The failure to observe any dipole–dipole coupling in the $N(CH_3)_4^+$ ion is not proof that the ion is not ordered. The increase in line width over the spectrum recorded for isotropic solutions leads us to expect nuclear quadrupole splitting for the deuterated ion in middle nematic phases. The N-14 spectrum is an even more sensitive test of small degrees of orientation.[10-12] Increasing the number of methyl groups in methylammonium ions must increase the ability of the ion to penetrate the electrical double layer of the phase and thus to reside partly in the lipophilic region. We are unable, without further study, to obtain evidence on this important question.

References and Notes

(1) Visiting professor, 1967–present. Research supported by the Banco Naçional de Desenvolvemento_Economico (BNDE), Conselho Naçional de Pesiquisas (CNPq), Fundaçao de Ampara à Pesquisa do Estado de Sao Paulo (FAPESP), The National Research Council of Canada (NRCC), and the Defense Research Board of Canada (DRB).

(2) (a) G. H. Brown, J. W. Doane, and V. D. Neff, "A Review of the Structure and Physical Properties of Liquid Crystals," Chemical Rubber Publishing Co., Cleveland, Ohio, 1971. (b) P. A. Winsor, Chem. Rev., 68, 1 (1968).

(3) T. J. Flautt and K. D. Lawson, J. Amer. Chem. Soc., 89, 5491 (1967).

(4) L. W. Reeves, A. S. Tracey, and M. M. Tracey, J. Amer. Chem. Soc., 95, 3799 (1973).

(5) L. W. Reeves, J. Sanches de Cara, M. Suzuki, and A. S. Tracey, Mol. Phys., 25, 1481 (1973).

(6) D. M. Chen and L. W. Reeves, J. Amer. Chem. Soc., 94, 4384 (1972).

(7) P. Deihl and C. L. Khetrapal, "NMR Basic Principles and Progress," Vol. 1, P. Delhi, E. Fluck, and R. Kosfeld, Ed., Springer-Verlag, New York, N.Y., 1969, Chapter 1.

(8) S. Meiboom and L. C. Snyder, Accounts Chem. Res., 4, 81 (1971).

(9) A. Saupe and G. Englert, Phys. Rev. Lett., 11, 462 (1963).

(10) F. Fujiwara, L. W. Reeves, and A. S. Tracey, J. Amer. Chem. Soc., 96, 5250 (1974).

(11) D. M. Chen, L. W. Reeves, A. S. Tracey, and M. M. Tracey, J. Amer. Chem. Soc., 96, 5251 (1974).

(12) F. Fujiwara, L. W. Reeves, A. S. Tracey, and L. A. Wilson, J. Amer. Chem. Soc., 96, 5249 (1974).

(13) L. W. Reeves and A. S. Tracey, J. Amer. Chem. Soc., 96, 1198 (1974).

(14) L. W. Reeves, M. Suzuki, A. S. Tracey, and J. A. Vanin, Inorg. Chem., 13, 999 (1974).

(15) L. W. Reeves, M. Suzuki, and A. S. Tracey, unpublished results.

(16) J. A. Ferretti, R. K. Harris, and R. B. Johannesen, J. Magn. Resonance, 3, 84 (1970).

(17) J. Lindgren and I. Olovsson, Acta Crystallogr., Sect. B, 24 549 (1968).

Reactions Involving Hydrogen Peroxide, Iodine, and Iodate Ion. V. Introduction to the Oscillatory Decomposition of Hydrogen Peroxide[1]

Herman A. Liebhafsky* and Lawrence S. Wu

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. Received April 10, 1974

Abstract: Apparatus is described that permits the simultaneous recording of three (oxygen, iodine, iodide) among the kinds of pulses that characterize the oscillatory decomposition of hydrogen peroxide in this reaction system. For two significant experiments of identical composition, such recordings joined to gas-buret readings give a body of evidence unusual in precision and extent for oscillatory reactions. This evidence makes possible a thorough test of an updated skeleton mechanism based upon extensive earlier work. The results of the test are encouraging but not conclusive.

