Table II. Residual CD[a] of the Complexes Studied

R_a	$R(AB_a{}^S)_{tot}$	$R(AB_a{}^R)_{tot}$	ΔR_{tot}
Me	0.90	0.73	0.16
Et	0.93	−0.57	0.36
i-Pr	0.94	−0.42	0.53

[a] As peak heights in units of $\Delta\epsilon$.

principle CD cotton effects occur between 550 and 400 nm (Figure 1). It is evident that the CD spectrum in the d–d region consists of two dominant peaks.

The $R(AB_a)$'s (vicinal effects)[9] were calculated by subtracting the CD of the glycine complex from the appropriate experimental spectra according to eq 12, as shown in Figure 2 for the (*R*)- and (*S*)-methylalanine complexes. The residual CD's (ΔR) were then obtained from the vicinal effects by application of eq 13, as shown in Figure 2 for the (*R*)- and (*S*)-methylalanine complexes. Similar results are observed for compounds **2b,d** with significant differences between $R(AB_a{}^R)$ and $R(AB_a{}^S)$. The $R(AB_a)$ and the ΔR values in Figure 2 are complicated by the presence of two dominant Gaussian peaks. Since it would be extremely difficult to deconvolute these unambiguously, we simply calculate $R(AB)_{tot}$ as the sum of the positive and negative contributions in the 400–500-nm range and ΔR_{tot} as the sum of the ΔR at 445 and 498 nm for comparison. These results are reported in Table II.

Experimental Section

Visible spectra were obtained on a Cary 17 spectrophotometer. CD spectra were obtained on a Cary 61 spectropolarimeter. The pH-stat used in the syntheses is described elsewhere.[14] Cation-exchange resin was Bio Rad AG 50W-X2, 200–400 mesh. Amino acids were purchased from Aldrich Chemical Co. Deconvolution and mathematical manipulation of CD data were carried out with the aid of a Hewlett-Packard 9825 programmable calculator. The previously described amino acid complexes[2] $\mathbf{2a}^R$, $\mathbf{2b}^S$, $\mathbf{2b}^R$, $\mathbf{2d}^S$, and $\mathbf{2d}^R$ were prepared under controlled conditions, as described below, and crystallized to constant CD, as the perchlorate salts from the major fractions (which were isolated via cation-exchange chromatography in cases where insufficient solubility difference existed to effect rapid purification by crystallization).

$\Lambda(-)_{436}$-β_2-[((2*S*,9*S*)-2,9-diamino-4,7-diazadecane)cobalt(III) (*R*)- or (*S*)-methylalaninate] Diperchlorate (2c). Methylalanine (4.0 mmol) was slurried with $\Lambda(-)_{436}$-α-(dichloro-2,9-diamino-4,7-diazadecane)cobalt(III) chloride[2] (4.0 mmol) in 10 mL of water. The slurry was stirred in a 48 °C water bath while the pH was maintained at 7 ± 0.1 by pH-stat with 1.0 M NaOH. After a few hours the solution had turned orange, and the base addition was complete. The product was precipitated from solution upon addition of excess $NaClO_4$: yield (of (*S*)-amino acid complex) 0.755 g (35%). Anal.: C, H, N.

Conclusion

The earlier assumption that the (*S*)-am complex is relatively free of steric interactions is supported by the slow increase of $R(ABa^S)_{tot}$ as the size of R_a increases. This slow increase is expected simply from the variation of the inducing power and is also found in other amino acid complexes in which steric interactions are absent.[15] The residual CD, however, increases dramatically with the size of the R_a group, indicating a more significant increase in the steric interactions in the (*R*)-am complexes between the R_a and the tetraaminecobalt(III) moiety. Thus the conclusion that the (*R*)-amino acids exhibit greater steric interactions is entirely consistent with the experimental observation that less (*R*)-alanine is formed upon decarboxylation of compound **1**.

This technique has considerable potential in that the amino acid may be used as a probe (manifested through the residual d–d CD) for steric interactions which may exist in solution.

Acknowledgment. We wish to thank the Colorado State University Agriculture Experiment Station and the Research Corp. for support of this research.

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Reactions Involving Hydrogen Peroxide, Iodine, and Iodate Ion. 7. The Smooth Catalytic Decomposition of Hydrogen Peroxide, Mainly at 50 °C

Herman A. Liebhafsky,* Ryusaburo Furuichi, and Glenn M. Roe

Contribution from the Department of Chemistry, Texas A&M University,
College Station, Texas 77843, and the Corporate Research and Development Center,
General Electric Company, Schenectady, New York 12345. *Received February 12, 1980*

Abstract: Substantial progress has been made in the ongoing search for a simple mechanism to describe this complex reaction system over wide concentration ranges. A reasonably good quantitative explanation has been found for the nonoscillatory (smooth catalytic) decomposition of H_2O_2 as it occurred in many early experiments. This explanation rests upon the "skeleton mechanism", which will need further modification to explain induction periods and oscillations. Computer evaluation of the skeleton mechanism proved that the overall rate of the "smooth catalysis" need not be first order with respect to the peroxide concentration even though each peroxide step in the mechanism has that distinction. Free radicals, though undoubtedly present, are not ipso facto involved in the smooth catalysis. In this evaluation, the experimental limiting value, 7.2 min^{-1} at 50 °C, was used as the specific rate for the "electrolytic dissociation" of I_2 into I^+ and I^-.

During the smooth catalytic decomposition ("smooth catalysis") of H_2O_2 in this reaction system,[1-7] the main reaction is

$$H_2O_2 = H_2O + {}^1/{}_2O_2 \qquad (A)$$

although the approximate proportionality of $[H_2O_2]$ and $[I_2]$[8] gives warning that this equation is deceptively simple. Ultimate simplicity would require $[I_2]$ to be constant, hence independent of $[H_2O_2]$. Nowhere is this true.

