analysis.

Except for runs at sodium methoxide concentrations above 0.04 M, the data fit the equation for the formation of an intermediate in a system of two pseudo first-order reactions.



$$(B) = \frac{k_1(A)_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

or

$$E_\lambda = \frac{k_1 \epsilon_\lambda l (A)_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (\text{eqn.1})$$

where A is 4,6-di(2-phenyl-2-propyl)pyrogallol, B the colored intermediate, E_λ its extinction and ϵ_λ its molar extinction coefficient at the wavelength of the experiment, l the path length of the cell and k_1 and k_2 the two pseudo first-order rate constants. Experiments at methoxide concentrations greater than 0.04 M deviate from eqn. 1 by showing higher extinctions than predicted at longer reaction times. In other words, k_1 appears to decrease with time. This effect is independent of the initial concentration of the pyrogallol, so it does not appear to be due to a decrease in the dissolved oxygen concentration with time. While concerned about the significance of this unexplained deviation, we have fit the data at shorter reaction times in these runs to eqn. 1 by a suitable choice of k_1 , k_2 and ϵ_λ . These parameters were estimated for each run by the least-squares method of ALCOCK et al. (3).

Kinetic curves for partially oxidized stock solutions of 4,6-di(2-phenyl-2-propyl)pyrogallol had high initial extinctions. These curves were analyzed by extrapolating the extinction back to a corrected zero time and then treating the data as before. This procedure is justified because the integrated rate equation for a case in which the initial concentration of B is less than $k_1(A)_0/(k_2 - k_1)$ is:

$$(B) = \frac{k_1 (A)_0}{k_2 - k_1} (e^{-k_1(t+\Delta)} - e^{-k_2(t+\Delta)})$$

where Δ is the zero time correction.

3. RESULTS

The air oxidation of 4,6-di(2-phenyl-2-propyl)pyrogallol in strongly alkaline methanolic solution is accompanied by the transient formation of two broad extinction bands in the visible region, one with λ_{\max} near 520 nm, the other at about 770 nm (Fig. 2). Strong product extinc-

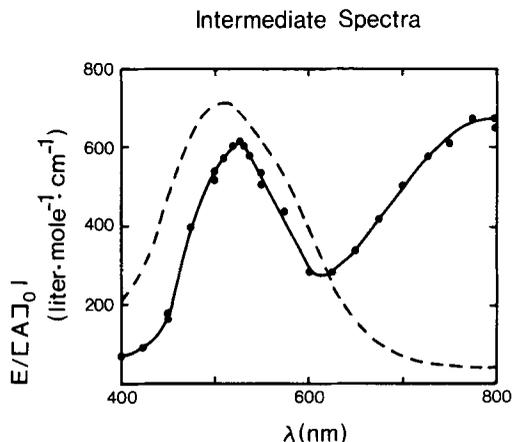


Figure 2. Spectra of the intermediates of air oxidation of 4,6-di(2-phenyl-2-propyl)pyrogallol.

●: $E_{\max}/(A)_0I$ in air saturated 0.02 M-sodium methoxide. $(A)_0 = 0.40$ mM. Broken line: spectrum of intermediate formed when 0.23 mM-4,6-di(2-phenyl-2-propyl)pyrogallol was oxidized for 30 seconds in 0.002 M-sodium methoxide and then neutralized with phthalic acid.

tion in the ultraviolet region hindered attempts to study intermediate extinctions below 400 nm. Extinction at 250 nm does rise to a maximum after about thirty seconds and then decays during the air oxidation in 0.002 M-sodium methoxide, and this transient extinction is stronger than those at 200 and 275 nm. Product extinction dominates between 300 and 350 nm, and the extinction at these wave lengths increases steadily during oxidation.

In the presence of excess dissolved oxygen, the two visible intermediate extinction bands form and decay with indistinguishable rates over the entire range of pH', oxygen concentration and pyrogallol reactant concentration studied. With the exception of experiments at sodium methoxide concentrations of 0.04 M or

greater, the extinction versus time curves are adequately described by eqn. 1. The curves at high methoxide concentration show decreasing rate constants for decay during the latter part of the reaction. Nevertheless, we have fit the early portions of these curves to eqn. 1 and ignored the deviations at longer times. While the values obtained for the kinetic constants in these experiments merit some scepticism, we feel that they indicate real trends in the high pH' range.

In applying eqn. 1, we have assumed that the larger of the two rate constants is k_2 and the smaller k_1 . The justification for this assumption of a slow reaction followed by a fast one is the observed change in extinction in solutions in which the pyrogallol reactant is in excess of the dissolved oxygen (see Section 4). In such cases, an initial rapid increase and decrease of extinction is followed by a slower formation and decay of the intermediates.

Figure 3 shows the influence of pH' on k_1 and k_2 and the extinction coefficients for reactions in air-saturated methanol at 25°C. There is no significant difference between the rate constants determined at 500 nm and those obtained under identical conditions at 770 nm. The values of k_1 at both wavelengths fit a curve describing a mechanism in which neutral reactant, monoanion and dianion react with pseudo first-order rate constants k^0 , k^- , $k^{=}$ respectively:

$$k_1 = \frac{k^0(H^+)^2 + k^-K_1(H^+) + k^{=}K_1K_2}{(H^+)^2 + K_1(H^+) + K_1K_2} \quad (\text{eqn. 2})$$

where K_1 and K_2 are the first and second dissociation constants. The following values give a reasonable fit of the data.

