Kinetics of the Interaction of HO_2 and O_2^- Radicals with Hydrogen Peroxide. The Haber–Weiss Reaction[1]

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Abstract: The rates of reaction of HO_2 and O_2^- with hydrogen peroxide, known as the Haber–Weiss reactions, were studied by ^{60}Co γ radiolysis as a function of pH at 23.5 °C. The numerical values for the two rate constants, $k_{HO_2+H_2O_2} = (0.50 \pm 0.09)$ $M^{-1}\,s^{-1}$ and $k_{O_2^-+H_2O_2} = (0.13 \pm 0.07)$ $M^{-1}\,s^{-1}$, were computed from molecular oxygen yields which result from the radiation-induced chain decomposition of aqueous hydrogen peroxide solutions. The experimental results are consistent with a chain mechanism which takes into account the dissociation of $HO_2 \rightleftharpoons O_2^- + H^+$ ($pK = 4.7$) and the competition between the Haber–Weiss reactions ($HO_2 + H_2O_2$ and $O_2^- + H_2O_2$) and the recombination reactions of the superoxide and perhydroxyl radicals ($HO_2 + HO_2$ and $HO_2 + O_2^-$).

Introduction

The reaction of perhydroxyl radical with hydrogen peroxide, reaction 3, was used by Haber and Weiss in 1934 to explain the chain decomposition of hydrogen peroxide by iron salts:[2]

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH + OH^- \qquad (1)$$

$$OH + H_2O_2 \rightarrow HO_2 + H_2O \qquad (2)$$

$$HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2 \qquad (3)$$

$$Fe(II) + OH \rightarrow Fe(III) + OH^- \qquad (4)$$

Subsequent studies of the photo- and radiation-induced chain decomposition of hydrogen peroxide proved that the Haber–Weiss step is necessary for the correct interpretation of the experimental results. A number of such studies included determinations of k_3 which are listed in Table I.[3-11] Early qualitative evidence against the occurrence of the Haber–Weiss step was found by George in mixtures of solid KO_2 and 95% hydrogen peroxide.[12] However, we now know that information about the Haber–Weiss step cannot easily be extracted from the kinetics of such heterogeneous mixtures. Some other studies published lately suggested that the reaction either does not occur or is very slow.[13,14] Similar conclusions were also drawn from thermodynamic and molecular orbital considerations.[15]

More recently a pressing question regarding the Haber–Weiss reaction was its efficiency of OH radical generation under physiological conditions. As is well known, exposure of biological compounds to OH radicals can result in such reactions as hydroxylation, oxidation, H-abstraction, addition to double bonds, and bond breakage.[16,17] To account for the occurrence of some of these reactions in biological systems in which both H_2O_2 and HO_2/O_2^- were being generated, the Haber–Weiss reaction was invoked.[16,17] While experimental observations in most cases were no doubt accurate, the interpretation of the results in terms of a Haber–Weiss reaction is questionable.

It should be noted that in most cases no effort was made to remove metal impurities, a situation which strongly invites speculations of a Fenton-type reaction mechanism.[18] Addition of chelating agents like EDTA is a dangerous practice as it may obscure rather than clarify the situation, since little is known about the complex chemistry between biological compounds and such metal chelates in the presence of hydrogen peroxide and/or superoxide radicals.[19] The subject of the involvement of the Haber–Weiss and the Fenton reaction[20] (reaction 1) in biological and related systems has been discussed in some detail in several recent articles.[16-18]

The purpose of this investigation was to systematically study the Haber–Weiss reaction as a function of pH in the range from 0.5 to 10.0 and to reduce as much as possible the role of metal impurities.

Experimental Section

Materials. Highly purified water was obtained by passing distilled water through a commercial ultrapurification system (Millipore Corp.). This water was found to be of equal or better quality than triply distilled water. It was discovered that contamination of solutions with particulate matter, possibly iron-containing dust, led to irreproducible results. Thus, all solutions were filtered through 0.2-μm fluorocarbon membranes prior to use. When solutions were prepared and handled in a laminar flow hood, it was not necessary to filter them again before use and the stability of concentrated hydrogen peroxide solutions increased dramatically. A filtered source of UHP nitrogen (99.999%, Matheson Co.) was used to deoxygenate solutions, if necessary.

