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Nickel Acetate Catalyzed Autoxidation of Benzoin

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Abstract: The autoxidation of benzoin in methanol catalyzed by nickel acetate is first order in each of benzoin and the catalyst and independent of the partial pressure of oxygen. The stoichiometry and product analysis demonstrate that benzoin reacts with oxygen to give benzil and hydrogen peroxide. A primary isotope effect of $k_H/k_D = 7$ has been observed. The rates of oxidation, relative to benzoin, of 4,4′-dichloro-, 4,4′-dimethyl-, and 4,4′-dimethoxybenzoin were respectively 2.4, 0.40, and 0.21. We suggest that the reaction involves equilibration of nickel acetate with a nickel acetate–benzoin complex. The rate-limiting step of the reaction involves abstraction of an α-hydrogen atom of the benzoin by an acetoxy group. Some intermediate must then react very rapidly with oxygen. Substituent effects indicate that in the slow step some net negative charge is introduced into the substrate group.

It is a well documented experimental fact[1] that the autoxidation of benzoin to benzil is catalyzed by transition metal acetates with a nearly quantitative yield. The reaction provides a good probe for the mechanisms of catalysis of oxidation reaction by metal ions. In a kinetic study of catalysis by ferrous chloride[2] we showed that benzoin and iron(II) reacted competitively in the fast step with the reactive transient iron(IV) which was first formed in the rate-limiting step from iron(II) and O_2. In this report we present the results of a study of catalysis by nickel acetate. The fact that the substance is a catalyst at all is surprising since neither nickel chloride, nickel perchlorate, nor nickel acetylacetonate showed any significant catalytic activity.

Results

The course of the autoxidation in methanol solution has been followed by different techniques including volumetric monitoring of oxygen uptake, polarographic determination of the fall in oxygen concentration in a closed system, spectrophotometric determination of benzoin and benzil, measurement of hydrogen peroxide iodometrically or with permanganate, and gravimetric determination of formaldehyde with dimedone.

Lithium acetate alone catalyzes oxidation but is inefficient relative to nickel acetate; the rate of autoxidation in the absence of added metallic salts is immeasurably slow under the conditions of our experiments. A solution prepared from nickel perchlorate and lithium acetate is essentially equivalent to nickel acetate. The reaction rate is much less sensitive to solvent than is oxidation catalyzed by ferrous chloride.[2] The rate for nickel acetate catalysis is 1.7 times slower in ethanol than in methanol. (Ferrous chloride catalysis is 20 times faster in ethanol than in methanol.) Some of the preliminary work was conducted with $Ni(OAc)_2 \cdot 4H_2O$. Later anhydrous nickel acetate was used exclusively. The rate is a little slower with the tetrahydrate.

Rate Law. The initial rates of oxygen uptake (Figure 1) were almost equal under pure oxygen and air at 1 atm of pressure. However, over a longer period of time a small reproducible difference in the values of ΔO_2 appeared with the rate apparently being very slightly faster under oxygen. The polarographic measurements clearly confirmed the fact that the rate is zero order with respect to oxygen.

In most experiments with the polarographic method the solutions were initially saturated with air and a large excess of benzoin was used. In several runs the solutions were initially saturated with oxygen. The rate is essentially constant within an individual run and there is no significant variation in the slopes observed in different runs with identical initial concentrations of benzoin and nickel acetate.

The order with respect to benzoin was investigated by polarographic monitoring of oxygen in runs in which the benzoin concentration was varied and by

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[1] M. Weiss and M. Appel, *J. Amer. Chem. Soc.*, 70, 3666 (1948).

[2] G. S. Hammond and C.-H. S. Wu, *Advan. Chem. Ser.*, No. 77, 186 (1968).

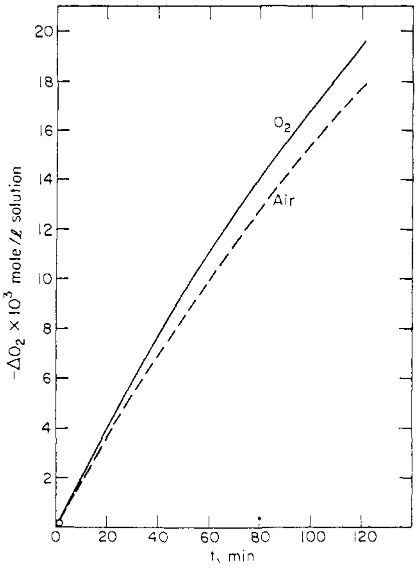

Figure 1. Consumption of oxygen by methanolic benzoin catalyzed by nickel acetate at 30°: $[\text{benzoin}]_0 = 0.051\ M$, $[\text{Ni(OAc)}_2] = 0.06\ M$; (solid line) 1 atm of O_2 maintained throughout the reaction; (broken line) the solution was initially saturated with 1 atm of air; the rate was determined by volumetric monitoring.

spectrophotometric determination of the rates of disappearance of benzoin and appearance of benzil. Results are shown in Figure 2. A logarithmic plot of the oxygen disappearance rates against benzoin concentration is linear with a slope of 0.9 and a logarithmic plot of benzoin concentration against time, with constant oxygen pressure, is also linear. We conclude that the reaction is first order with respect to benzoin.

The order with respect to nickel acetate was investigated by all the analytical methods in runs with varying catalyst concentration. Rates obtained by the polarographic method are summarized in Table I. The pseudo-first-order constants calculated from data obtained in the concentration range from 0.007 to 0.10 M were essentially constant. At even lower concentrations the calculated rate constants (not shown) increase slightly, an effect probably associated with ionic dissociation of nickel acetate. We conclude that the rate law under most of the conditions studied is given by the following equation.

$$-\frac{d[O_2]}{dt} = \frac{d[\text{benzil}]}{dt} = k[\text{benzoin}][\text{Ni(OAc)}_2]$$

Table I. Dependence of Rate of Oxidation of Benzoin on the Catalyst in Methanol at 30°

$[\text{Ni(OAc)}_2]$,[a] M	R_0[b] × 10^5 M min^{-1}	k,[c] M^{-1} min^{-1}
0.0068	2.46	0.075
0.0136	4.44	0.067
0.0282	8.17	0.063
$[\text{Ni(OAc)}_2]$,[d] M		
0.015	4.4	0.067
0.022	7.2	0.074
0.033	9.5	0.066
0.049	14.9	0.068
0.065	16.9	0.058
0.081	22.1	0.061
0.098	26.4	0.061

[a] $[\text{Benzoin}]_0 = 0.049\ M$, $\text{Ni(OAc)}_2 \cdot 4H_2O$. [b] $R_0 = (-d[O_2]/dt)_0$ by polarographic monitoring of $[O_2]$. [c] $k = R_0/[\text{Ni(OAc)}_2][\text{benzoin}]_0$. [d] $[\text{Benzoin}]_0 = 0.045\ M$, anhydrous Ni(OAc)_2.