$$k^0 = 4 \times 10^{-4} \text{ sec}^{-1}; \quad k^- = 0.016 \text{ sec}^{-1}; \\ k^{=} = 0.20 \text{ sec}^{-1}$$

$$K_1 = 2.5 \times 10^{-13}; \quad K_2 = 1 \times 10^{-16}$$

The data presented in Fig. 3b indicate that k_2/k_1 ratios are independent of pH'. This can be seen from the fit of the k_2 values to a theoretical curve calculated from assumption $k_2 = 5k_1$ where k_1 is calculated from eqn. 2. While there

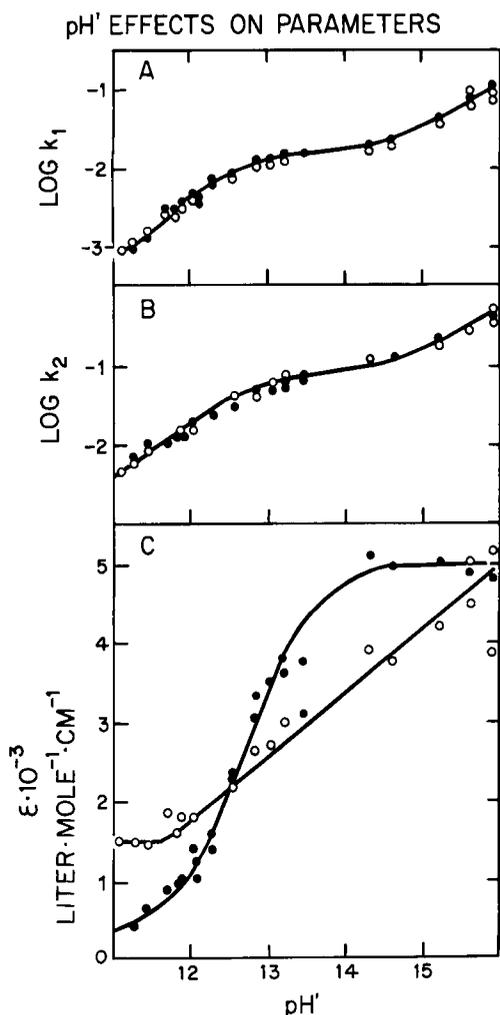


Figure 3. The effect of pH' on k_1 , k_2 and extinction coefficients. All experiments were performed in air-saturated methanol at 25°C. o: results at 500 nm; ●: results at 770 nm. 3a: $\log k_1$ versus pH'. The solid curve is drawn according to eqn. 2. For the parameters $k^0 = 4 \times 10^{-4} \text{ sec}^{-1}$, $k^- = 0.016 \text{ sec}^{-1}$, $k = 0.20 \text{ sec}^{-1}$, $K_1 = 2.5 \times 10^{-13}$, $K_2 = 1 \times 10^{-16}$; 3b: $\log k_2$ versus pH'. The solid curve is drawn for $k_2 = 5k_1$, where k_1 is given by eqn. 2 and the parameters listed in 3a.; 3c: extinction coefficients versus pH'. The extinction coefficients are calculated according to eqn. 3 assuming $r = 5$.

is considerable scatter in the individual estimates of k_2/k_1 , all values for this ratio are in the 1.9-7.6 range, and 40 out of 42 fall in the 3-7 range. There is no apparent trend in the individual estimates with pH'.

The maximum extinction observed during a run (E_{\max}) increases with pH' both at 500 nm and 770 nm. A plot of ϵ versus pH' (Fig. 3c) shows these effects. In computing ϵ , we have assumed a constant k_2/k_1 ratio (r) equal to five and used the equations (11).

$$(B)_{\max} = (A)_0 r^{-r/r-1}$$

$$\epsilon = \frac{E_{\max}}{(B)_{\max} l} = \frac{E_{\max} r^{r/r-1}}{(A)_0 l} \quad (\text{eqn. 3})$$

in order to avoid scatter due to random variations in the individual estimates of r . The 770 nm intermediate is completely absent at low pH', the only extinction at this wavelength being due to the 500 nm intermediate. The extinction coefficient at 770 nm increases to a constant value of 5.0×10^3 liter \cdot mole $^{-1}$ \cdot cm $^{-1}$ above pH' 14, and the inflection point for this increase occurs at about pH' 12.7. Extinction at 500 nm is constant at an ϵ value of 1.5×10^3 liter \cdot mole $^{-1}$ \cdot cm $^{-1}$ below pH' 12 but gradually rises with increasing pH' to about 5×10^3 liter \cdot mole $^{-1}$ \cdot cm $^{-1}$ in the 15-16 pH' range. It is not clear from the data whether this is a steady increase or whether it involves an inflection point.

The 770 nm intermediate reacts very rapidly with H^+ . This is shown by an experiment in which the intermediates were allowed to accumulate by oxidation for thirty seconds in 0.002 M-sodium methoxide and the solution was then acidified by addition of methanolic phthalic acid. Rapid acidification causes an immediate loss of extinction at 770 nm (Fig. 2) even though the rate of oxidative decay of this intermediate is slow at low pH'. It also appears that the 770 nm intermediate forms by a rapid reaction between methoxide ion and an intermediate formed in neutral solution. To demonstrate this, we allowed a neutral solution of 4,6-di(2-phenyl-2-propyl) pyrogallol to slowly oxidize and then added it to pH' 11.7 phthalate buffer in one case and 0.002