All glassware was cleaned with HF–HNO_3–Alconox cleaning solution, thoroughly rinsed, and preirradiated. Quartz vessels were used for storage of solutions.

Buffer solutions were prepared from specially purified[21] Na_3PO_4 (Baker analyzed product) and double distilled 70% $HClO_4$ in Vycor (G. Frederick Smith Co.), containing less than 0.01 ppm Fe.

Two samples of hydrogen peroxide were used. Mallinckrodt analyzed reagent grade 30% hydrogen peroxide (without stabilizer) was used after millipore filtration. Ultrapure 30% hydrogen peroxide, distilled in Vycor from Apache Chemical Co., was studied with and without filtration. Absolute concentrations were determined by the ceric sulfate method[22] using a molar extinction coefficient of $\epsilon_{320\,nm}^{Ce(IV)}$ 5580 $M^{-1}\,cm^{-1}$ in 0.8 N sulfuric acid.

Apparatus and Techniques. Determination of the rate of the Haber–Weiss reaction involves measuring the yield of oxygen produced by ^{60}Co γ radiolysis in deoxygenated hydrogen peroxide solutions. The radiation-induced decomposition of hydrogen peroxide is always accompanied by thermal decomposition, a process catalyzed by metal impurities. That metallic impurities are involved in the thermal mechanism is demonstrated by the quenching effect of added EDTA on the thermal rate of oxygen production as shown in Table II.

It was found that rigorous cleaning of glassware and the use of ultrapure chemicals slows down the thermal rate of decomposition to a tolerable level. To correct for the thermal decomposition in a radiation experiment, samples of unirradiated blanks were analyzed for oxygen content immediately before and after the irradiated sample. Experiments showed that the thermal oxygen production is linear with time over the short interval of a radiation experiment (less than 10 min); hence oxygen present in the irradiated solutions from thermal decay was calculated by interpolation. In typical runs the thermal reaction accounted for 5–10% of the observed oxygen; in the worst case at pH 10 and in 2 M hydrogen peroxide the contribution was as high as 40%.

Oxygen concentrations were measured with a Yellow Springs Instrument oxygen electrode, which has a sensitivity of ±0.5 ppm. The

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Table I. Values of the Haber-Weiss Rate Constant k_{HW} in Aqueous Solutions[a]

method	H_2O_2, M	pH	temp, °C	k_{HW}, $M^{-1}\,s^{-1}$	ref
^{60}Co γ-radiolysis and UV photolysis	8×10^{-5}	natural	RT ± 5	530.0	3
^{60}Co γ-radiolysis	1-20	natural	0	1.10	4
and UV photolysis	1-20	natural	25	3.70	
^{60}Co γ-radiolysis and UV photolysis	1-40	1.0	10	0.01	5
^{60}Co γ-radiolysis	0.1-5.0	0.4	RT (?)	0.20	6
		1.0		0.28	
		1.5		0.65	
UV photolysis	0.12-4.2	neutral	RT (?)	16.00	7
UV photolysis in presence of H_2	3×10^{-4}	2.0	RT (?)	5.0	8
Reevaluation of ^{60}Co γ-radiolysis data			RT	~10.0	9
^{60}Co γ-radiolysis	0.003-0.2	5.4-7.85	RT	2.25 ± 0.02	10
KO_2 in H_2O	0.16	7.5-9.4	25	10^{-4}	11
^{60}Co γ-radiolysis	0.08-1.5	0.5-3.5	23.5	0.50 ± 0.09	this report
	0.08-1.5	7.0-9.9	23.5	0.13 ± 0.07	

[a] Here, depending upon the pH, k_{HW} can be $k_{HO_2+H_2O_2}$, $k_{O_2^-+H_2O_2}$, or a combination of both.