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* To whom correspondence should be addressed at Texas A&M University.

(1) Part 1: W. C. Bray and H. A. Liebhafsky, *J. Am. Chem. Soc.*, **53**, 38 (1931).

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(3) Part 3: H. A. Liebhafsky, *J. Am. Chem. Soc.*, **53**, 896 (1931).

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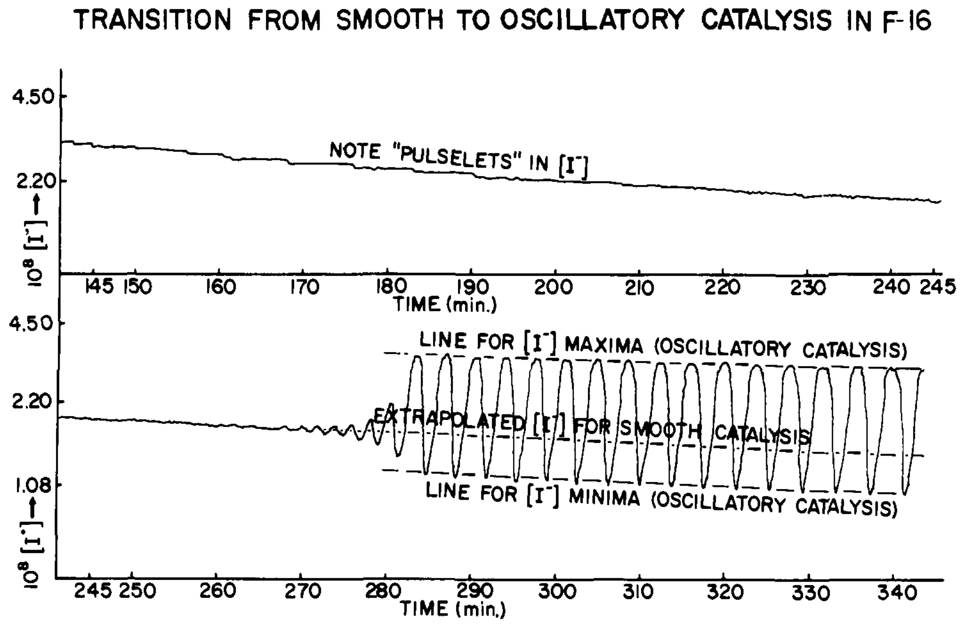

Figure 1. Photograph of center section of [I$^-$] record (millivolts output from specific [I$^-$] electrode) for F-16. The induction period (not shown) is like that in ref 9, Figure 2. The smooth catalysis (145–260 min) is marked by a rough proportionality between [I$^-$] and time (or [H_2O_2]) and by the presence of "pulselets" (random fluctuations?) in [I$^-$]. The interval 260–284 min shows the best record we have of a *gradual transition* from smooth to oscillatory catalysis. From the first fully developed [I$^-$] pulse (near 284 min), [I$^-$] oscillations of *virtually constant amplitude* and *decreasing frequency* were recorded until 53 min, when the experiment was ended, [H_2O_2] being near zero. Note the three parallel broken lines at the lower right. Discussion follows.

In 1928 alone, when the intensive investigation of this reaction system was begun, more than a hundred rate measurements of oxygen evolution (of R_{O_2})[8] were made on reaction A. The results were bewildering. Nothing like them was found in the literature. The oscillatory catalysis, spectacular though it is, was at the time only one more enigmatic feature of a complex reaction system that could not be explained by the results of R_{O_2} measurements alone, important though these are as *numerical tests* of proposed mechanisms.

Recent investigations (parts 5 and 6) deal with an approach to reaction A from the "iodine side"; i.e., with [I_2] initially much larger than it will be when reaction A becomes the "main reaction". In the approach from the "iodate side", H^+, IO_3^-, and H_2O_2 are mixed to make an initially colorless reaction mixture. Here is what happens when such a mixture is agitated. During the *induction period*, taken here as the time to reach $R_{O_2(\max)}$, the iodine color deepens until $R_{O_2(\max)}$ is reached. Thereafter, R_{O_2} and [I_2] decrease smoothly until oscillations set in or until H_2O_2 is exhausted, when the iodinaceous species, some inaccessible to measurement, readjust their concentrations.

Any mechanism worth its salt must explain the smooth catalysis. Because this could not be done in 1931, a qualitative summary (part 1, p 39) was published instead. Since then, methods have been developed[9–11] for the *simultaneous measurement* of [I_2], [I$^-$], and R_{O_2} during reactions taken *virtually to completion*: complete reaction, which sometimes requires 10 h or more, was recognized in 1928 as requisite for a comprehensive picture of the reaction system.

Detailed analysis of a modern experiment, F-16, and computer modification of the *skeleton mechanism* (part 6) have greatly improved our understanding of the many R_{O_2} measurements made in 1928–1929.

Gas burettes were used to measure R_{O_2} in F-16 as in 1928–1929, but the reaction mixtures were differently agitated now and then, an important point because supersaturation plays a critical role in the mechanism of Edelson and Noyes.[12] During the early work, the reaction mixtures, submerged in black oil, were mechanically given some 120–130 "double shakings" each minute in their flasks;[13] all modern experiments were done with magnetic stirring.