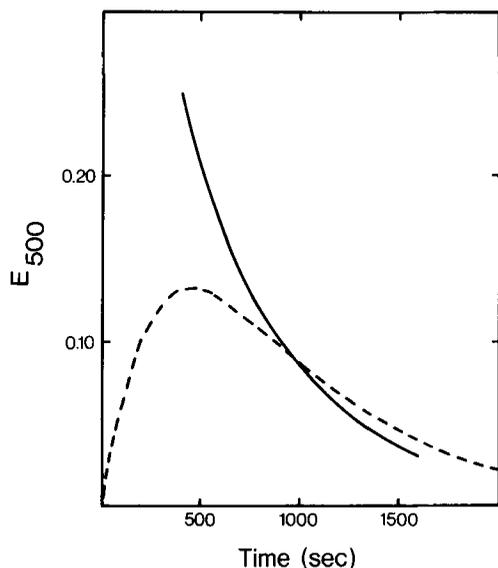
Decay of E_{500} in acidified solutions

Figure 4. Change in ϵ_{500} after acidification of a partially oxidized solution.

Solid line: E_{500} after 3.0 ml. of 0.38 mM-4,6-di(2-phenyl-2-propyl) pyrogallol was oxidized for 30 seconds in 0.0023 M-sodium methoxide and then neutralized with 25 μ l 0.20 M-phthalic acid. The time scale has been displaced 400 seconds to the right. *Broken line:* 0.38 mM-pyrogallol reactant in the buffer formed from 3.0 ml 0.0023 M-sodium methoxide and 25 μ l 0.20 M-phthalic acid.

M-sodium methoxide in another and observed the extinction changes at 770 nm using fast reaction techniques. In both cases the initial extinction was high, and the extinction reached its maximum more quickly than with fresh reactant stock solutions.

In contrast, the 500 nm extinction does not respond rapidly to acidification (Fig. 2 and 4). The extinction immediately after acidification of a partially oxidized solution is approximately the same as at high pH' and nearly twice the maximum extinction obtained when the pyrogallol reactant was oxidized in the buffer formed by adding the same amount of phthalic acid to the same volume of sodium methoxide. The constants estimated for oxidation in the low pH' buffer are $k_1 = 0.0013 \text{ sec}^{-1}$, $k_2 = 0.0039 \text{ sec}^{-1}$ and $\epsilon_{500} = 1.8 \times 10^3 \text{ liter-mole}^{-1}\text{cm}^{-1}$. The

extinction change after acidification of the partially oxidized solution fits the equation:

$$E = 0.205e^{-0.0016t} + 0.045e^{-0.0036t}$$

The close agreement between the rate constants for oxidation in the buffer and the exponential terms found in the acidification experiment will be discussed in section 4.

Table I shows the effect of the initial concentration of 4,6-di(2-phenyl-2-propyl)pyrogallol on the apparent rate constants. Within the limited range of concentration (0.07-0.34 mM) allowed by the sensitivity of the spectroscopic method and the requirement of a large excess of dissolved oxygen, the apparent k_1 values at both wavelengths and pH' values appear to be independent of reactant concentration. The situation is not as clear for the less precise estimates of k_2 , and we have used two other criteria concerning the constancy of the k_2/k_1 ratio. If this rate is constant, k_1 should be inversely proportional to the time it takes for the extinction to reach a maximum (t_{\max}), and E_{\max} should be proportional to $(A)_0$. This seems to be the case for both wavelengths at pH' 13.76. The data at pH' 11.70 show a slight increase in $k_1 t_{\max}$, both at 500 and 770 nm, as reactant concentration decreases. In the case of the 770 nm intermediate, E_{\max} appears to be proportional to reactant concentration while E_{\max} at 500 nm does not rise as much as reactant concentration.

Table II contains data obtained in oxygen-saturated solutions and, for comparison, in air-saturated solutions at the same pH'. Increased oxygen concentration increases both rate constants and, to judge from the constancy of E_{\max} and $k_1 t_{\max}$, both rate constants are affected to the same extent. This increase in rate constant is a factor of about 3.5. While this is considerably less than the 4.8-fold increase in oxygen concentration predicted by Henry's law, the data are not precise enough to decide whether or not the pseudo first-order rate constants are strictly proportional to the concentration of dissolved oxygen.

The two extinction bands are affected differently by an insufficiency in dissolved oxygen, the extinction at 770 nm being weaker

Table I

Effect of concentration of 4,6-di(2-phenyl-2-propyl) pyrogallol on rate constants

(A) ₀ (mM)	t _{max} (sec)	E _{max}	k ₁ × 10 ² (sec ⁻¹)	k ₂ × 10 ² (sec ⁻¹)	ε × 10 ⁻³ (liter × mole ⁻¹ × cm ⁻¹)
A. Experiments at 500 nm pH' 13.96					
0.342	30	0.164	1.11 ± 0.01	7.9 ± 0.1	4.77 ± 0.88
0.187	32	0.0960	1.11 ± 0.02	7.2 ± 0.2	4.7 ± 0.1
0.098	32	0.0495	1.22 ± 0.08	6.3 ± 0.2	3.9 ± 0.1
pH' 11.70					
0.340	190	0.0850	0.251 ± 0.002	0.97 ± 0.01	1.54 ± 0.02
0.171	220	0.0500	0.261 ± 0.003	0.80 ± 0.01	1.52 ± 0.02
0.069	240	0.0223	0.286 ± 0.008	0.58 ± 0.02	1.30 ± 0.05
B. Experiments at 770 nm pH' 13.96					
0.342	35	0.217	1.18 ± 0.02	5.6 ± 0.1	4.5 ± 0.1
0.187	40	0.0930	1.70 ± 0.05	3.7 ± 0.1	2.11 ± 0.08
0.098	35	0.0600	1.33 ± 0.02	5.3 ± 0.1	3.8 ± 0.1
pH' 11.70					
0.340	180	0.0410	0.281 ± 0.007	0.96 ± 0.03	0.68 ± 0.03
0.171	200	0.0235	0.45 ± 0.06	0.5 ± 0.2	0.4 ± 0.2
0.069	230	0.0096	0.271 ± 0.007	0.58 ± 0.06	0.58 ± 0.06