Pyrex vessel shown in Figure 1 was designed to incorporate features necessary to achieve reproducibility in the oxygen measurements; no rubber, plastic, metal, or ground glass contacts the solution at any time. The response of the O_2 electrode was tested in the presence of up to 4 M hydrogen peroxide and it was found that the response was constant and independent of H_2O_2 concentration.

Two ^{60}Co γ-ray sources were used for irradiation. The respective intensities were measured periodically by the ferrous dosimeter, $G(Fe^{3+}) = 15.5$.[23] At a particular time their intensities were for source no. 1 7.60×10^{-5} M and for source no. 2 1.16×10^{-5} M of ferric iron formed per minute. The G value represents the number of molecules formed per 100 eV energy dissipated in the system. Samples in which the Haber-Weiss reaction was studied were irradiated from 0.5 to 4 min. All reactions and measurements were carried out at 23.5 °C.

Table II. Effect of EDTA Concentration on the Spontaneous O_2 Generation at 23.5 °C in (a) 1.0 M H_2O_2[a] at pH 4.8 and (b) 0.1 M H_2O_2[b] at pH 10.0

EDTA, μM	(a) O_2, μM/min	(b) O_2, μM/min
0	1.15	1.60
2	0.80	0.73
10	0.38	0.32
20	0.16	0.12
50	0.11	0.08
100	0.09	0.05

[a] Apache Chemical Co. [b] Mallinckrodt Chemical Co.

Results and Discussion

In the present study measurements of the Haber-Weiss reactions have been carried out in the pH range from 1 to 10.

$$HO_2 \rightleftharpoons O_2^- + H^+$$
$$\times K_{HO_2} = (2.05 \pm 0.4) \times 10^{-5}\ M \qquad (5, -5)$$

Because of the pH dependence of the equilibrium[24] it is necessary to redefine the Haber-Weiss reaction as the sum of reactions 3 and 6 as both HO_2 and O_2^- react with hydrogen peroxide:

$$HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2 \qquad (3)$$

$$O_2^- + H_2O_2 \rightarrow OH + OH^- + O_2 \qquad (6)$$

Reactions 3 and 6 cannot be monitored spectrophotometrically in concentrated hydrogen peroxide solutions because of the rapid regeneration of O_2^- by reaction 2. An alternative way of following these reactions is by either observing the disappearance of H_2O_2 (which has the disadvantages of being a small change in a large number) or by measuring the formation of molecular oxygen (the method used in this study). To minimize the experimental error in the oxygen measurements, the peroxide solutions were deoxygenated before use.

The overall chain mechanism by which molecular oxygen is generated in deoxygenated hydrogen peroxide solutions irradiated with ^{60}Co γ-rays is described by three sets of equations, initiation, propagation, and termination reactions:

initiation:

$$H_2O \rightsquigarrow OH\ (2.74),\ e^-_{aq}\ (2.76),\ H\ (0.55),$$
$$H_2O_2\ (0.72),\ H_2\ (0.55),\ H_3O^+\ (2.76) \qquad (1)^{25}$$

$$e^-_{aq} + H_2O_2 \rightarrow OH + OH^-$$
$$k_7 = (1.2 \pm 0.1) \times 10^{10}\ M^{-1}\,s^{-1} \qquad (7)^{26}$$

$$H + H_2O_2 \rightarrow OH + H_2O$$
$$k_8 = (9.0 \pm 1.0) \times 10^{7}\ M^{-1}\,s^{-1} \qquad (8)^{27}$$

propagation:

$$OH + H_2O_2 \rightarrow HO_2 + H_2O$$
$$k_2 = 4.5 \times 10^{7}\ M^{-1}\,s^{-1} \qquad (2)^{28}$$

$$HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2$$
$$k_3 = (0.5 \pm 0.09)\ M^{-1}\,s^{-1} \qquad (3)$$