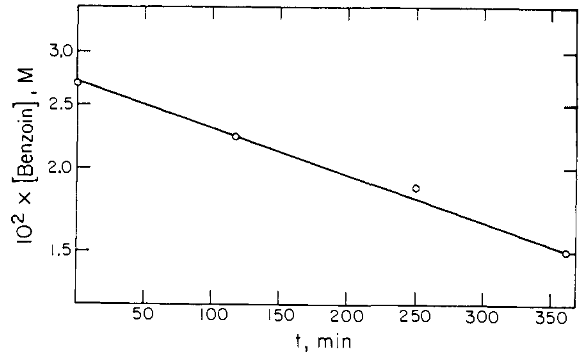

Figure 2. Linear relation of logarithm of [benzoin] *vs.* time in autoxidation of benzoin in methanol at 30° $[\text{Ni(OAc)}_2] = 0.020\ M$. The reaction mixture was in equilibrium with 1 atm of oxygen.

Kinetic Isotope Effect. α-Deuteriobenzoin was prepared by a standard method for synthesis of the unlabeled compound.[3] Analysis by nmr showed that the product was 75% deuterated in the α position. The rate of autoxidation of the deuterated material was followed by both volumetric and polarographic methods. In polarographic runs three different Ni(OAc)_2 concentrations were used and in volumetric runs the stoichiometry of consumption of oxygen and benzil and of the appearance of hydrogen peroxide were determined. All results as summarized in Table II pointed to a ratio $k_H/k_D = 7$ to 8. Unreacted benzoin was recovered after 6.25 hr reaction and the α-C–D content was found to have increased from 75 to 92%. The expected deuterium content was calculated to be 90%, in very reasonable agreement with the value found. The calculation took account of the expected extent of oxidation (65% for undeuterated substrate) and a kinetic isotope effect of 7. This internal consistency indicated that the C–deuterium exchange with solvent is slow under oxidation conditions.

Table II. Deuterium Isotope Effect on the Rate of Autoxidation of Benzoin in Methanol at 30°, Catalyzed by Ni(OAc)_2

$[\text{Ni(OAc)}_2]$, M	$[\text{Benzoin}]_0$, M	$[\text{Benzoin-}d]_0$,[a] M	k_H/k_D
0.0031	0.0506	0.0502	7.2
0.0155	0.0506	0.0502	7.5
0.0785	0.0506	0.0502	7.2
0.0540[b]	0.0810	0.0800	7.7

[a] Benzoin-*d* is 75% α-deuterated benzoin; k_D is the adjusted rate constant representing 100% α-deuterated benzoin. [b] Volumetric runs, at 6.25 hr: $\Delta O_2 : \Delta\text{benzil} : \Delta H_2O_2$ was 1:1.03:0.074 and 1:103:083 for benzoin and benzoin-*d*, respectively.

Since the rate-determining step apparently does not involve oxygen, the behavior of the system in the absence of oxygen was examined. A solution of deuterated benzoin and nickel acetate in methanol was deoxygenated and allowed to stand for 24 hr. The

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(3) M. Gomberg and W. E. Bachman, *J. Amer. Chem. Soc.*, **49**, 2584 (1927).

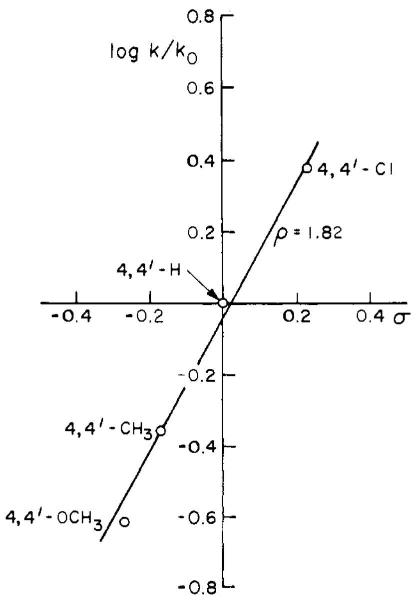

Figure 3. $\rho\sigma$ plot of the rate of autoxidation of substituted benzoin at 30° in methanol. Catalyzed by nickel acetate. Reaction conditions: $[\text{benzoin}]_0 = 0.06\ M$, $[\text{Ni(OAc)}_2] = 0.016\ M$, $[O_2] = 0.00154\ M$. σ values are taken from L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N.Y., 1940, p 188.

benzoin was then separated and analyzed by nmr. The C–D content was reduced to 14% indicating that, in the absence of oxygen, exchange with the solvent is induced by nickel acetate.

Substituent Effects. The rates of oxidation of 4,4′-dichloro-, 4,4′-dimethyl-, and 4,4′-dimethoxybenzoin were measured and compared with benzoin. The results are shown in Table III. The kinetic law remained unchanged with the substituted substrates. The data fit the Hammett equation with a ρ value of 1.82 as shown in Figure 3.

Table III. Substituent Effect on Rate of Autoxidation of Benzoin[a] in Methanol at 30°, Catalyzed by Ni(OAc)_2

Substituents	Relative rate	k, M^{-1} min^{-1}
4,4′-Dichloro-	2.4	0.173
None	1.0	0.072
4,4′-Dimethyl-	0.42	0.031
4,4′-Dimethoxy-	0.23	0.017

[a] $[\text{Benzoin}]_0 = 0.60\ M$, $[\text{Ni(OAc)}_2] = 0.016\ M$, the reaction mixture was initially saturated with air under atmospheric pressure. The polarographic method was used for rate determination.

Activation Parameters. Rates of oxidation were measured at temperatures ranging from 10 to 50° using the polarographic method for monitoring. The solubilities of oxygen at the various temperatures were calculated from reported data[4] using 1 atom total pressure and correcting for the variation in the vapor pressure of methanol with temperature.[5] The results are summarized in Table IV. A plot (Figure 4) of log k against T^{-1} is linear and gives an Arrhenius activation energy, E_a, of 15.1 kcal mol^{-1}. At 30°, $\Delta H^{\ddagger}$, $\Delta F^{\ddagger}$, and $\Delta S^{\ddagger}$ have the values of 14.5 kcal mol^{-1}, 19.1 kcal mol^{-1}, and -15.0 cal deg^{-1} mol^{-1}.