relative to the 500 nm band when 4,6-di(2-phenyl-2-propyl)pyrogallol is in excess of dissolved oxygen (Fig. 5). Furthermore, as can be seen from the spectrum recorded at the end of the reaction with oxygen from the atmosphere, the 770 nm band disappears slightly before the 500 nm extinction. This effect is visible to the naked eye as a color shift from violet to red shortly before the cessation of oxygen uptake. A similar color change was observed by SCHULZE and FLAIG (24) in the case of 4,6-di-*tert*-butylpyrogallol.

4. DISCUSSION

Two broad extinction bands, one with λ_{max} near 520 nm and the other near 770 nm, form and decay during the air oxidation of 4,6-di(2-phenyl-2-propyl)pyrogallol in alkaline methanol, and these colored intermediates disappear when oxygen uptake ceases. The extinction band at 520 nm resembles the spectrum observed by SALFIELD (23) for carbon

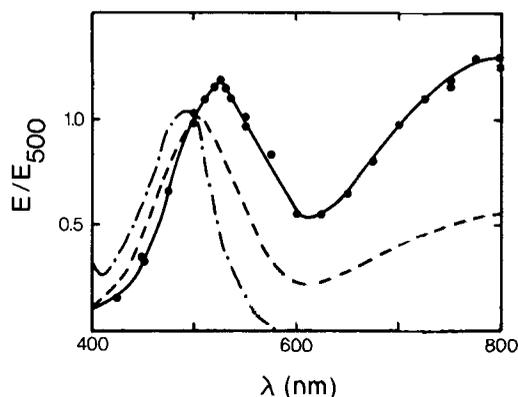
Effect of O₂ deficiency on Spectra

Figure 5. Effect of O₂ deficiency on the intermediate spectra.

●: E/E₅₀₀ for E_{max} values when 0.40 mM-4,6-di(2-phenyl-2-propyl)pyrogallol was oxidized in 0.02 M-sodium methoxide;-----E/E₅₀₀ for 4.6 mM-pyrogallol reactant oxidized in 0.2 M-sodium methoxide for seven minutes (E₅₀₀ = 0.813). The initial O₂ concentration was 1.6 mM; -·-·-E/E₅₀₀ after 23 minutes oxidation (E₅₀₀ = 0.088).

Table II

Effect of O₂ concentration on rate constants

pH'	solution	t _{max} (sec)	E _{max}	k ₁ × 10 ² (sec ⁻¹)	k ₂ × 10 ² (sec ⁻¹)	ε × 10 ⁻³ (liter·mole ⁻¹ ·cm ⁻¹)
A. Experiments at 500 nm						
13.96	air sat. 0.342mM A	30	0.164	1.11 ± 0.01	7.9 ± 0.1	4.77 ± 0.08
13.96	O ₂ sat. 0.325mM A	11	0.176	4.3 ± 0.1	15.9 ± 0.7	3.3 ± 0.2
11.70	air sat. 0.340mM A	190	0.0850	0.251 ± 0.002	0.97 ± 0.01	1.54 ± 0.02
11.70	O ₂ sat. 0.325mM A	75	0.0770	0.77 ± 0.01	2.49 ± 0.05	1.30 ± 0.03
B. Experiments at 770 nm						
13.96	air sat. 0.342mM A	35	0.217	1.18 ± 0.02	5.6 ± 0.1	4.5 ± 0.1
13.96	O ₂ sat. 0.325mM A	10	0.244	4.1 ± 0.1	18.4 ± 0.9	5.2 ± 0.3
11.70	air sat. 0.340mM A	180	0.0410	0.281 ± 0.007	0.96 ± 0.03	0.68 ± 0.03
11.70	O ₂ sat. 0.325mM A	45	0.0476	1.23 ± 0.04	2.7 ± 0.1	0.61 ± 0.02
11.70	0.325mM A	55	0.0450	1.3 ± 0.2	1.8 ± 0.3	0.44 ± 0.3

tetrachloride solutions of 4,6-di-*tert*-butylpyrogallol which had been oxidized by silver oxide. SALFIELD ascribes this spectrum to the corresponding 3-hydroxy-*o*-quinone on the basis of the solution's infrared spectrum.

Although both extinction bands form and decay with indistinguishable rates over the entire pH' range studied, there is definite evidence that they are not solely due to a single intermediate or two intermediates in rapid equilibrium with each other. The first piece of evidence is the decrease in E₇₇₀/E₅₀₀ ratio near the end of the reaction when the pyrogallol reactant is in excess of dissolved oxygen. The second piece of evidence, involving the difference in the rates of response of the two extinctions to rapid acidification, will be discussed in more detail later.

As ALCOCK et al. (3) have pointed out, there is an ambiguity in describing extinction versus

time curves for the intermediate of two first-order processes since two sets of the parameters k₁, k₂ and ε fit the experimental curve equally well. The two sets of rate constants differ in that the numerical values of k₁ and k₂ are interchanged. If the hypothesis that a fast second step follows a slow initial step is chosen, then the estimate of ε will be greater than the estimate based on the reverse hypothesis (first step fast, second slow) by the factor k₂/k₁. One solution to this problem would be to measure the rate of consumption of the reactant, but extinctions of the intermediate or products obscure reactant extinction at all wavelengths tried, and we have not developed any other sufficiently rapid technique for measuring the decrease in reactant concentration.