$$O_2^- + H_2O_2 \rightarrow OH + OH^- + O_2$$
$$k_6 = (0.13 \pm 0.07)\ M^{-1}\,s^{-1} \qquad (6)$$

termination:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$
$$k_9 = (8.60 \pm 0.62) \times 10^{5}\ M^{-1}\,s^{-1} \qquad (9)^{24}$$

$$HO_2 + O_2^- \xrightarrow{H_2O} H_2O_2 + O_2 + OH^-$$
$$k_{10} = (1.02 \pm 0.49) \times 10^{8}\ M^{-1}\,s^{-1} \qquad (10)^{24}$$

$$O_2^- + O_2^- \xrightarrow{2H_2O} H_2O_2 + O_2 + 2OH^-$$
$$k_{11} < 0.35\ M^{-1}\,s^{-1} \qquad (11)^{24}$$

The numerical values in eq 1 are G values for the respective species. In the presence of hydrogen peroxide the reducing radicals e^-_{aq} and H are converted to OH radicals by reactions 7 and 8. Hence the resulting total yield of OH radicals in this system is $G(R) = G_{OH} + G_H + G_{e^-_{aq}} = 6.05$. All the OH radicals are in turn converted to HO_2/O_2^- radicals in the

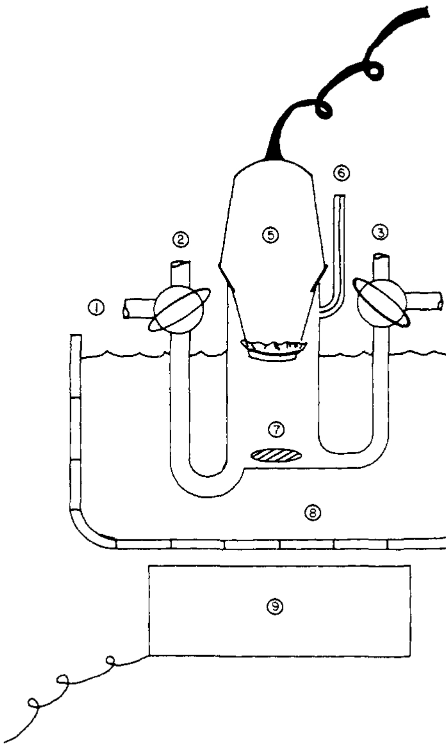

Figure 1. Apparatus for the determination of oxygen concentrations in aqueous solutions with a Yellow Springs Instrument oxygen electrode: 1, vacuum drain; 2, sample inlet; 3, rinse-water inlet; 4, N_2-purge inlet; 5, oxygen electrode; 6, capillary tubing open to atmosphere for equilibration of pressure; 7, Teflon stirring-bar; 8, constant temperature bath; 9, magnetic stirrer.

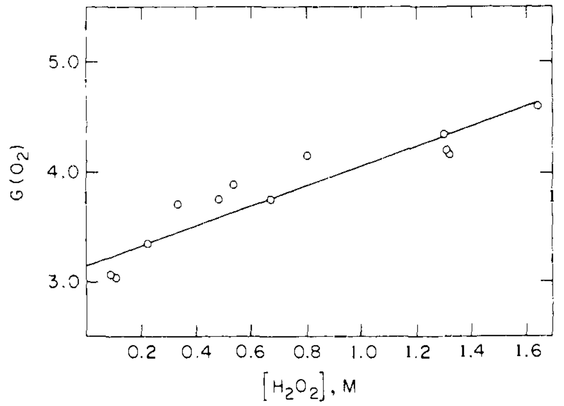

Figure 2. Illustration of linear relationship between $G(O_2)$ and $[H_2O_2]$ at a ^{60}Co γ-ray flux of $I = 4.85 \times 10^{-7}$ M radicals/s and pH 2.21 ± 0.07; temperature 23.5 °C.

propagation step (reaction 2) thus starting the chain reaction. Our mechanism does not include the hypothetical $H_2O_2^+$ radical,[6,29,30] as our experiments show no evidence for such a species in the pH range studied. Also, we neglect reaction 11 as a termination step because of the small rate constant.