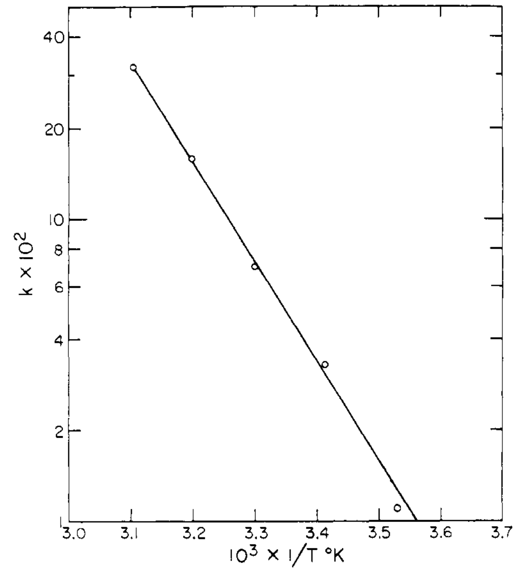

Figure 4. Arrhenius plot of the autoxidation rate of benzoin in methanol catalyzed by nickel acetate at a temperature range of 10 to 50°. Rate measured by polarographic method. Reaction conditions: $[\text{benzoin}]_0 = 0.027\ M$, $[\text{Ni(OAc)}_2] = 0.0175\ M$, the solution was initially saturated with air.

Table IV. Solubility of Oxygen in Methanol and Rate of Autoxidation of Benzoin at One Atmosphere of Pressure and Various Temperatures

Temp, °K	$[O_2]$,[a] $M \times 10^2$	k,[b] M^{-1} min^{-1}
283.4	0.192	0.011
293.0	0.174	0.033
303.0	0.154	0.070
312.3	0.126	0.160
322.0	0.088	0.320

[a] The atmospheric pressure is 740 mm; the vapor pressure of methanol has been taken into consideration in obtaining the solubility of oxygen. [b] The reaction conditions: $[\text{benzoin}]_0 = 0.027\ M$, $[\text{Ni(OAc)}_2] = 0.0175\ M$, $[O_2]_0$ corresponded to 1 atm of air.

Reaction Products. In solutions made up from benzoin and nickel acetate in methanol, formaldehyde was produced almost as rapidly as benzil and there was very slow accumulation of hydrogen peroxide as shown in Figure 5. However, if 0.1 to 0.5 M acetic acid was added initially, the rate of production of formaldehyde was slowed substantially and hydrogen peroxide accumulated to rather high concentrations. Initially the rates of production of hydrogen peroxide and benzil were equal within experimental error (Figure 6). Separate experiments to determine the rates of oxygen uptake and production of benzil showed them to be essentially the same. We conclude that the primary reaction can be expressed by

$$C_6H_5CHOHCOC_6H_5 + O_2 \xrightarrow[CH_3OH]{Ni(OAc)_2} C_6H_5COCOC_6H_5 + H_2O_2 \quad (1)$$

Reaction 1 must be followed by

$$CH_3OH + H_2O_2 \xrightarrow{Ni(OAc)_2} CH_2O + 2H_2O \quad (2)$$

Reaction 2 is obviously catalyzed by nickel acetate since solutions of hydrogen peroxide in methanol are

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(4) C. B. Kretschmer, J. Nowakowska, and R. Wiebe, *Ind. Eng. Chem.*, **38**, 506 (1946).

(5) "International Critical Tables," Vol. III, McGraw-Hill, New York, N. Y., 1928.

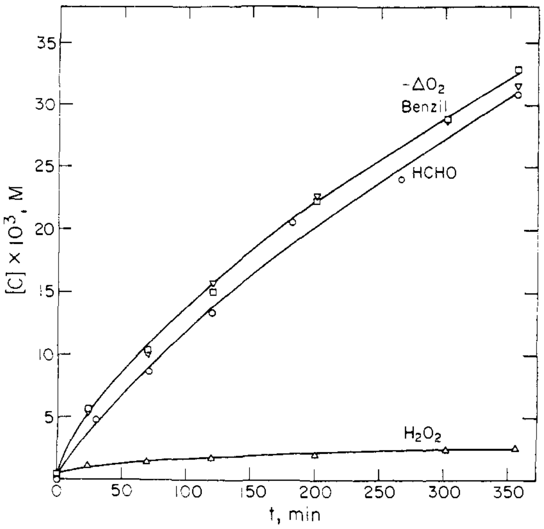

Figure 5. Products distribution of autoxidation of benzoin catalyzed by nickel acetate in methanol at 30°: (□) benzil; (▽) oxygen; (○) formaldehyde; (△)hydrogen peroxide. Reaction conditions: $[\text{benzoin}]_0 = 0.051$ *M*, $[Ni(OAc)_2] = 0.060$ *M*, $[O_2] = 0.077$ *M* (*i.e.*, 1 atm of oxygen throughout the reaction).

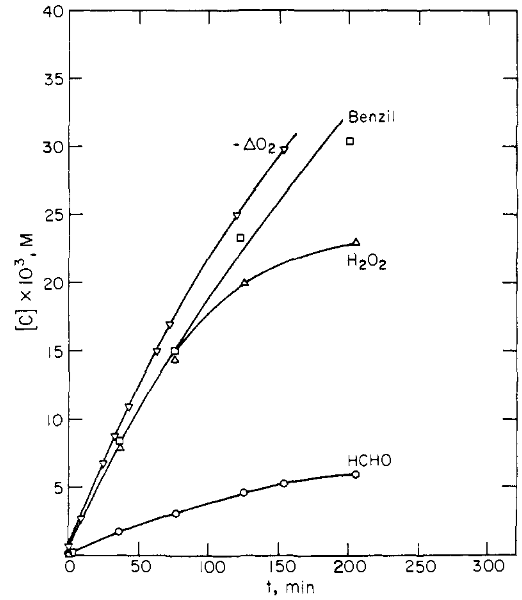

Figure 6. Products distribution of autoxidation of benzoin catalyzed by nickel acetate at 30° in methanol containing 0.5 *M* acetic acid: (□) benzil; (▽) oxygen; (○) formaldehyde; (△) hydrogen peroxide. Reaction conditions: $[\text{benzoin}]_0 = 0.052$ *M*, $[Ni(OAc)_2] = 0.061$ *M*, $[O_2] = 0.077$ *M* (*i.e.*, 1 atm of oxygen throughout the reaction).

quite stable. A number of experiments were carried out to demonstrate the identity of the catalyzed reaction by monitoring the behavior of solutions of hydrogen peroxide in methanol containing various other constituents involved in our experiments. The results are summarized graphically in Figure 7.