1928–1929 Experiments. An extensive survey of the reaction system culminated in two sets of results, L71-90 at 60 °C and L(1)–(34) at 50 °C. The main features of the smooth catalysis were established at the higher temperature and then confirmed at the lower, which was chosen as the preferred temperature for subsequent investigations, largely to reduce the volatility of I_2. "Oscillatory catalysis" was not found at 60 °C, where $[H^+]_0$ = 0.0715 was the lowest acid concentration investigated. At 50 °C, oscillatory catalysis was often found in the narrow range between $[H^+]_0$ = 0.0645 and 0.0430; these experiments do not belong here. Table I contains the results of all other 1928–1929 experiments at 50 °C. In these, only smooth catalysis was then thought to occur after the induction period.

The results of the earlier work at 60 °C supplement those in Table I. At $t = \infty$, titrations showed that final [I_2] at 60 °C increased from 10^{-6} to 7 (10^{-3}) as $[H^+]_0$ increased above 0.0715, an indication that increased [I_2] was needed to support high R_{O_2}. Initial addition of I_2 (L-74) markedly changed the smooth catalysis. Temperature coefficients (about 3 for the jump from 50 to 60 °C) were usually high and variable, another sign of complexity.

In the first three experiments of Table I, I_2(s) precipitated and I$^-$ formed at concentrations high enough to be measured in 1928. Sometimes, dissolution of I_2(s) to form I_3^- may have occurred.

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(4) Part 4: H. A. Liebhafsky, *J. Am. Chem. Soc.*, **53**, 2074 (1931).

(5) Part 5: H. A. Liebhafsky and L. S. Wu, *J. Am. Chem. Soc.*, **96**, 7180 (1974).

(6) Part 6: Herman A. Liebhafsky, William C. McGavock, Robert J. Reyes, Glenn M. Roe, and Lawrence S. Wu, *J. Am. Chem. Soc.*, **100**, 87 (1978).

(7) In the past Roman numerals have been used to cite the six references just given.

(8) Conventions are those of part 5: time, minutes or seconds, as indicated; concentrations, mol/L, represented by brackets; stoichiometric equations, =; kinetic processes, → for irreversible, and ⇄ for reversible reactions; rates, *R*'s, and specific rates, *k*'s, are identified by subscripts. *R* with a numerical subscript is always the *net* rate of the reaction in question.

(9) J. H. Woodson and H. A. Liebhafsky, *Anal. Chem.*, **41**, 1894 (1969).

(10) I. Matsuzaki, J. H. Woodson, and H. A. Liebhafsky, *Bull. Chem. Soc. Jpn.*, **43**, 3317 (1970).

(11) I. Matsuzaki, R. B. Alexander, and H. A. Liebhafsky, *Anal. Chem.*, **42**, 1690 (1970).

(12) D. Edelson and R. M. Noyes, *J. Phys. Chem.*, **83**, 212 (1979).

(13) A "double shaking" was a complete mechanical oscillation of the reaction flask. The reaction mixture collided violently with the flask walls at each end of the oscillation. The evolved oxygen passed through a copper pipe overhead to the gas burette.

Table I. Results of 1928–1929 Measurements of R_{O_2} during Smooth Catalysis at 50 °C

no.[b]	$[H^+]_0$[a]	$[IO_3^-]_0$	$10^2\kappa_1$,[c] min^{-1}	$10^2\kappa_2$,[c] min^{-1}	κ_1/κ_2[c]
L(15)	0.01637	0.1063	4.18		
L(14)	0.0328	do	4.18		
L(17)	0.0430	do	4.18		
L(19)	0.0645	do	1.27	0.455	2.79
L(22)	0.0645	0.2018	2.20	0.807	2.73
L(21)	0.0646	0.2882	2.85	1.12	2.54
L(10)	0.0715	0.1063	1.10	0.463	2.43
L(11)	0.0715	0.2018	1.83	1.15	1.59
L(7)	0.1437	0.1063	0.808	0.539	1.50
L(8)	0.3564	do	0.808	0.562	1.44
L(5)	0.7144	do	0.866	0.608	1.42
L(6)	1.495	do	1.25	0.723	1.73
L(9)	2.997	do	2.27	1.33	1.71
L(1)	2.997	do	2.13	1.38	1.54
L(2)	4.583	0.0937	5.28	4.31	1.23
L(3)	6.111	0.0908	14.2	10.8	1.31
L(12)	6.171	0.0938	9.5	8.2	1.16
L(13)	7.040	0.0908	21.5	16.4	1.31

[a] The subscript identifies this as an initial concentration. As always, the brackets denote mol/L. Reaction mixtures made with KIO_3 and $HClO_4$ except at $[H^+]_0 = 4.583$ and above, where HIO_3 was used to forestall possible precipitation of $KClO_4$. Volume of reaction mixtures usually 150 cm³. Throughout H_2O_2 was nominally 0.576. [b] Numbers give sequence of experiments. [c] κ_1 and κ_2 are initial and final specific-rate "constants" evaluated graphically from the slopes of $a - x$ plots against t as abscissa on "semilog" paper: a and x are the volumes of oxygen evolved at $t = \infty$ and $t = t$ min, measured in "actual" cm³, i.e., of gas assumed saturated with water vapor at room temperature and pressure. Were the smooth catalysis first order with respect to $[H_2O_2]$, the experimental points on such a plot would obey the relationship $kt = 2.303 \log a/(a - x)$, where k is the first-order specific rate, which will reappear later. This simple relationship never held over an extended time for the smooth catalysis. Instead, the experimental points after the induction period conformed initially to a line of slope corresponding to κ_1. Toward the end of the smooth catalysis, the points conformed to a line of lower slope corresponding to κ_2. The intermediate points lay on a smooth connecting curve of decreasing slope. The κ_1 and κ_2 values in Table I are those of 1928–1929. Their ratio will be used later.