The oxygen has its origin in two sources: (1) the dismutation of HO_2 and O_2^- in reactions 9 and 10 in which every two radicals produce one molecule of molecular oxygen and (2) the Haber-Weiss reactions (reactions 3 and 6) which yield one oxygen molecule for every turnover of the chain. Use of the steady-state approximation for (OH), (HO_2), and (O_2^-) radicals leads to the following expression for the molecular oxygen yield produced by ^{60}Co γ irradiation of intensity I:

$$G(O_2) = \tfrac{1}{2}G(R) + (H_2O_2)[G(R)/ID]^{1/2} \times [k_3 + k_6K_{HO_2}/(H^+)] \quad (II)$$

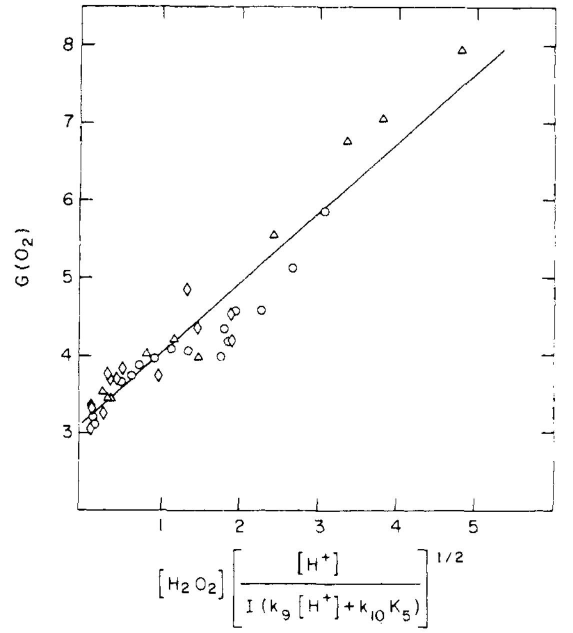

Figure 3. Data showing the linear relationship between $G(O_2)$ and $[H_2O_2][[H^+]/I(k_9[H^+] + k_{10}K_{HO_2})]^{1/2}$ in the pH range 0.5-3.0 and a hydrogen peroxide concentration range from 0.08 to 1.5 M: ○, H_2O_2 Mallinckrodt irradiated in source 1; △, H_2O_2 Apache irradiated in source 1; ◇, H_2O_2 Apache irradiated in source 2.

where

$$D = 2[k_9 + k_{10}K_{HO_2}/(H^+)] \quad (III)$$

The expression for $G(O_2)$ is valid over the entire pH range.

Equation II indicates that a plot of $G(O_2)$ as a function of hydrogen peroxide concentration for a fixed radiation intensity and pH will be linear. Such a plot is shown in Figure 2. The rate constants for reactions 3 and 6 are obtained from the limiting forms of eq II at low and high pH, respectively.

Determination of k_3. For pH less than 3.0, eq II reduces to a form which upon rearrangement yields

$$G(O_2) = \tfrac{1}{2}G(R) + k_3[H_2O_2]\left[\frac{G(R)[H^+]}{2I(k_9[H^+] + k_{10}K_{HO_2})}\right]^{1/2} \quad (IV)$$

A plot of $G(O_2)$ vs. $[H_2O_2][[H^+]/I(k_9[H^+] + k_{10}K_{HO_2})]^{1/2}$ is linear as shown in Figure 3 for the pH range 0.5-3.0 and a hydrogen peroxide concentration ranging from 0.08 to 1.5 M. These results comprise two sets of data (see legend of Figure 3) obtained with Mallinckrodt and Apache hydrogen peroxide solutions. Applying the "t" test[31] to the means of the two sets of data, it can be shown that there is a 70% probability that the two sets have a common mean. Hence these data were averaged together, to give a mean value of $k_3 = 0.50 \pm 0.09$ M^{-1} s^{-1}, where the range is the 95% confidence interval. In these computations we used the experimentally determined values for $G(O_2)$, $[H_2O_2]$, $[H^+]$, I (radiation intensity), and the value of $\tfrac{1}{2}G(OH) = 3.12$ obtained from the intercept of the least-squares line in Figure 3.