Effect of Acetic Acid. Figures 5 and 6 also indicate that addition of acetic acid can increase the rate of reaction 1. This effect is further documented in Figure 8. With a fixed concentration of nickel acetate, addition of small amounts of either acetic or propionic acid increases the oxidation rate, with the two acids being essentially equivalent. The accelerating effect levels off above 0.1 *M* and addition of larger amounts of acetic acid leads to a reduction in rate. As is shown in Figure 9, addition of lithium acetate depresses the rate, with the effect being largest in the experiments with the lowest initial concentration of nickel acetate. We believe that the primary effect must be due to participation of the additives in the solvolytic equilibrium.

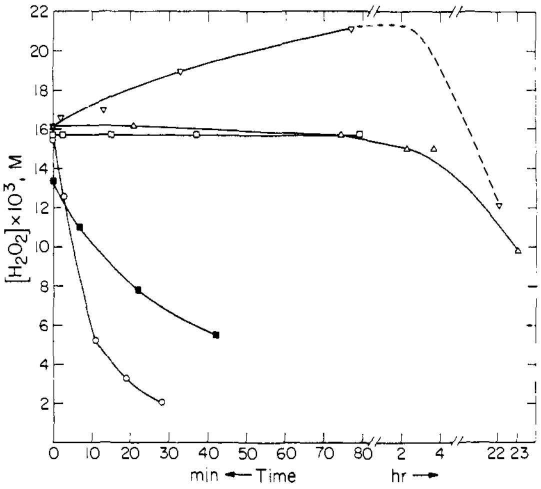

Figure 7. Stability of methanolic hydrogen peroxide at 25° in 1 atm of air in the presence of various constituents: (□) [benzoin] = 0.05 *M*; (○) $[Ni(OAc)_2] = 0.05$ *M*; (■) $[\text{benzoin}]_0 = 0.044$ *M*, $[Ni(OAc)_2] = 0.015$ *M*; (△) [HOAc] = 0.5 *M*, $[Ni(OAc)_2] = 0.05$ *M*; (▽) [HOAc] = 0.5 *M*, $[Ni(OAc)_2] = 0.05$ *M*, $[\text{benzoin}]_0 = 0.05$ *M*.

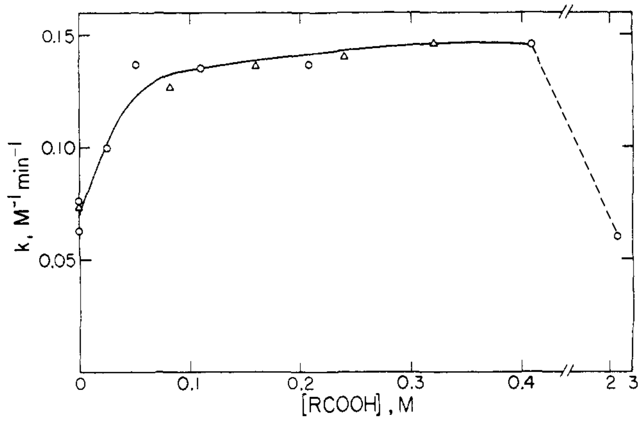

Figure 8. Acetic acid effect on the rate of autoxidation of benzoin in methanol catalyzed by nickel acetate at 30°. Reaction conditions: $[\text{benzoin}]_0 = 0.051$ *M*, $[Ni(OAc)_2] = 0.04$ *M*. The solution was initially saturated with 1 atm of air or oxygen. The rate was monitored by the polarographic method: (△) propionic acid, (○) acetic acid.

$$Ni(OAc)_2 + CH_3OH \rightleftharpoons Ni(OAc)(CH_3OH)^+ + AcO^- \quad (3)$$

$$Ni(OAc)(CH_3OH)^+ + CH_3OH \rightleftharpoons Ni(CH_3OH)_2{}^{2+} + AcO^- \quad (4)$$

$$AcO^- + HOAc \longrightarrow (AcO\cdots HOAc)^- \quad (5)$$

For reasons that will be discussed in the following sections, we believe that the second ionization step, eq 4, is not very important at the concentrations of nickel acetate used in our work. With this assumption we infer that catalytic activity is greatest in solutions containing the greatest amounts of the solvated Ni(OAc)$^+$ ion. However, the fact that the inhibitory effect of acetate ion appears to reach a limit asymptotically (Figure 9) indicates that solutions containing no significant amounts of ionized nickel species still have substantial activity.

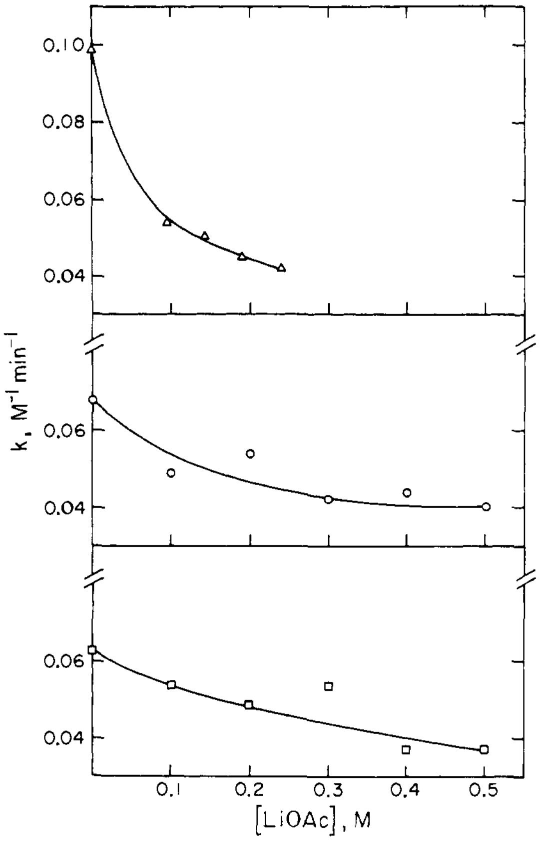

Figure 9. Inhibitory effect of lithium acetate on the rate of autoxidation of benzoin in methanol at 30° catalyzed by nickel acetate. Reaction conditions: $[benzoin]_0 = 0.044$ *M*; $[Ni(OAc)_2]$ (△) 0.0087 *M*, (○) 0.015 *M*, (□) 0.033 *M*. The rate was monitored by the polarographic method.