Smooth catalysis at low $[H^+]_0$ appeared to proceed by a different mechanism in this, the "iodide zone".

One of the frustrating complexities in Table I will now be identified and dismissed. No one familiar with salt effects, equilibrium and kinetic, and with the thermodynamic complexity of iodate solutions[14] will be surprised to see divergent rate behavior above $[H^+]_0 = 1$.

A second complexity cannot be dismissed, for it has mechanistic significance. Experience with smooth catalyses in other reaction systems shows the rate of reaction A to be strictly first order with respect to $[H_2O_2]$. The variable κ's of Table I consequently engender misgivings made more serious by the work of Haber and Weiss[15] and recently deepened by that of Edelson and Noyes,[12] because such behavior suggests radical and chain reactions.

Revised Skeleton Mechanism: 1928–1929, 1972, and 1980 Results Intercompared. The intercomparisons were far too extensive for detailed record here. Table II is a partial record of one of the most significant, which involves L(10) (1928), F-16 (1972), and **F-16** (1980).[16]

The intercomparison in Table II is for $[H^+] = 0.0715$, an acidity chosen because it lies low enough so that salt effects and iodate complications do not wreak havoc, yet high enough so that no oscillatory decomposition was found in 1928. Figure 1 shows that 1972 brought a different story. Oscillatory catalysis began in F-16 after smooth catalysis had been under way long enough to reveal its nature.

We retain the earlier subdivision (part 6) of the skeleton mechanism into UP reactions (in which H_2O_2 *raises* the oxidation number of an iodine species), DOWN reactions (in which H_2O_2 *lowers* this oxidation number with liberation of O_2), and IODINE reactions that control H_2O_2 decomposition although they *do not involve* H_2O_2 directly.

Progress requires that we evaluate $[H_2O_2]$ as a function of t. This can only be done by assuming that $R_U = k_U[H_2O_2] = R_D = k_D[H_2O_2]$, and $R_{H_2O_2} = (k_U + k_D)[H_2O_2] = k[H_2O_2]$,[17] so that $k_U + k_D = k$. (U and D of course mean "UP" and "DOWN".) Were matters simple, we should have $k = \kappa_1 = \kappa_2$.

One of the great difficulties of working in this reaction system is that $[H_2O_2]$ cannot be determined but must be calculated from $[H_2O_2]_0$, and one or another of the relationships of the preceding paragraph, usually in conformity with reaction A. When a gas burette is used, a, the "actual" volume of gas measured at $t = \infty$, is the best way of establishing $[H_2O_2]$. More later.

The skeleton mechanism (part 6) to be revised is

$$I_2 + H_2O \rightleftarrows HIO + H^+ + I^- \text{ (IODINE)} \qquad (1)$$

$$I_2 \rightleftarrows I^+ + I^- \text{ (IODINE)} \qquad (2)$$

$$2H^+ + IO_3^- + I^- \rightleftarrows HIO + HIO_2 \text{ (IODINE)} \qquad (3)$$

Oxidation of I^+

$$I^+ + H_2O_2 \rightarrow H^+ + HIO_2 \text{ (UP)} \qquad (4)$$

Reduction of HIO

$$HIO + H_2O_2 \rightarrow H^+ + I^- + H_2O + O_2 \text{ (DOWN)} \qquad (5)$$

Irreversible reactions forming HIO

$$2H^+ + IO_3^- + 2I^- \rightarrow 2HIO + IO^- \text{ (IODINE)} \qquad (6)$$

$$HIO_2 + H^+ + I^- \rightarrow 2HIO \text{ (IODINE)} \qquad (7)$$

$$H_2O_2 + HIO_2 \rightarrow HIO + H_2O + O_2 \text{ (DOWN)} \qquad (8)$$

$$H_2O_2 + H^+ + I^- \rightarrow HIO + H_2O \text{ (UP) (usually negligible)} \qquad (9)$$

Additional formation of HIO_2

$$H_2O_2 + IO_3^- + H^+ \rightarrow HIO_2 + H_2O + O_2 \text{ (DOWN)} \qquad (10)$$

For a detailed intercomparison, specific rates obtained by integration will not serve. Data for closely-spaced individual values of t are needed. Many such were calculated, and barely enough for a satisfactory intercomparison are given in Table II.

Comments on Table II. (1) The 1928–1929 H_2O_2 contained an inhibitor, probably acetanilide or a stannous salt. The lengths of the induction periods (Table II, footnote "e") for L(10) and F-16 indicate that about 20 min sufficed to destroy the inhibitor at this $[H^+]_0$; at higher values, the time needed was shorter. After the induction periods, L(10) and F-16 were more nearly similar than Table II indicates, although L(10) never gave a maximum R_{O_2} as great as did F-16. Fuller discussion of induction periods belongs in the future, but this may be said now: the presence of inhibitor in the 1928–1929 H_2O_2 does not destroy the usefulness of Table I as a guide to mechanism.

It is gratifying that F-16 and **F-16** have nearly identical induction periods.

(2) The skeleton mechanism (part 4) was modified by changing three specific rates to give the revised mechanism for **F-16**: k_{2f}

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(14) (a) R. Furuichi and H. A. Liebhafsky, *Bull. Chem. Soc. Jpn.*, **48**, 745 (1975). (b) H. A. Liebhafsky and G. M. Roe, *Int. J. Chem. Kinet.*, **11**, 693 (1979). The thermodynamic complexity of acid iodate solutions makes it impracticable to establish for use in rate laws either $[H^+]$ or a function related thereto. Even $[IO_3^-]$ is kinetically doubtful, for such solutions contain species with more than one iodine atom. At 25 °C, glass-electrode measurements gave a pH of 1.685 (H^+ activity, 0.0207 mol/L) for reaction mixtures in which $[H^+]_0$ was 0.0715. We know further[14b] that the Dushman reaction will consume H^+ to a significant extent when $[I^-]$ becomes appreciable, as it does when $[H^+]_0$ is low. To the difficulties just described must be added the uncertainties in $[H_2O_2]$ described in the text. Fortunately, it seems that the use of $[H^+]_0$, $[IO_3^-]_0$, and $[H_2O_2]$ as calculated are correct enough *relatively* to allow the reaching of sound conclusions.