Our value of k_3 is in relatively good agreement with the value(s) reported earlier for the acid pH range by Ferradini et al.[6] (see Table I, 1969).

Determination of k_6. For the high pH range (pH >7), eq II yields

$$G(O_2) = \tfrac{1}{2}G(R) + k_6[H_2O_2]\left[\frac{G(R)K_{HO_2}}{2k_{10}[H^+]I}\right]^{1/2} \quad (V)$$

The rate constant k_6 was determined from the slope of the plots of $G(O_2)$ vs. $H_2O_2/([H^+]I)^{1/2}$ shown in Figure 4 for pH

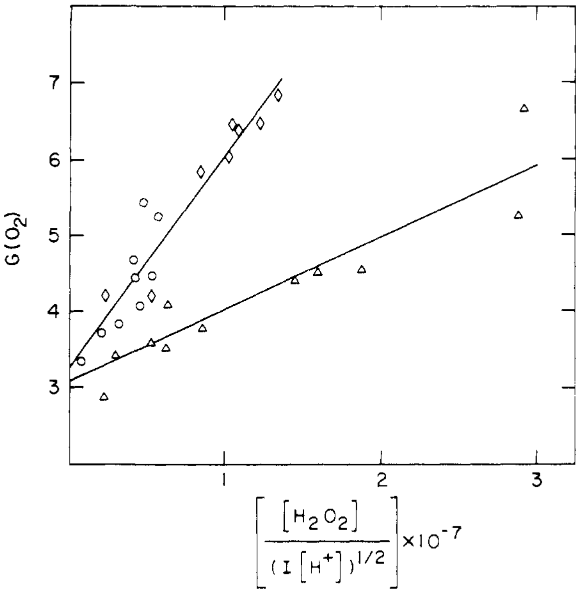

Figure 4. Data showing the linear relationship between $G(O_2)$ and $[H_2O_2]/(I[H^+])^{1/2}$ in the alkaline pH range from 7.0 to 9.9 and a hydrogen peroxide concentration range from 0.08 to 1.3 M: △, H_2O_2 Mallinckrodt irradiated in source 1, computed $k_6 = 0.13 \pm 0.07$ M^{-1} s^{-1}; ○, H_2O_2 Apache irradiated in source 1; ◊, H_2O_2 Apache irradiated in source 2. The computed rate constant from these two runs is $k_6 = 0.24 \pm 0.07$ M^{-1} s^{-1}.

7.0–9.5 and a hydrogen peroxide concentration range from 0.08 to 1.3 M. The two sets of data in Figure 4 represent results obtained with the Mallinckrodt and Apache hydrogen peroxide solutions, respectively. Application of the "t" test[31] to the means of these two sets of data indicates that they cannot belong to a single population. Hence there is a genuine difference in reactivity of the two types of peroxide solutions toward O_2^- for wich the corresponding rate constants are $k_6^M = 0.13 \pm 0.07$ M^{-1} s^{-1} and $k_6^A = 0.24 \pm 0.07$ M^{-1} s^{-1} (the superscripts stand for M = Mallinckrodt and A = Apache).