We favor the hypothesis that fast reactant follows an initial slow step because of the

observation that, when 4,6-di(2-phenyl-2-propyl)pyrogallol is present in excess of dissolved oxygen, a rapid initial increase and decrease in extinction is followed by a slower formation and decay of colored intermediates. The initial rapid changes represent the relatively rapid reactions with dissolved oxygen, and the subsequent slower processes occur as additional oxygen diffuses from the atmosphere into the solution. Since the rates of both reaction steps increase with increasing dissolved oxygen concentration (see table II), it is likely that both steps require O_2 . If the second step were slow compared to the first, the intermediate would be unable to compete with the large excess of reactant for the available dissolved oxygen, and the intermediate would continue to accumulate until the reactant was nearly depleted. The rapid decay of the initial extinction indicates that the colored intermediates are more reactive than the pyrogallol reactant.

The pH' dependence of k_1 fits a scheme in which neutral 4,6-di(2-phenyl-2-propyl)pyrogallol, its monoanion and dianion all react with oxygen, the reaction rate increasing with the negative charge of the species. The two apparent dissociation constant obtained from the pH' dependence, 2.5×10^{-13} and 1×10^{-16} , are reasonable values for the first and second dissociation constant of a pyrogallol in methanol. The two dissociation constants of pyrogallol in water are 9.67×10^{-10} and 2.3×10^{-12} (1), and the pK_a values of neutral acids tend to be four to six units higher in alcohol than in water (7).

The shape of the k_1 versus pH' curve is reminiscent of that found by MARKLUND and MARKLUND (17) for the rates of air oxidation of pyrogallol in aqueous alkaline solutions. These authors found proportionality between rate and hydroxide concentration below pH9, pH independence in the range 9-10, and a further proportional increase at higher pH, a dependence which fits a scheme in which the pyrogallol dianion reacts more rapidly than the monoanion. The apparent differences between the current results and those of MARKLUND and MARKLUND may be due to unsolved experimental difficulties in our work. The first difference is that the increase in rate at high pH' is not as large as found for pyrogallol. This

may be in error because of the difficulty in measuring the rapid reactions in the more concentrated sodium methoxide solutions and the fact that the kinetic curves at very high pH' did not fit eqn. 1 over the entire course of the reaction. The other difference, the slow neutral reaction observed in the current work, may be due to trace metal ion contamination. MARKLUND and MARKLUND, having observed such a reaction, suppressed it with EDTA. Because of the insolubility of EDTA salts in methanol, this procedure was not applicable to the present work. We have observed that neutral solutions of 4,6-di(2-phenyl-2-propyl)pyrogallol in technical grade methanol darken more rapidly than solutions in reagent grade solvent.

The pH' dependence of k_2 is nearly identical to that of k_1 . This similarity indicates that the intermediate responsible for extinction is a diprotic acid with dissociation constants similar to those of the pyrogallol. Furthermore, the relative reactivities of the neutral intermediate, its anion and dianion appear to resemble those of the various protonation forms of the pyrogallol. Since the 3-hydroxy-*o*-quinone (Fig. 1, III) has only one dissociable proton, it is unlikely that this species is solely responsible for either extinction band. The corresponding semiquinone (IV), with two acidic hydrogens and an electronic structure similar to the pyrogallol, provides a far better model for the pH' dependence.

Electron spin resonance signals of semiquinones have been observed during the air oxidation of alkaline pyrogallol solutions (14), and of 4,6-di-*tert*-butylpyrogallol in alkaline dimethylformamide (21). REIN and RISTAU (22) have observed the kinetics of semiquinone formation during the iodate oxidation of pyrogallol in aqueous solutions. Their results indicate two consecutive second order processes, both involving an oxidant molecule.

The 770 nm extinction appears to be due to the conjugate base of a species with a dissociation constant of about 2×10^{-13} . The apparent ϵ values at 770 nm, based on an assumed two-step process and a pH' independent k_2/k_1 ratio, fit a sigmoid curve when plotted versus pH', and the inflection point for this curve is about pH' 12.7.

Rapid acidification experiments show that the reaction of the 770 nm species with acid is, as expected for a proton transfer, too fast to measure in our experiments. In view of the agreement between the inflection point pH' , and the value of the first dissociation constant found from the pH' dependence of k_2 , the most reasonable hypothesis is that the 770 nm extinction is due to the semiquinone monoanion.

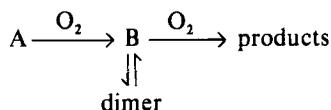
We have assumed that the mechanism involves consecutive bimolecular reactions with O_2 , but more complex reaction schemes deserve consideration. One such possibility is bimolecular disproportionation of the semiquinone. VARTANYAN et al. (28) have proposed a reversible, base induced semiquinone disproportionation to explain an apparent paradox in the kinetics of air oxidation of propyl gallate. These authors found that the observed oxidation rates were constant with time for up to 50% reaction even though the initial oxidation rates were proportional to the propyl gallate concentration. On the other hand, REIN and RISTAU (22) found that the rate of decay of pyrogallol semiquinone in base is strictly proportional to iodate concentration, an indication that the semiquinone is relatively stable and does not decay by non-oxidative pathways.