(15) F. Haber and J. Weiss, *Proc. R. Soc. London, Ser. A*, **147**, 332 (1934), translated and revised for publication (after Professor Haber's death) in English by O. H. Wainsborough-Jones.

(16) **Computer data** are identifiable via **boldface type**. The identification is direct when data are so printed or indirect when they are so headed.

Table II. L(10), F-16, and **F-16** Intercompared[a]

time, min	$\bar{R}_{O_2}$,[c] "actual" cm^3			$[H_2O_2]$[d]			10^2k, min^{-1}			$10^8[I^-]$		$10^3[I_2]$	
	L(10)	F-16	**F-16**	L(10)	F-16	**F-16**	L(10)	F-16	**F-16**	F-16	**F-16**	F-16	**F-16**
1		0.30	1.50		0.576	0.576		0.028	0.111	5.0	11.0	0.055	0.031
3		0.35	3.51		0.576	0.573		0.033	0.303	11.2	21.1	0.17	0.11
5		1.05	5.38		0.575	0.569		0.098	0.490	13.7	26.8	0.30	0.18
7	0.06	2.15	6.94	0.574	0.573	0.562	0.006	0.20	0.655	13.6	30.4	0.45	0.24
9	0.81	6.00	8.15	0.573	0.569	0.554	0.081	0.56	0.792	9.0	32.8	0.52	0.30
11	0.91	11.70	9.03	0.572	0.560	0.545	0.090	1.12	0.900	8.4	34.3	0.56	0.33
14	1.10	13.70[e]	9.81	0.570	0.539	0.529	0.109	1.36	1.017	8.2	35.5	0.58	0.37
20	4.10	11.50	10.09	0.565	0.499	0.496	0.413	1.23	1.127	7.7	35.5	0.56	0.39
40	9.34[e]	7.80	7.74	0.469	0.396	0.396	1.13	1.05	1.089	6.5	29.8	0.49	0.30
100	4.17	3.50	3.33	0.238	0.223	0.225	1.00	0.84	0.824	4.3	17.6	0.29	0.13
200	1.56	1.35	1.21	0.103	0.106	0.112	0.86	0.68	0.600	2.4	9.3	0.12	0.047
260[b]	0.86	0.76	0.75	0.068	0.073	0.080	0.72	0.55	0.521	1.9	6.9	0.11	0.029

[a] For initial composition of reaction mixture, see Table I. [b] Onset of oscillations definite here. See Figure 1. [c] $\bar{R}_{O_2}$ is an average for time t calculated thus: $\bar{R}_{O_2} = ([(a-x)_{t-\Delta t}] - [(a-x)_{t+\Delta t}])/2\Delta t$, where a and x are experimental quantities explained in the text. For **F-16**, the rates entered are exact values as printed out by the computer. Volumes of reaction mixtures: L(10), 150 cm^3; F-16, 143 cm^3. $\bar{R}_{O_2}$ for L(10) was reduced accordingly. Temperature for L(10) was 49.6 °C and for F-16 and **F-16** 50 °C; no adjustment was made. [d] Calculated on the basis of reaction A from experimental values of $a-x$ for L(10) and F-16. Computer prints out value corresponding to $[H_2O_2]_0 = 0.576$. [e] Induction periods (minutes to maximum R_{O_2}): L(10), 34; F-16, 14; **F-16**, 20; all approximate. Presence of inhibitor responsible for long induction period of L(10), in which the failure of measurable gas evolution to appear before 7 min is likely evidence of supersaturation: the inhibitor should not have affected reaction 10, which produces 0.22 "actual" cm^3 O_2 per minute initially.

was reduced from 22 to 7.2 and k_7 from 1E9 to 5E7; k_8 was increased from 1 to 25 (for clarification, see part 6, p 91, note 16). The changes bring the mechanism closer to experiment (see part 5). The eventually most useful value of k_{2f} is still in doubt. See part 6, p 91.

(3) The comparison of F-16 with **F-16** is a cruel test of the skeleton mechanism because it demands *numerical agreement* with *three* measured quantities ($[I^-]$, $[I_2]$, R_{O_2}) plus *one* derived (k). As the rate constants inaccessible to experiment are interdependent, revising the skeleton mechanism can easily degenerate into an endless numbers game of discouraging complexity. Many sets of postulated specific rates were tried.

(4) An important point: for the smooth catalysis (i.e., after the induction period, however defined), **F-16** shows a continuously decreasing **k**. This is *proof positive* that the skeleton mechanism, in which every reaction involving H_2O_2 is *first order* with respect to $[H_2O_2]$, can give an overall rate for reaction A that is *not* thus first order. This failure of constancy in k therefore does *not* prove that radical or chain reactions are occurring. The κ's of Table I are not true constants.

(5) The skeleton mechanism will have to be modified, perhaps supplemented by other reactions, if induction periods and oscillations are to be explained.