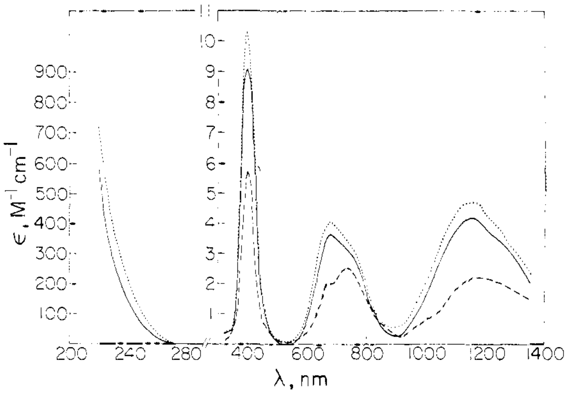

Figure 10. Uv, visible, and near-ir spectra of nickel perchlorate and nickel acetate in methanol: (---) $Ni(ClO_4)_2 \cdot 2H_2O$, 0.0170 *M*; (——) $Ni(OAc)_2$, 0.0176 *M*; (.....) 0.0176 *M* $Ni(OAc)_2$ + 0.013 *M* LiOAc. A 5-cm path width quartz cell and a Cary 14 spectrophotometer were used. The appropriate solution was used as a blank in the reference cell.

Table V. Variation of Ligand Field Transitions on Addition of LiOAc to $Ni(ClO_4)_2$[a]

$[LiOAc]/[Ni(ClO_4)_2]$	λ_{max}, nm	ϵ	λ_{max}, nm[d]	ϵ	λ_{max}, nm[d]	ϵ	λ_{max}, nm	ϵ
40.4[b]	402	8.8	675	3.40	735	2.94	1140	4.35
20.2[b]	402	8.8	675	3.50	735	3.06	1140	4.47
7.7[b]	402	9.0	675	3.30	735	2.94	1140	4.12
4.0[b]	402	9.0	675	3.40	735	2.94	1140	4.12
4.0[c]	402	10.6	675	4.08	735	3.67	1140	4.72
2.0[c]	402	9.60	675	3.43	735	3.29	1140	4.21
1.50[c]	401	8.75	667	3.33	735	3.33	1140	4.11
1.00[c]	400	7.80	667	2.94	735	3.10	1155	3.53
0.70[c]	400	7.06	667	2.61	735	2.88	1160	3.00
0.50[c]	400	6.68	665	2.41	735	2.80	1170	2.82
0.20[c]	400	6.05	665	2.15	735	2.58	1170	2.53
0.00[c]	400	5.76	665	1.97	735	2.53	1180	2.21

[a] All solutions 0.017 *F* $Ni(ClO_4)_2 \cdot 2H_2O$. [b] Formal ionic strength maintained at 0.574. [c] Formal ionic strength maintained at 0.058 with $LiClO_4$. [d] Maximum not clearly developed with solutions more concentrated in LiOAc.

Ionization of Nickel Acetate in Methanol. Figure 10 shows the electronic absorption spectra of solutions of nickel acetate and nickel perchlorate which are typical of octahedral coordinated Ni(II) complexes.[6a] Although the spectra are similar there are clear-cut differences which we attribute to the difference in ligands attached to nickel in different states of electrolytic ionization. The perchlorate solutions show the lowest intensity of absorption in the region around 1150 nm and also show definite double peaked maxima at both 660 and 750 nm, whereas the acetate solutions show a maximum and a shoulder. The intensity of the sharp band maximum at 400 nm is greatest in the acetate solutions. Addition of lithium acetate to solutions of nickel acetate accentuates the differences between perchlorate and acetate solutions. The effect of changing the dominant counterion from perchlorate to acetate is also shown in Figure 10. The monotonous increases in intensity of absorption at 400 and 1140 nm probably are associated with essentially complete conversion of Ni^{2+} and $Ni(OAc)^+$ to $Ni(OAc)_2$. Table V summarizes data for extinction coefficients of the three Laporte-forbidden d–d transition bands[7] for solutions made up by addition of varying amounts of lithium acetate to 0.017 *F* $Ni(ClO_4)_3 \cdot 2H_2O$. It seems fruitless to attempt to evaluate ionization constants from the spectrophotometric data for several reasons. First, the changes in ϵ_{obsd} are not large; second, the values of ϵ are dependent on the total electrolyte concentration; and third, the limiting values of ϵ_{max} are reached at values of $[LiOAc]/[Ni(ClO_4)_2]$ not much greater than 2.

The small increases in intensity which accompany attachment of one or two acetoxy ligands to Ni^{2+} are consistent with the notion that the octahedral crystal field reduces its symmetry as acetate ions replace solvent molecules in the inner coordination sphere of Ni^{2+}. This interpretation presumes that $Ni(ClO_4)_2$ is highly ionized in methanol solution, which is supported by the agreement between our spectral data with that of the others.[7,8] Table VI shows the analysis of the spectral data including assignment of transitions to the bands, the values of 15*B* and β (the nephelauxetic parameter), and a comparison with Drago's values. The calculations of 15*B* and β are based on the crystal field theory.[6b,7]

We also examined the absorption spectra of nickel acetate in methanol in the concentration range 0.02 to 0.2 *M* (see Figure 11). This is the range in which rate data were obtained to establish the kinetic order with respect to nickel acetate. The result showed that Beer's law was obeyed with small deviation which assured us that the major species of the nickel catalyst in this concentration range is $Ni(OAc)_2$.

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(6) (a) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 264; (b) *ibid.*, p 81.

(7) V. Imhof and R. S. Drago, *Inorg. Chem.*, **4**, 427 (1965).

(8) D. A. Fine, *Inorg. Chem.*, **5**, 197 (1966).