Our data show little or no evidence of an irreversible disproportionation of the 770 nm intermediate or its reversible formation of a dimer which then reacts with oxygen. Either of these cases would produce a kinetic system in which an irreversible second-order or pseudo second-order process follows an irreversible pseudo first-order process. TALAT-ERBEN (26) has shown that in such systems $k_1 t_{\text{max}}$ decreases sharply and $(B)_{\text{max}}/(A)_0$ decreases gradually as $(A)_0$ is increased. Neither of these effects occurs at high pH' , while the evidence for changes in $k_1 t_{\text{max}}$ or $E_{\text{max}}/(A)_0$ at low pH' is marginal.

If the 770 nm intermediate is the semiquinone, the current results support the conclusions of REIN and RISTAU (22) concerning the absence of irreversible semiquinone disproportionation. Although the reversible disproportionation proposed by VARTANYAN et al. (28) can also fit the apparent constancy of $k_1 t_{\text{max}}$ and $E_{\text{max}}/(A)_0$, the evidence in support of

this hypothesis is weak. It is based on observations of a reaction with oxygen gas, and complications involved in the rate of diffusion of O_2 from the gas bubbles into the solution may be the source of the apparent kinetic paradox. Since diffusion from gas bubbles into a reactant solution is a very complicated kinetic system, the observation that oxidation rates were independent of the rate of introduction of O_2 does not disprove the significance of diffusion effects.

Several authors (for example, 23) describe colorless dimers of the *o*-quinone, and NISHINAGA et al. (21) report that the dimer formed by oxidation of 4,6-di-*tert*-butylpyrogallol decomposes to the semiquinone in alkaline dimethylformamide. These observations raise the possibility that an intermediate is in equilibrium with a colorless dimer that does not lie on the oxidation pathway.



If such an equilibrium strongly favored the dimer, E_{max} would be proportional to the square root of the initial reactant concentration. The data in table I do not show this effect.

It is difficult to explain the pH' dependence of ϵ at 500 nm. Rapid acidification of a partially oxidized solution of 4,6-di(2-phenyl-2-propyl)pyrogallol does not produce an immediate decrease in extinction at 500 nm, so the lower extinction coefficients at lower pH' are not due to an acid-base equilibrium of the intermediate. The kinetic curve for the extinction changes of a rapidly acidified solution fits the integrated rate equation for a two-step reaction in which the initial concentration of intermediate, $(B)_0$, is greater than the maximum concentration attainable by oxidation at the low pH' :

$$(B) = \frac{k_1(A)_0}{k_2 - k_1} e^{-k_1 t} + \left[(B)_0 - \frac{k_1(A)_0}{k_2 - k_1} \right] e^{-k_2 t}$$

$$(B)_0 > \frac{k_1(A)_0}{k_2 - k_1}$$

The difficulty is that since there is no apparent change in k_2/k_1 with pH' , it is hard to see how the concentration of B accumulating at high pH' could be greater than the maximum concentration at low pH' .

The explanation of the effect of pH' on E_{max} at 500 nm may lie in a more complex mechanistic scheme, but we have been unable to develop a mechanistic proposal that deals

with the observations satisfactorily. We will consider two such schemes and their inadequacies.

The first scheme is a three-step reaction in which the 500 nm intermediate is formed from the 770 nm intermediate or its conjugate acid.

The first scheme is a three-step reaction in which the 500 nm intermediate is formed from the 770 nm intermediate or its conjugate acid.



$$(C) = k_1 k_2 (A)_0 \left[\frac{e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} - \frac{e^{-k_2 t}}{(k_2 - k_1)(k_3 - k_2)} + \frac{e^{-k_3 t}}{(k_3 - k_1)(k_3 - k_2)} \right]$$

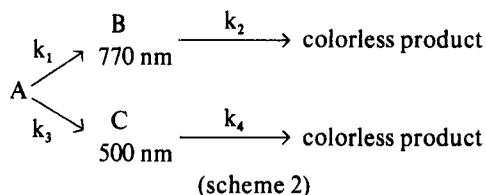
In order for this scheme to fit the observed kinetics, k_3 must be much larger than k_2 . Otherwise, the formation of the 500 nm intermediate would lag behind the formation of the 770 nm species, and the kinetic curves at 500 nm would have inflection points on their ascending sides. Neither of these effects is apparent in the data. If k_3/k_2 were large, the kinetics at 500 nm would approximate those at

770 nm. Furthermore, changes in k_3/k_2 would affect E_{max} at 500 nm without altering the ratio of the apparent rate constants. However, rapid acidification experiments definitely rule out the possibility of large k_3 values. According to the integrated rate equation for scheme 1 in which the initial concentration of the reactant and the two intermediates are $(A)_0$, $(B)_0$ and $(C)_0$ respectively,

$$(C) = \frac{k_1 k_2 (A)_0 e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} + \frac{k_2}{k_3 - k_2} \left[(B)_0 - \frac{k_1 (A)_0}{k_2 - k_1} \right] e^{-k_2 t} + \left[(C)_0 + \frac{k_1 k_2 (A)_0}{(k_3 - k_1)(k_3 - k_2)} \right] e^{-k_3 t}$$

After acidification of a partially oxidized solution, the extinction would decay with an initial rate (k_3) that is much faster than the rates apparent from the oxidation at the low pH' . No such rapid initial decay occurs, and the kinetic constants for decay of the acidified solution match those found for oxidation at the low pH' .