(6) As was to be expected from part 6 and earlier work, Table II shows for both F-16 and **F-16** the rough proportionality between $[I_2]$ and $[H_2O_2]$ describable at low $-R_{I_2}$ by eq D in part 6

$$-R_{I_2} = 7.2[I_2] - F[H_2O_2]$$

and interpretable as deriving from reaction 2 with $R_{2f} \gg R_{2r}$. In **F-16**, k_{2f} = 7.2 min^{-1} was used because it is the highest *measured* value of this important datum.

(7) During smooth catalysis, the recorded outputs of spectrophotometer (absorbance) and specific I^- electrode (millivolts) remain nearly linear and parallel as they decrease with time or $[H_2O_2]$: see the $[I^-]$ trace (140–260 min) in Figure 1. The relationship of output to concentration differs in the two cases. For $[I_2]$, absorbance and concentration remain proportional until deviations from Beer's law make themselves felt; careful calibration compensated for the deviations. For $[I^-]$, Nernst's law prescribes that millivolts be proportional to log $[I^-]$.

Computer data show that the product ($[HIO][I^-]$) is virtually constant for fixed $[I_2]$. This fact is of mechanistic significance. In general, $[I^-]$ is the concentration most revealing of mechanism. Accordingly, one would ascribe the "pulselets" in Figure 1 to an increase (perhaps initially only a random fluctuation) in $[I^-]$. But, in light of the first sentence in this paragraph, how can one be sure that the cause is not a compensating decrease in [HIO]?

More Light on Table I. Representative computer values, κ_1 and κ_2, for the intermediate $[H^+]_0$ range in Table I are

no.	L(10)	L(11)	L(7)	L(8)
$10^2\kappa_1$,[a] min^{-1}	1.057	1.580	1.051	1.109
$10^2\kappa_2$,[b] min^{-1}	0.579	0.965	0.531	0.562

no.	L(5)	L(6)	L(9)	L(1)
$10^2\kappa_1$,[a] min^{-1}	1.216	1.457	1.780	1.796
$10^2\kappa_2$,[b] min^{-1}	0.651	0.913	1.396	1.373

[a] κ_1 is computed for the interval 0–t_1. At t_1 min, log $[a/(a-x)] = 0.1$. [b] κ_2 is computed for the interval 0–t_2, where $t_2 = 9t_1$ min. This approximation of κ_2 (Table I) suffices for the present purpose.

This approximation of κ_2 (Table I) suffices for the present purpose. The computations show that conclusions drawn from the intercomparisons of Table II apply to Table I. To link the two tables more firmly, κ_1 and κ_2 were calculated from the experimental data of F-16. The results: $10^2\kappa_1$ = 1.175 min^{-1} from 14 to 30 min; $10^2\kappa_2$ = 0.435 min^{-1} from 283 to 383 min. The agreement with L(10) leaves little doubt that the reaction mixtures shaken in 1928 and those stirred magnetically in 1972 gave nearly the same R_{O_2} values under the same conditions.

The effect on the reaction system of changing $[H^+]_0$ must be considered under at least four headings: (1) thermodynamic complexities (already mentioned); (2) induction periods; (3) R_{O2} (κ_1, κ_2, and k); (4) onset of oscillations (see below). Revealing data follow for items 2 and 3 (see Table I for other information):

expt	$[H^+]_0$	induction period,[a] min	$10^2\kappa_1$	min to completion
L(13)	7.040	2	21.5	40
L(7)	0.1437	8	0.808	840
L(15)	0.01637	270	4.18	400

[a] Inhibitor in H_2O_2 must be destroyed before induction period can end.

In 1928, the region bounded by L(17) and L(15) was called the "iodide zone" and thought to result from a change in mechanism. The computer has shown that the skeleton mechanism cannot account for this region. It should not be expected to do so.

Highlights of the Smooth Catalysis. Thanks to the computer, it is possible to see in Table III certain highlights called for by the skeleton mechanism. These point up the differences between smooth catalysis here and in simpler systems.[17,18]

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(17) H. A. Liebhafsky, *J. Am. Chem. Soc.*, **54**, 1792 (1932). Contains information about stirring and R_{O_2} and references to earlier work by others. When UP reactions are absent, $k = k_D$.

Table III. Guideposts for the Smooth Catalysis: Computer Data for F-16

t, min	$[H_2O_2]$	$[H^+]$	$[IO_3^-]$	$10^3[I_2]$	$10^8[I^-]$	$10^8[HIO]$	$10^{10}[I^+]$	$10^2[HIO_2]$	mol of O_2	10^3k_D, min^{-1}	10^3k_U, min^{-1}
0	0.576	0.0715	0.1063								
1	0.576	0.0714	0.1062	0.031	11.0	1.63	0.281	0.0197	0.0003	0.4162	0.2218
3	0.573	0.0712	0.1060	0.106	21.1	2.91	0.971	0.0553	0.0016	0.9728	0.7634
5	0.569	0.0711	0.1059	0.180	26.8	3.91	1.663	0.0895	0.0041	1.488	1.297
7	0.562	0.0709	0.1057	0.245	30.4	4.69	2.29	0.120	0.0076	1.921	1.761
9	0.554	0.0708	0.1056	0.296	32.8	5.27	2.81	0.144	0.0117	2.256	2.133
11	0.545	0.0707	0.1055	0.335	34.3	5.70	3.23	0.164	0.0165	2.499	2.410
14	0.529	0.0706	0.1054	0.371	35.5	6.11	3.68	0.184	0.0244	2.714	2.668
20	0.496	0.0705	0.1053	0.388	35.5	6.41	4.11	0.204	0.0411	2.792	2.795
40	0.396	0.0707	0.1055	0.301	29.8	5.91	4.00	0.196	0.0910	2.142	2.167
100	0.225	0.0711	0.1059	0.129	17.56	4.28	3.02	0.148	0.1760	0.9214	0.9298
200	0.112	0.0713	0.1061	0.0467	9.33	2.91	2.20	0.107	0.232	0.3344	0.3367
260	0.080	0.0714	0.1061	0.0290	6.94	2.42	1.91	0.093	0.248	0.2077	0.2090

Here Are the Highlights of Table III. (1) Between 6 and 7 min, R_3 changes sign, which signals that the Dushman reaction (regarded as reversible) from then on *produces*, not *consumes*, I^- and IO_3^-.