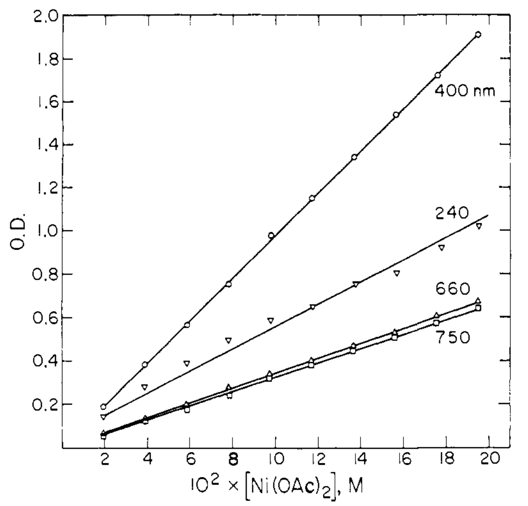


Figure 11. A Beer's law plot of methanolic $Ni(OAc)_2$ of concentration range 0.02 to 0.2 M. All solutions were prepared from nickel acetate tetrahydrate. Absorbances (OD) at 400, 660, and 750 nm were determined on a Beckman DU spectrophotometer with a 1-cm path length quartz cell. The absorbance at 240 nm was determined on a Cary 14 spectrophotometer with a 0.05-cm path width quartz cell.

Table VI. Spectral Data for Nickel(II) Complexes in Methanol[a]

	$Ni(CH_3OH)_4$-$(OAc)_2$[b]	$[Ni(CH_3OH)_6^{2+}][2ClO_4^-]$[c]	
$\nu_1(^3A_{2g} \rightarrow {}^3T_{2g})$	8772	8475	8431
ϵ_1	4.72	2.21	2.4
$\nu_2(^3A_{2g} \rightarrow {}^3T_{1g}(F))$	14,815, 13,600	15,040, 13,600	14,226
ϵ_2	4.23, 3.67	1.97, 2.53	4
$\nu_3(^3A_{2g} \rightarrow {}^3T_{1g}(P))$	24,876	25,000	25,000
ϵ_3	10.6	5.76	6.3
15B	12,874	13,896	13,936
Nephelauxetic parameter	0.82	0.88	0.88

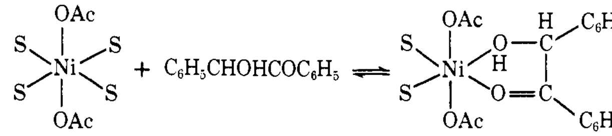
[a] ν in cm^{-1}. [b] Our data. [c] First column our data, second column from ref 7.

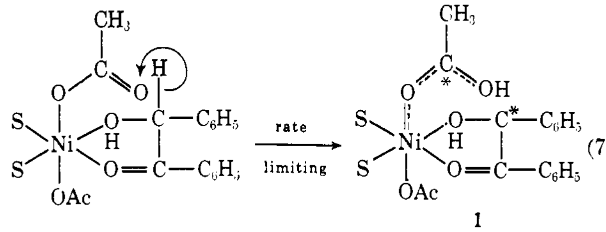
Discussion

Combination of the kinetic data and the kinetic isotope effect indicates that the rate-determining step in oxidation involves a reaction of nickel(II) species with benzoin. Since nickel perchlorate, chloride, and acetylacetonate have no catalytic activity, we assume that acetoxy groups play a unique role. Because of the influence of acetic acid and lithium acetate on rates and spectra, we infer that there are paths involving both monoacetatonickel and diacetatonickel. Although we do not know the dissociation constant for $Ni(OAc)_2$ in methanol, the data show that it must be rather small. Consequently, rate constants calculated in terms of $Ni(OAc)^+$ would be considerably larger than those calculated for $Ni(OAc)_2$.

The structure of nickel acetate in methanol solution is probably octahedral with two acetate ions and four solvent molecules bound to the central ion; both stereoisomers should be present in an equilibrated mixture of some unknown composition. Ionization simply replaces acetate in the inner coordination sphere with methanol. In the solutions which are not anhydrous, *e.g.*, made up from nickel acetate tetrahydrate, some of the nickel probably has water in place of one of the methanol molecules in the inner sphere. This is the most likely cause of the slight rate depression when small amounts of water are known to be present.

A reasonable mechanistic model for reaction with benzoin is given in eq 6–9, where S represents a solvent molecule.


(6)



(7)

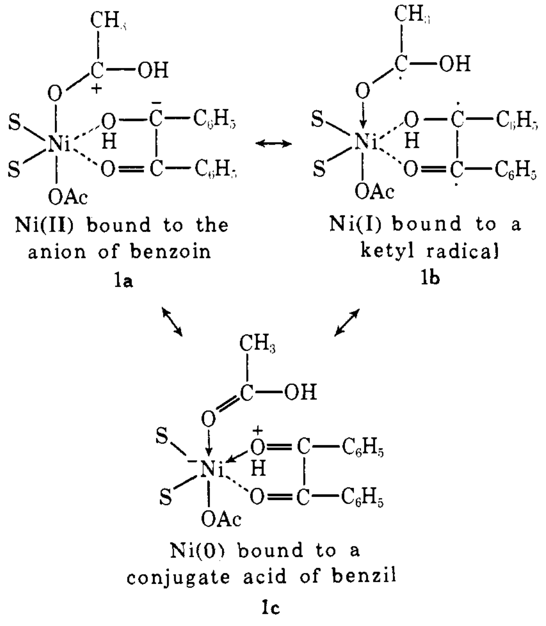
1

$$\mathbf{1} \longrightarrow Ni(0) + 2HOAc + C_6H_5COCOC_6H_5 \quad (8)$$

$$Ni(0) + O_2 + 2HOAc \longrightarrow Ni(OAc)_2 + H_2O_2 \quad (9)$$

Equations 8 and 9 are stoichiometric representations of the overall transformation that must occur after the rate-limiting step, eq 7. Mechanistic details cannot be revealed by our kinetic evidence which only gives the composition of the transition state for (7). The fact that C–D exchange occurs in the absence of oxygen indicates that reversal can occur when there is no scavenger for reducing intermediates present. It is, of course, possible that oxygen reacts directly with **1**. If dissociation of **1** occurs as suggested above, we have no strong prejudice as to the identity of the species labeled Ni(0). For example, nickel(II) hydride would probably fill the requirements quite well.

Asterisks in formula **1**, the reducing intermediate, beg the question of detailed electronic structure of the species. If we were to visualize the process as abstraction of a hydrogen atom, **1** would be described as a complex in which a ketyl radical is bound to Ni(I). On the other hand, formulation of the process as a proton abstraction would imply that **1** is a complex of Ni(II) with the enolate ion as a ligand. The difference between the two descriptions is, perhaps, largely semantic. Since the two unsaturated centers are coupled through the nickel atom, a proper description in resonance notation may be the following.