To resolve the question as to which set of data should be accepted, we observed the decay of O_2^- absorption in peroxide solutions at 280 nm. In the presence of 0.09 M Mallinckrodt peroxide the observed value for the O_2^- decay at pH 8.24 was $k_{obsd} = (2.7 \pm 0.3) \times 10^4$ M^{-1} s^{-1} and $k_{obsd} = (2.9 \pm 0.4) \times 10^4$ M^{-1} s^{-1} upon addition of 5×10^5 M EDTA (note that the ratio of H_2O_2:EDTA is such that OH scavenging by EDTA is negligible). A similar series of experiments carried out in 0.08 M Apache peroxide yielded $k_{obsd} = (1.3 \pm 0.3) \times 10^4$ M^{-1} s^{-1} and $k_{obsd} = (1.5 \pm 0.3) \times 10^4$ M^{-1} s^{-1} in the presence of 5×10^{-5} M EDTA. These values of k_{obsd} should be compared to the accepted value of the rate constant for spontaneous decay of O_2^- at pH 8.24: $k_{obsd} = 3.0 \times 10^4$ M^{-1} s^{-1}. As is apparent, while the Mallinckrodt results are within experimental error of the expected value, the results for the Apache runs are off by a factor of 2. This effect was even more pronounced at pH 7.5, where again the Mallinckrodt results were within experimental error of the expected value while the Apache rates were low by a factor of 5–7.

At present we have no explanation for the rate lowering effect of the impurity in the Apache peroxide. Most likely the impurity is organic in nature since from our experience the effect of metallic impurities can be suppressed by the addition of EDTA. As our data show EDTA had no significant effect upon the observed rates. Similar discrepancies between the two types of hydrogen peroxide do not exist in the acid range. In our opinion the data obtained in this study with the Mallinckrodt hydrogen peroxide are more reliable and we accept therefore for k_6 the value of 0.13 ± 0.07 M^{-1} s^{-1}.

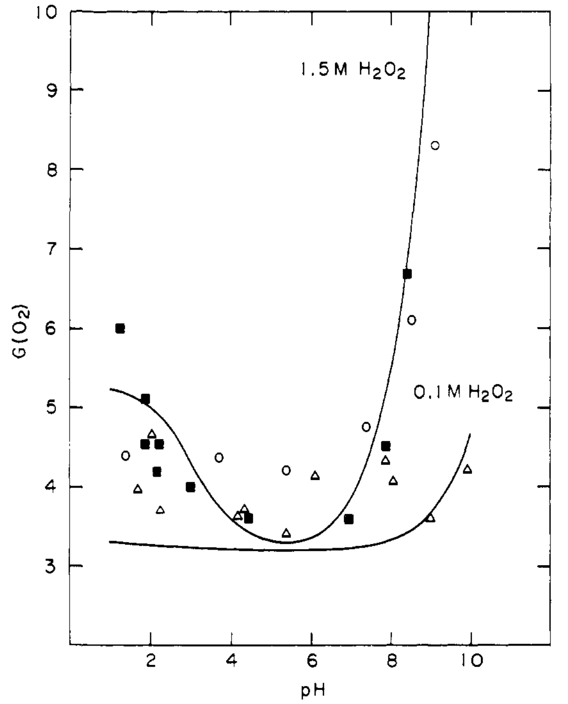

Figure 5. Illustration of the change in $G(O_2)$ with pH for different hydrogen peroxide concentrations as predicted by eq II. The solid lines were computed for the two extreme hydrogen peroxide concentrations used in this study, using the average values for $k_3 = 0.50 \pm 0.09$ M^{-1} s^{-1} and $k_6 = 0.13 \pm 0.07$ M^{-1} s^{-1}: ■, 1.5 M H_2O_2 Mallinckrodt; ○, 0.9 M H_2O_2 Apache; △, 0.3 M H_2O_2 Mallinckrodt.

Using the two values for k_3 and k_6, the pH dependence of $G(O_2)$ can be evaluated from eq II. This calculation is illustrated in Figure 5 for two peroxide concentrations. The two solid lines in the figure are computed for 1.5 and 0.1 M hydrogen peroxide solutions, the upper and lower concentration limits used in this study. The experimental data points, although scattered, follow the overall trend of the solid lines which, according to our mechanism, should pass through a minimum at the pH where the termination reactions (reactions 9 and 10) compete most effectively.