(2) $[H^+]$ and $[IO_3^-]$ decrease equimolarly as required by reaction 10.

(3) The induction period as here defined ends near 20 min, where R_{O_2} is maximum. Concentration maxima occur as follows: $[I_2]$, [HIO], $[I^+]$, $[HIO_2]$, all at 20 min; by then, $[I^-]$ is slightly below its maximum. Note that $[I_2]$ and $[HIO_2]$ are of comparable magnitude and much larger than [HIO], $[I^+]$, or $[I^-]$.

(4) From their maxima, all these concentrations decline continuously. These declines continue beyond 260 min because the skeleton mechanism has not so far proved capable of producing significant oscillations.

(5) By 260 min, the O_2 formed by a liter of reaction mixture is half the moles of H_2O_2 decomposed, even though k_D and k_U are never equal.

(6) The conclusion just drawn is confirmed by the last two columns of Table III, which contrast sharply with what is found in simpler cases.[17,18]

The last two highlights are of stoichiometric, as well as mechanistic, significance. One serious problem with this reaction system is that the concentration of the principal reagent, H_2O_2, cannot be measured precisely: it must be calculated, in one way or another, on the basis of reaction A. But, as Table III indicates, there is a continuing imbalance between k_D and k_U.

The reliability of the gas burette, in which equilibrium does not necessarily exist (especially at large R_{O_2}), is a related question. For $[H_2O_2]_0 = 0.576$, as in Table I, *a* = "actual" cm³ of O_2 should be 1094. For the full size reaction mixtures from which no gas was lost, the measured values were

no.	L(14)	L(17)	L(19)	L(10)	L(11)
a, "actual" cm³	1307	1293	1045	1062	1071

no.	L(7)	L(8)	L(5)	L(6)	L(9)
a, "actual" cm³	1052	1065	1081	1092	1061

One point is incontrovertible: at the two lowest values of $[H^+]_0$, *a* exceeds 1094 cm³ by enough to show that DOWN reactions dominate UP in what was once called the "iodide zone". This dominance is to be expected from the $I_2(s)$ and the high $[I^-]$ found there.

In F-16, 1074 "actual" cm³ was found for *a* as against 1040 cm³ calculated. The calculation, as always, assumed the measured gas to be saturated with water vapor at 25 °C and 1 atm total pressure—reasonable *average* conditions, deviations from which would make for a discrepancy.

According to the last two columns of Table III, varying differences will exist throughout an experiment between the actual values of $(a - x)$ and those calculated on the basis of reaction A. This discrepancy complicates, but does not vitiate, the drawing of broad conclusions about mechanism. The computer escapes this uncertainty because it gives $[H_2O_2]$ values virtually accurate for the information input.

From Smooth to Oscillatory Catalysis. The three parallel lines in the lower right of Figure 1 are strong evidence that the same reactions occur, though surely at different rates, on both sides of the transition from smooth to oscillatory catalysis.

In F-16, R_{O_2} pulses could never be measured. Pulses in $[I_2]$, though very weak, were definite to the end and always synchronous with the pulses in $[I^-]$, which (see caption, Figure 1) continued to the end of the experiment. We believe that the pulses and their relationships in F-16 are like those in part 5, Figures 1 and 2. The greater weakness of the R_{O_2} and $[I_2]$ pulses in F-16 must be due mainly to differences in $[H^+]$ and $[H_2O_2]$. The parallelisms (see the nine lines drawn tangent to the photographed pulse recordings of part 5) no doubt exist also for the weaker pulses of F-16. The great virtue of Figure 1 is that it shows parallelisms to persist during the transition from smooth to oscillatory catalysis.

About Oscillations. In 1928, oscillatory catalysis was found between $[H^+]_0 = 0.0645$ and 0.0430 at $[H_2O_2]_0 = 0.576$ and $[IO_3^-]_0 = 0.1063$ (Table I), and the oscillatory catalysis *came early*. In F-16, oscillatory catalysis was found at $[H^+]_0 = 0.0715$, and it *came late*. The profound influence of such small changes in $[H^+]_0$ is the most intriguing feature of this reaction system. F-16 lays the groundwork for the understanding of this feature, to wit:

(1) Oscillatory behavior could not have been found in 1928 at $[H^+]_0$ values of 0.0645 and above because, as F-16 has shown, R_{O_2} pulses are too weak. Nevertheless, there is sound evidence based on κ_1/κ_2 ratios that undetected oscillatory catalysis did then occur. In Table I, the first four κ_1/κ_2 ratios are much higher than the rest, and they agree well with 2.70, the value for F-16. The contrast between the four high ratios and the rest in Table I indicates that the overall R_{O_2} during oscillatory decomposition is *less* than it would have been had the catalysis remained smooth.

(2) We now know that the slight increase in $[H^+]_0$ from 0.0573 (F-12) to 0.0715 (F-16) delays the appearance of oscillations by some *200 min*. Further increases in $[H^+]_0$ betoken longer delays and eventual extinction of all oscillations at some *upper* limit—all for $[H_2O_2]_0 = 0.576$.