Ni(II) bound to the anion of benzoin
1a

Ni(I) bound to a ketyl radical
1b

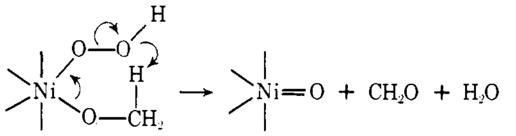
Ni(0) bound to a conjugate acid of benzil
1c

The question of the spin state of **1** is not semantic. Low spin Ni(II) complexes have triplet ground states. The easy, intuitive approach would suggest the proton transfer would be an adiabatic process[9] so that **1** is produced initially as a triplet. The resonance structure **1b** might be the better representation of triplet.

An electron-withdrawing substituent, *p*-Cl, accelerates the reaction and an electron-donating substituent slows the reaction. We would expect substituent effects in the opposite direction on the equilibrium constant for formation of complex since electron withdrawal should make the substrate a weaker base. Consequently, the effects suggest that in reaction 7 there is a net increase in electron density in the benzoin–benzil unit. However, the effect is much smaller than would be anticipated if an uncomplexed enolate ion were the product. Obviously, if the proton transfer model is preferred, it must be accompanied by the stipulation that a large fraction of the negative charge is transferred to the nickel atom. The rate of the reaction also compels the same conclusion. Oxidation catalyzed by lithium acetate probably does involve formation of the benzoin enolate and is very much slower than the nickel catalyzed reaction even though free acetate should be a much stronger base than complexed acetate.

The apparent higher rate of reaction by way of Ni(OAc)+ is easily accounted for. The cationic species may have a larger association constant for formation of the chelate complex and any net transfer of electron density to nickel should be encouraged by replacement of acetate by methanol, a nucleophile of lower ligand field strength.

We have no detailed information of the nickel-catalyzed oxidation of methanol by hydrogen peroxide. Since the reaction is inhibited by acetic acid, the reaction may involve the reaction of methoxide with hydrogen peroxide in some form. Possibly the two species react when they are both bound to the metal, as shown below.



(10)

Conclusion

We have found an unusual mechanism for catalysis of oxidation by a metallic species. Most mechanisms probably involve some kind of primary reaction between oxygen and the metal, usually leading to a higher oxidation state of the latter. Catalysis of oxidation of benzoin by iron(II) is an example.[2] In the present case the mechanism apparently involves interaction of the metal with the substrate to produce a highly reactive reducing agent, which then reacts rapidly with oxygen. The activity of the nickel catalyst is highly ligand specific, being restricted to acetate and propionate in our work. This specificity has been built into the cyclic mechanism involving transfer of the α-hydrogen atom of benzoin to a ligated acetoxy group.

Experimental Section

Materials. **Nickel acetylacetonate** was prepared by the procedure reported earlier.[10] **Nickel acetate tetrahydrate** was recrystallized from 40% acetic acid and dried *in vacuo* over sodium hydroxide pellets. Recrystallized and reagent grade material showed the same kinetic behavior. **Anhydrous nickel acetate** was obtained from the tetrahydrate by dehydration at 100° *in vacuo* over phosphorus pentoxide. *Anal.* Calcd for $NiC_4H_6O_4 \cdot 4H_2O$: Ni, 23.60. Found: Ni, 23.60. Calcd for $NiC_4H_6O_4$: Ni, 33.21. Found: Ni, 33.31. **Nickel perchlorate dihydrate** was obtained by dehydration of the reagent grade hexahydrate *in vacuo* at 100° over phosphorus pentoxide. *Anal.* Calcd for $NiCl_2O_8 \cdot 2H_2O$: Ni, 19.98. Found: Ni, 20.20. The analysis of nickel was obtained by the dimethylglyoxime gravimetric[11] method. **Lithium acetate,** reagent grade, was dried *in vacuo* over phosphorus pentoxide at 100° to constant weight. **Methanol and ethanol,** reagent grade, were either treated with aluminum amalgam[12a] or with iodine-activated magnesium[12b] and then distilled through a 70 × 1 cm Hempel column. The solvents gave invariant kinetic results irrespective of treatment. Acetic acid was purified accordingly[13] by reflux with chromium trioxide and followed by distillation over phosphorus pentoxide. **Formaldehyde,** Mallinckrodt 37% reagent grade, was used as received and assayed by the gravimetric dimedone method.[14] **Hydrogen peroxide** (80%, assayed by iodometry) from the Becco Division of Food Machinery Corp. was used. **Benzoin,** Matheson Coleman reagent, was twice recrystallized from 95% ethanol under nitrogen: mp 134.5°, ϵ_{247}^{max} 12,300 in methanol. **Benzil,** Matheson Coleman reagent, was recrystallized twice from 95% ethanol: mp 95°, ϵ_{259}^{max} 20,200 in methanol. **4,4′-Dimethoxybenzoin,** Aldrich Chemical Co., was recrystallized twice from 95% ethanol under nitrogen, mp 111°. **4,4′-Dimethylbenzoin** was prepared by condensation of 4-methylbenzaldehyde according to the procedure[15] described for the preparation of benzoin, mp 88°. **4,4′-Dichlorobenzoin,** K and K laboratories, was recrystallized twice from *n*-heptane under nitrogen, mp 88° (reported value,[16] 88°).

Preparation of Deuteriobenzoin. $C_6H_5CDODCOC_6H_5$ was prepared by reduction of benzil with the binary system of magnesium–magnesium iodide[3] followed by hydrolysis of the reaction mixture with 1 *N* D_2SO_4 in D_2O.

MgI_2 Solution. Fresh magnesium (0.02 g atom, in small pieces), 30 ml of mixed solvent (diethyl ether and benzene 1:2 by volume), and 0.01 mol of iodine were stirred together for 10 min until the exothermic reaction subsided. It was then heated to and kept at vigorous reflux until the solution became transparent and nearly colorless; 5 ml more of the mixed solvent was added to avoid over saturation. After cooling to room temperature, the unreacted magnesium was filtered off. This MgI_2 solution should be used immediately in the next step.