The investigations to which this series belongs are separated chronologically as follows: 1916–1917, when the oscillatory decomposition was discovered;[2] 1927–1933, when the whole reaction system was surveyed and the isolation of individual reactions was begun;[3-5] 1967 to the present,[6-14] when modern experimental methods were introduced and necessary ancillary work was done.

Extensive experiments, many of which, though useful, will not be published because they were exploratory in nature, have led to an updated skeleton mechanism to be tested here against the results of two of the most significant experiments among the multitude.
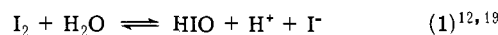
Updated Skeleton Mechanism

The complex chemistry of this reaction system (ref 2, Table I) implies a complicated mechanism in which the same set of reactions must vary widely enough in rate at different concentrations of hydrogen peroxide, acid, iodate, iodine, and iodide to explain the results observed. By "skeleton" is meant that species such as HIO_3, $H_2I_2O_6$, and congeners,[15] $H_2I_2O_3$ and congeners,[5,10,16,17] and free radicals; all these will be reserved for future introduction if needed.
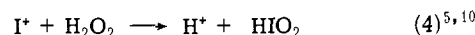
The original point of departure[2] for the present mechanism was the "simplest direct line between iodide and periodate in acid solution," which is I^-, HIO, HIO_2, IO_3^-, IO_4^-.

Thermodynamics establishes the likelihood that H_2O_2 can oxidize each substance in this line except the last and reduce each except the first. Periodate species are safely dismissed from further consideration.[3] Thermodynamics thus predicts the possibility that H_2O_2 will be catalytically decomposed in reaction systems containing the first four iodine species in the line, but only kinetic experiments can establish whether such catalysis actually occurs, by what mechanism, and of what nature (smooth, oscillatory, or both). The H_2O_2-Br_2-Br^- reaction system,[18] in which only smooth decomposition occurs, is valuable as a simple standard of comparison for the present system, which is now presumed to have the following mechanism.

Reversible reactions

$$I_2 + H_2O \rightleftharpoons HIO + H^+ + I^- \qquad (1)^{12,19}$$

$$I_2 \rightleftharpoons I^+ + I^- \qquad (2)^{10,20}$$

$$2H^+ + IO_3^- + I^- \rightleftharpoons HIO + HIO_2 \qquad (3)^{5,11,16}$$

Oxidation of I^+

$$I^+ + H_2O_2 \longrightarrow H^+ + HIO_2 \qquad (4)^{5,10}$$

Reduction of HIO

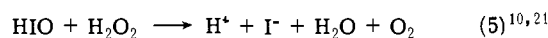$$HIO + H_2O_2 \longrightarrow H^+ + I^- + H_2O + O_2 \qquad (5)^{10,21}$$

Table I. Analysis of Experiment W-24 ($[H^+]^a = 0.0572$; $[IO_3^-] = 0.212$; 50°; Gas Buret)