(3) A *lower* $[H^+]_0$ limit for oscillations exists because, according to the first three experiments in Table I, the induction periods become longer and longer as $[H^+]_0$ is lowered. Eventually, most of the H_2O_2 added at low acid will decompose during the induction period.

(4) It has long seemed probable that the $[I^-]$ pulses were fundamentally different from those in $[I_2]$ or R_{O_2} because the iodide pulses represent the shifts in the iodine hydrolysis (near) equilibrium during the oscillatory catalysis, of which changes in $[I_2]$ are a probable cause, and R_{O_2} one result. The demonstration in F-16 that the $[I^-]$ pulses continue undiminished in amplitude until H_2O_2 is virtually gone and the other pulses undetectable makes this probability a certainty.

Variation in Iodate Concentration. Even though acid iodate solutions are discouragingly complex, we cannot avoid examining $[IO_3^-]_0$ variation because increasing $[IO_3^-]$ increases the frequency

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(18) W. C. Bray and R. S. Livingston, *J. Am. Chem. Soc.*, **45**, 1251 (1923).

of oscillations. The computer shows that the skeleton mechanism requires approximately the increase of R_{O_2} with $[IO_3^-]$ that is reflected in the κ's of Table I. As proof, compare with these κ's the following computed values of κ and those in column 10, Table II. These are for $[IO_3^-]_0 = 0.3$ (as opposed to 0.1063) and $[H^+]_0$ and $[H_2O_2]_0$ unchanged.

t, min	1	3	5	7	9	11
10^2k	0.304	0.789	1.202	1.415	1.734	1.876
t, min	14	20	40	100	200	260
10^2k	1.987	2.01	1.719	1.186	0.820	0.703

At $[IO_3^-]_0 = 0.3$, the "Dushman reversal", previously mentioned, occurs between 3 and 4 min–earlier than in **F-16**.

The agreement of the **k**'s above with the κ's of Table I is all that could be expected, for the κ's are average values. The increased R_{O_2} values following upon $[IO_3^-]_0$ increases exceed what can be directly accounted for by the rates of reactions in which IO_3^- is consumed. The R_{O_2} increases result because the entire reaction system readjusts itself to increasing $[IO_3^-]_0$, and it is gratifying that the skeleton mechanism provides for this readjustment.

The Skeleton Mechanism Today. This mechanism was designed to be revised as the examination of progressively more complex experimental material proceeds. It has yielded a surprisingly good *quantitative* description of the smooth catalysis as recorded in Table I—a description that included the *rates* of H_2O_2 decomposition, which are the most important single measure of the catalysis. However, such success does not prove mechanism; for, as long hours at the computer have shown, many combinations of the assignable and interdependent specific rates can yield plausible descriptions.

Questions Remain. Why (see Table II) are initial computed R_{O_2} values greater than those measured? Supersaturation (preceded by saturation and N_2 displacement) may not be the whole answer. Why was it best to use $k_{2f} = 7.2$ min^{-1} (its maximum measurable value) here when 3 times that value was preferable in part 6? The skeleton mechanism may have to be modified by the addition of free-radical reactions, which would take it closer to that used by Edelson and Noyes[12] to simulate oscillations and move it further from that with which a similar result was achieved on a molecular basis.[19]

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Redox Properties of Metalloporphyrin Excited States, Lifetimes, and Related Properties of a Series of Para-Substituted Tetraphenylporphine Carbonyl Complexes of Ruthenium(II)

D. P. Rillema,*[1a] J. K. Nagle,[1b] L. F. Barringer, Jr.,[1a] and T. J. Meyer*[1b]

Contribution from the Departments of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514, and Charlotte, North Carolina 28223. *Received January 21, 1980*

Abstract: Excited-state and redox properties of Ru(*p*-XTPP)(CO), X = MeO, Me, H, F, Cl, H and Br, have been defined. Emission bands were centered at 730 ± 3 nm and excited-state lifetimes were in the range of 30 ± 10 μs. Two one-electron oxidations in CH_2Cl_2 ranged from 0.74 to 0.86 V for the first step and from 1.18 to 1.27 V for the second one. A one-electron reduction process in $(CH_3)_2SO$ ranged from −1.35 to −1.24 V. Excited-state lifetimes and redox potentials exhibit a weak dependence on the Hammett σ_p function. In general, redox potentials increase as the electron-withdrawing power of the substituents increases, whereas excited-state lifetimes decrease. The first oxidation step (0.74–0.86 V) and the reduction step are, respectively, assigned to π-electron removal or acceptance by the porphyrin ring. The second oxidation is assigned to removal of an electron from the ruthenium(II) center. The excited state is shown to be the $T(\pi-\pi^*)$ state of the porphyrin ring and to exhibit photoredox behavior involving both oxidative and reductive quenching. Redox product separation occurred in flash photolysis quenching experiments and back-reactions took place at near-diffusion-controlled rates. The redox potential of the $Ru(TPP)(CO)^{+/*}$ couple was estimated from emission and redox data to be −0.57 ± 0.03 V; it was determined from oxidative quenching studies to be −0.56 ± 0.10 V. Comparison to the excited-state properties of $Ru(bpy)_3^{2+}$ is made, and the utility of porphyrin complexes as potential solar energy storage catalysts is examined.

Introduction

Prior studies have shown that photoexcited states of metal–polypyridyl complexes can undergo oxidative[2] and reductive[3] quenching. The ability of the exicted states to undergo electron transfer has been utilized in a number of recent investigations for generating reactive redox intermediates. The excited states have provided the basis for energy related applications aimed at the eventual splitting of water photochemically. For example, hydrogen[4] and oxygen[5] have been produced separately in photoe-

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