Reduction of Benzil. The reaction vessel consisted of a three-necked round bottom flask provided with a magnetic stirrer. A two-way stopcock for alternative evacuation and passing N_2, one outlet fitted with a gas bubbler, another outlet with serum cap for introducing acidic D_2O for hydrolysis, was used. The system was kept under nitrogen. Purified benzil (0.01 mol) was placed in the flask and the predeoxygenated MgI_2 solution (0.01 mol) was introduced, followed by clean magnesium (0.011 mol, in small pieces). This reaction mixture was stirred at room temperature in a slightly positive nitrogen atmosphere. This spontaneous reduction reaction took 2.5 hr to reach completion as indicated by the change from dark opaqueness to yellow transparency.

Hydrolysis with D_2O. D_2SO_4 (1 *N*, 28 ml, predeoxygenated) was introduced and it was stirred vigorously under nitrogen for 1 hr. Then the reaction mixture was open to air. The aqueous layer was

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(9) The reaction involves breaking of a carbon–hydrogen bond, normally a kinetically slow process. Since the concentration of the complex is too small to detect spectroscopically, the specific rate of reaction 7 must be rather high and perhaps incompatible with the view that C–H bond breaking and spin pairing occur in the same step.

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discarded and the organic layer was stirred with 100 ml of benzene and 50 ml of chloroform to dissolve the products. The resultant turbid suspension was filtered to remove magnesium hydroxide, unreacted magnesium, and polymeric substance. The filtrate was evaporated to dryness and the product was further dried *in vacuo* at room temperature over P_2O_5, giving deuteriobenzoin, a white solid, at 95% yield, mp 132°.

Characterization of Deuteriobenzoin. Infrared spectra were measured on a Model 225 Perkin-Elmer spectrophotometer using KBr pellets and freshly prepared $CHCl_3$ solutions. Both showed absorption bands at 3460 (OH), 2540 (OD), and 2330 (CD) cm^{-1}. The CH absorption at 2900 cm^{-1} (KBr pellet) in benzoin did not appear as a resolved maximum in the spectrum of deuteriobenzoin. The ultraviolet spectrum was measured on a Cary 14 spectrophotometer and superimposable on that of benzoin. The nmr spectra were measured on a Varian A-60 spectrometer in $CDCl_3$ solution with TMS as the internal reference. By integration of α-CH and OH peak areas, using the total integral for the five aromatic protons as internal standard and comparing quantitatively the spectra of benzoin and benzil, it was determined that the material was 99% benzoin and at least 75% C deuterated.

Kinetic Procedures. The volumetric oxygen monitoring procedure was essentially the same as previously reported.[2] Besides the same gas monitoring apparatus[2] which was semiautomatic, we have assembled a new automatic gas apparatus based on the same principle as reported in the literature[17] with modification of the mechanism of automatic recording.[18] The closed reaction system can be maintained at a constant pressure with sensitivity of 1 mm or less. A selenium photocell (Model B2M, International Rectifier Corporation, El Segundo, Calif.) was used as the sensing device of the pressure regulator. The output of the photocell, which was proportional to the pressure change, was connected in series to a preamplifier, a servo motor amplifier, then to a servo motor. The later was mounted on a vertical long spindle column carrying the mercury leveling bulb which adjusted the amount of mercury in the gas buret. The rotation of the spindle coupled with a potentiometer which was connected to a automatic recorder. This monitoring apparatus,[18] like the other one,[2] is useful for both gas evolution and gas absorption reactions. The results from these two apparatus agreed within 5%.

The polarographic monitoring was made on the Model 53 Yellow Springs Instrument (YSI) biological oxygen monitor. The sample solution (3 to 5 ml) was stirred 5 min in the reaction chamber either open to atmospheric air or 1 atm of oxygen to assure saturation solubility. Then the electrode was inserted and properly seated. After thermal equilibrium was reached (5–10 min stirring), as indicated by the steady value of $[O_2]$, the stirring was momentarily stopped, the catalyst solution was injected through the side groove in the electrode, then stirring was immediately resumed, and zero time was marked. A smooth constant stirring was maintained through the reaction course. The progress of the reaction was automatically recorded. It was essential to follow the instruction manual of this YSI instrument. Standard solution of which $[O_2]$ is known and standard reaction were used frequently to check the reliability of the electrode and the reproducibility of the results.

Analytical Methods. Benzoin and **benzil** were determined spectrophotometrically. The absorbance of a series of solutions of each compound and solutions of both compounds in methanol showed that Beer's law is followed at 260, 270, and 280 nm, at which wavelength the extinction coefficients vary five- to sevenfold. An isosbestic point at 235 nm also follows Beer's law and may be used to check the total concentration of the two species. Hydrogen peroxide and formaldehyde did not affect the absorbance at these wavelengths under our experimental conditions. For analyses, samples of reaction mixtures were diluted to suitable concentrations and the concentrations of the two species were calculated using data for absorbance at all three analytical wavelengths and the isosbestic point.

Formaldehyde was determined gravimetrically using 5,5-dimethyl-1,3-cyclohexadione (dimedone).[13] Before precipitation of the formaldehyde dimedone condensation product, it was necessary to remove benzoin, benzil, and hydrogen peroxide. Calibration for mechanical loss of the gravimetric method was made by control analyses of a series of authentic samples of known composition. For solutions of very low concentration of formaldehyde, the mechanical loss became appreciable and a correction was necessary. The following is a typical procedure. A solution containing 25 ml of 0.5 *N* sulfuric acid and five drops of 3% ammonium molybdate solution was placed in an erlenmeyer iodometry flask and was deaired by addition of a small quantity of solid sodium bicarbonate. Two grams of potassium iodide was then dissolved in the mixture. A 5-ml sample from the reaction mixture was added and the iodine released was titrated immediately with a standard solution of sodium thiosulfate. A small amount of 0.2% starch solution was added as the end point was approached to serve as an indicator. A 50-ml solution of a pH 4.5–4.6 acetate buffer was then added. The mixture was cooled to ice temperature for 20 min and then filtered through a glass Buchner funnel to remove precipitated benzoin and benzil. The filtrate was further diluted with an additional 200 ml of the acetate buffer and 0.028 *M* aqueous dimedone solution (at least 10% excess) was added. The mixture was allowed to stand for 18 hr at room temperature with occasional shaking. The precipitated condensation product was then collected with a preweighed M sintered glass Buchner funnel, washed with small portions of water, and dried to constant weight at 60°.

Hydrogen Peroxide. Iodometric determination[11] is described above since it was carried out as a part of the sequence leading to determination of formaldehyde. Hydrogen peroxide was also determined by titration with permanganate,[19] which agreed with the result from iodometry. This indicated that no other peroxide beside hydrogen peroxide was present in the reaction mixture.

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