It should be noted that the best fit between the predicted and observed results is at the extreme ends of the pH range studied. In the pH range between 4 and 7 the experimental data obtained in this study were always higher than the values predicted from k_3 and k_6. Preliminary studies of the Haber-Weiss reactions in very concentrated hydrogen peroxide solutions and in presence of very low concentrations (μM) of EDTA indicate that the metal impurities we are dealing with have an optimal activity in the neutral region ($G(O_2)$ is affected by addition of EDTA). This observation is consistent with our findings in the present study which suggests that both protonation as well as hydroxylation reduces the catalytic activity of the remaining impurity(ies) in our system.

It has been shown in this study that rigorous purification of reagents allows the rate constants for the Haber-Weiss reactions to be deduced from a simple kinetic treatment without invoking $H_2O_2^{+}$[6] or HO_2-H_2O_2 complexes[3] and that the magnitude of the rate constants k_3 and k_6 eliminates the Haber-Weiss reactions as potential OH radical sources in biological systems because of the relatively rapid dismutation of the HO_2/O_2^- radicals at physiological pH. In view of the fact that most of our attempts to exclude metal impurities led to lower values of the rate constants k_3 and k_6, we should probably view these numbers as upper limits.

Despite the exorcism of the Haber-Weiss reaction, there is convincing evidence for the involvement of hydroxyl radicals in reactions which use superoxide radicals as precursors.[16,17] Metal ions are strongly implicated in these reactions and there is evidence that superoxide radicals form metastable complexes with metal ions[32-34] which might then participate in a Haber–Weiss type reaction.

Alternatively, the superoxide radical can serve as a source of hydroxyl radicals by reducing Fe(III), thus permitting a Fenton reactions:[20]

$$O_2^- + \mathrm{Fe(III)} \rightarrow \mathrm{Fe(II)} + O_2 \qquad (12)$$

$$\mathrm{Fe(II)} + H_2O_2 \rightarrow \mathrm{Fe(III)} + OH + OH^- \qquad (1)$$

That Fenton-type reactions can occur even with complexed metal ions, e.g., ferric ethylenediaminetetraacetate, has already been demonstrated.[19,35] Thus the present status is that unless some very convincing evidence is produced in favor of singlet molecular oxygen ($^1O_2$, a species also in high fashion),[17,36] accumulating evidence is tipping the scales in the direction of the "Walling concepts"[18] of metal catalysis.

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References and Notes

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A Coordination Chemistry Study of a Nickel Surface. The Chemistry of Ni(111) with Triply Bonded Molecules

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Abstract: The chemistry of the (111) surface of nickel has been investigated for a series of molecules with unsaturated bonds: acetonitrile, methyl isocyanide, cyanogen, acetylene, 2-butyne, carbon monoxide, and ethylene. Acetonitrile, as in coordination chemistry, was weakly bound to the nickel surface and was readily and completely displaced by carbon monoxide at 300 K. This nitrile formed a simple ordered surface structure at 300 K; the observed (2 × 2) unit cell would accommodate acetonitrile molecules, normal to the surface, on every other nickel atom. The isomeric methyl isocyanide molecule was strongly bound to the surface, was not reversibly desorbed on temperature increase, and was not displaced by carbon monoxide. Dehydrogenation of the isocyanide occurred at ~380 K and above 800 K N_2 evolved to leave only carbon on the nickel crystal surface. Cyanogen was also strongly chemisorbed: thermal desorption gave N_2 at ~800 K in contrast to platinum surfaces which reversibly desorb cyanogen. Cyanogen on the Ni(111) surface formed an extremely stable, ordered (6 × 6) structure at ~400 K. Acetylene, 2-butyne, and ethylene were irreversibly chemisorbed on the nickel surface.

Introduction

Although a clean metal surface has absolutely no analogue in coordination chemistry,[4] metal surfaces with monolayers of chemisorbed molecules may have close analogues within coordination chemistry—mononuclear complexes, dinuclear compounds, and discrete molecular metal clusters. Experimental evidence qualitatively supports the analogy.[6-9] However, despite the diversity of supportive data, the evidence is

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