The second scheme involves parallel reactions.



$$(B) = \frac{k_1 (A)_0}{k_2 - k_1 - k_3} \left[e^{-(k_1 + k_3)t} - e^{-k_2 t} \right]$$

$$(C) = \frac{k_1 (A)_0}{k_4 - k_1 - k_3} \left[e^{-(k_1 + k_3)t} - e^{-k_4 t} \right]$$

Because of the indistinguishable kinetics at 500 and 700 nm, k_2 and k_4 would have to be nearly identical. The attractive feature of scheme 2 is that, if k_3 were much smaller than k_1 , changes in the k_3/k_1 ratio would not affect the ratio of the apparent kinetic constant but would influence the maximum concentration of C.

$$(B)_{\max} = \frac{k_1(A)_0}{k_1 + k_3} r^{-r/r-1}$$

$$(C) = \frac{k_3(A)_0}{k_4 - k_1 - k_3} e^{-(k_1 + k_3)t} + \left[(C)_0 - \frac{k_3(A)_0}{k_4 - k_1 - k_3} \right] e^{-k_4 t}$$

$$(C)_{\max} = \frac{k_3(A)_0}{k_1 + k_3} r^{-r/r-1}$$

$$\text{where } r = \frac{k_2}{k_1 + k_3} \sim \frac{k_4}{k_1 + k_3}$$

Changes in k_3/k_1 could have a large effect on E_{\max} at 500 nm but practically no influence at 770 nm. The equation for decay after acidification can easily be accommodated to the experimental data,

the high $(C)_0$ value being explained by a larger k_3/k_1 value at high pH.

The difficulties with scheme 2 arise when one attempts to substitute molecular structures for the abstract symbols of the kinetic system. It hardly seems reasonable that B and C, having different structures, would show identical rate constants for decay over such a wide pH' range. It is particularly improbable since one of the more likely intermediates, the 3-hydroxy-*o*-quinone (Fig. 1, III), is a monoprotic acid incapable of the second dissociation required by the pH' dependence of k_2 at 500 nm. Furthermore, a two-electron oxidation of the pyrogallol to its *o*-quinone is highly improbable because of spin restrictions on electron transfer from triplet O_2 to a singlet organic molecule (27). Finally, it is hard to imagine how the 770 nm intermediate, if it is a semiquinone, could react with oxygen and not form the quinone.

A more likely explanation is that the 500 nm extinction arises from at least two distinct, non-equilibrating species, one of which is the species absorbing at 770 nm or its conjugate acid. Extinction due to the 770 nm species could obscure the kinetics of the non-equilibrating species. One piece of evidence that at least two species are contributing to extinction at 500 nm is the downward shift in λ_{\max} of the 500 nm peak with time when air

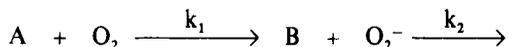
oxidation occurs in the presence of deficient dissolved oxygen (Fig. 5).

The most likely candidate for the non-equilibrating 500 nm species is the 3-hydroxy-*o*-quinone. Although pyrogallol oxidation produces polymeric products such as diphenyls (12) and triphenoquinones (19), these products and the polymeric intermediates leading to them do not appear to be important in the case of pyrogallols containing bulky substituents in the 4 and 6 positions. The rationale behind the first studies of the air oxidation of 4,6-di-*tert*-butylpyrogallol (24) was the presumed steric suppression of polymerization, and all the air oxidation products are monomeric (9). The isolated products of the air oxidation of 4,6-di(2-phenyl-2-propyl) pyrogallol, comprising over 60% of the theoretical yield, are also monomeric (2).

The possibility that species other than triplet O_2 oxidizes a colored intermediate deserves consideration. MARKLUND and MARKLUND (17) have demonstrated superoxide involvement in the air oxidation of pyrogallol in weakly basic solutions. MELUZOVA and VASSILEV (18) have interpreted the chemiluminescence accompanying the oxidation of pyrogallol in alkaline solutions as an indication of the transient formation of singlet O_2 . DOSKOCIL (10) and VARTANYAN et al. (28) have detected

hydrogen peroxide in pyrogallol oxidation by polarographic and chemical means.

The insensitivity of k_2/k_1 to oxygen concentration argues against a scheme of the sort



in which superoxide is the sole oxidant of B, and the only fate of the superoxide is to react with B. In such a case, the superoxide concentration would always equal (B). Increased oxygen concentration does not alter the maximum concentration of the intermediate but does increase k_2 , a result that is inconsistent with the proposed scheme. The effect of oxygen concentration might be consistent with superoxide involvement if the majority of the superoxide ions undergo dismutation. In such a case, increased oxygen concentration would raise the steady state concentration of superoxide and increase k_2 .

The air oxidation mechanism probably involves subsequent oxidation steps not involving detectable concentrations of colored intermediates since it requires the removal of four electrons to oxidize the pyrogallol reactant to its major oxidation product 3,5-di(2-phenyl-2-propyl)2pyrone-6-carboxylic acid (Fig. 1, II) (2). The reaction must either involve a complex system of one-electron transfers and possibly disproportionations, or two-electron transfers must occur. The latter possibility is unlikely in view of electron spin restrictions.

5. ACKNOWLEDGEMENTS

Preliminary kinetic and spectroscopic investigations were ably performed by L. K. WONG. We would like to thank JACK JOHANSEN for the loan of the rapid mixing apparatus and LISBETH SEJERSEN for writing the computer program for evaluation of rate constant and extinction coefficients.

REFERENCES

1. ABICHANDANI, C. T. & S. K. K. JATKAR: Dissociation constants of *o*-, *m*- and *p*-hydroxybenzoic acids, gallic acid, catechol, resorcinol, hydroquinone, pyrogallol and phloroglucinol. *J. Indian Inst. Sci.* 21A, 4.7-441 (1938)
2. ABRASH, H. I. & C. NIEMANN: Steric hindrance in α -chymotrypsin-catalyzed reaction. *Biochemistry* 2, 847-853 (1963)
3. ALCOCK, N. W., D. J. BENTON & P. MOORE: Kinetics of series first-order reactions. Analysis of spectrophotometric data by the method of least squares and an ambiguity. *Trans. Faraday Soc.* 66, 2210-2213 (1970)
4. AULD, D. S. & T. C. FRENCH: Cell for spectrophotometric titrations with small volumes. *Anal. Biochem.* 34, 262-274 (1970)
5. BATES, R. G.: Determination of pH. Theory and Practice, John Wiley & Sons (New York) pp. 222-229 (1964)
6. *ibid.* p. 183.
7. *ibid.* pp. 151-152.
8. BROSER, W. & H. FLEISCHAUER: Substituenteffekte bei Triphenylmethanfarbstoffen II. Eine Pufferreihe für das methanolische Medium. *Z. Naturforsch.* 25b, 1389-1394 (1970)
9. CAMPBELL, T. W.: The oxidation of di-*t*-butylpyrogallol by oxygen in alkaline solution. *J. Am. Chem. Soc.* 73, 4190-4195 (1951)
10. DOSKOCIL, J.: Polarography of some orthophenols and their oxidation products. *Collect. Czechoslov. Chem. Commun.* 15, 599-613 (1950)
11. FROST, A. A. & R. G. PEARSON: Kinetics and Mechanism, John Wiley & Sons (New York) p. 155 (1953)
12. HARRIES, C.: Ueber die Autoxydation des Pyrogallols. *Chem. Ber.* 35, 2954-2959 (1902)
13. HATHWAY, D. E.: Autoxidation of polyphenols. I. Autoxidation of methyl gallate and its O-methyl ethers in aqueous ammonia. *J. Chem. Soc.* 519-523 (1957)
14. HOSKINS, R. H. & B. R. LOY: Paramagnetic resonance in solutions of oxidized pyrogallol. *J. Chem. Phys.* 23, 2461-2462 (1955)
15. WASHBURN, E. W., ed.: International Critical Tables of Numerical Data. Physics, Chemistry and Technology, McGraw-Hill (New York) Volume III p. 262 (1928)
16. JÖNSSON, Å: Studies on Antimetabolites. I. Synthesis D,L- α -neophenylalanine, D,L- α -neotyrosine and D,L- α -neo-3,5-diiodo-tyrosine, the β , β -dimethyl analogues of optically inactive phenylalanine, tyrosine and 3,5-diiodotyrosine. *Acta Chem. Scand.* 8, 1203-1210 (1954)

17. MARKLUND, S. & G. MARKLUND: Involvement of the superoxide anion radical in the autoxidation of pyrogallol and a convenient assay for superoxide dismutase. *Eur. J. Biochem.* 47, 469-474 (1974)
18. MELUZOVA, G. B. & R. F. VASSILEV: Stoichiometry of chemiluminescent oxidation of pyrogallol by oxygen in aqueous solutions. *Mol. Photochem.* 2, 251-257 (1970)
19. NIERENSTEIN, M.: An oxidation product of pyrogallol. *J. Chem. Soc.* 107, 1217-1220 (1915)
20. NILSSON, R.: On the mechanism of peroxidase catalyzed oxidations studied by means of chemiluminescence measurements. *Acta Chem. Scand.* 18, 389-401 (1964)
21. NISHINAGA, A., T. ITHARA & T. MATSUURA: Base catalyzed oxygenation of 3,5-di-*t*-butylpyrocatechol and its related compounds. *Bull. Chem. Soc. Japan* 47, 1811-1812 (1974)
22. REIN, H. & O. RISTAU: Elektronenspinresonanz – Untersuchungen über die Oxydationskinetik von Phenylverbindungen. I. Mitteilung: Die Kinetik der Radialbildung bei der Oxydation des Pyrogallols. *Z. Phys. Chem. (Leipzig)* 239, 115-123 (1968)
23. SALFELD, J.-C.: Über die Oxydation von Pyrogallol und Pyrogallolderivaten, II, Die Konstitution dimerer 3-Hydroxy-*o*-benzochinone. *Chem. Ber.* 93, 737-745 (1960)
24. SCHULZE, H. & W. FLAIG: Zur Kenntnis der Huminsäuren IV, Mitteilung Über die Ringsprengung mehrwertiger Phenole mit Sauerstoff in alkalischem Medium. *Ann.* 575, 231-241 (1952)
25. TABAGUA, I. S.: Dissociation constants of some acids in methanol and its mixtures with water. *Tr. Sukhumsk. Gos. Ped. Inst.* 15; 119-133. *Ref. Chem. Abstracts* 60, 14373d (1964)
26. TALAT-ERBEN, M.: Displacement of the maximum in the concentration-time diagram of uni-bi, bi-uni, and bi-bimolecular consecutive reactions. *J. Chem Phys.* 26, 75-77 (1957)
27. TAUBE, H.: Mechanism of oxidations with O. *J. Gen. Physiol.* 49 Pt. 2, 29-50 (1965)
28. VARTANYAN, L. S., L. M. STRIGUN & N. M. EMANUEL: Kinetics of the autoxidation of propyl gallate in aqueous solution. *Dokl. Akad. Nauk. SSSR.* 148, 97-100 (1963)