Row	Data									
1	Number of pulse	0	1	2	3	4	5	6	7	8
					Concentration Data					
2	t (min) at $[I^-]_{min}{}^b$	0	7.7	14.8	22.5	30.3	38.5	47.0	55.6	64.8
3	$[H_2O_2]^b$	0.112	0.098	0.092	0.087	0.082	0.077	0.073	0.068	0.064
4^c	$10^3 k$ (min⁻¹)			8.9	8.0	7.9	7.8	7.5	7.6	7.5
5^d	$10^8[I^-]_{min}$	1.0	5.3	5.1	4.9	4.8	4.7	4.3	4.3	4.0
6^e	$10^4[I_2]_{max}$	15	3.0	3.0	2.8	2.6	2.5	2.4	2.2	2.1
7^d	$10^8[I^-]_{max}$		22	21	21	20	20	19	18	18
8^e	$10^4[I_2]_{min}$	2.0	1.8	1.8	1.7	1.6	1.5	1.5	1.4	1.4
9	$10^3[I_2]_{max}/[H_2O_2]$		3.06	3.26	3.22	3.17	3.25	3.29	3.23	3.28
10	$[I^-]_{max}/[I^-]_{min}$		4.2	4.1	4.3	4.2	4.3	4.4	4.2	4.5
11	$[I_2]_{max}/[I_2]_{min}$		1.67	1.67	1.64	1.63	1.67	1.60	1.57	1.50
					Measured Rates					
12^f	$10^5(+R_{I_2})_{max}$		3.0	3.0	2.4	2.6	1.86	1.45	1.21	0.75
13^f	$10^5(-R_{I_2})_{max}$	500	61	61	52	52	33	45	34	36
				Average Temporal Relationships for Pulses 1–8						
14	$t[I^-]_{min} = t[I_2]_{max} + 0.3$ min									
15	$= t[I_2]_{min} - 0.3$ min									
16	$= t[I^-]_{max} + 1.6$ min									

^{a} Brackets represent mol/l. added to make reaction mixture. Perchloric acid and potassium iodate, reagent quality, were used. ^{b} Brackets represent mol/l., present or calculated to be present, in reaction mixture. Estimation of $[H_2O_2]$ explained in text. ^{c} Specific rates calculated from 2.303 log $[(0.098)/[H_2O_2]_t] = k(t - 7.7)$. ^{d} Obtained by using Nernst equation at 50° for interpolation of chart as recorded. Ordinate values for chart established by calibration. ^{e} Obtained by interpolation from chart as recorded. value at $t = 0$ excepted. Ordinate values from calibration curve. Value at $t = 0$ calculated according to Dushman reaction from iodide added prior to $t = 0$. ^{f} Rates (R's) are in mol/l.(min⁻¹) of substance represented by subscript.

Irreversible reactions forming HIO

$$2H^+ + IO_3^- + 2I^- \longrightarrow 2HIO + IO^- \qquad (6)^{5,13,22}$$

$$HIO_2 + H^+ + I^- \longrightarrow 2HIO \qquad (7)^{10}$$

$$H_2O_2 + HIO_2 \longrightarrow HIO + H_2O + O_2 \qquad (8)^{10}$$

$$H_2O_2 + H^+ + I^- \longrightarrow HIO + H_2O \qquad (9)^{10,23}$$
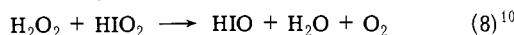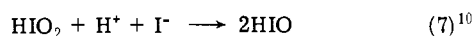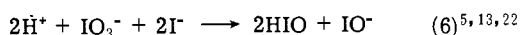
Additional formation of HIO₂

$$H_2O_2 + IO_3^- + H^+ \longrightarrow HIO_2 + H_2O + O_2 \qquad (10)^4$$

After introduction of the appropriate numerical factors, these reactions can be summed to give the stoichiometric changes that occur during any time interval. Once a reaction has gone through the induction period, the *principal* stoichiometric change is

$$H_2O_2 = H_2O + \tfrac{1}{2}O_2 \qquad (11)$$
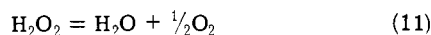
In the Br_2–Br^- system, reaction 11 is the *only* stoichiometric change at the steady state; the mechanism consists only of the analogs of reactions 1, 5, and 9, and the system at the steady state is a classic case to which the Bodenstein steady-state approximation is *exactly* applicable. In the present system, reaction 11 is never the only stoichiometric change over an interval of time; all ten reactions in the skeleton mechanism combine to establish what occurs; and the Bodenstein steady-state approximation is of limited usefulness.

Experimental Section

Method. Simultaneous recording[8] of the rate of oxygen evolution of (I^-) and of (I_2) is mandatory for an understanding of the reaction system and was accomplished by using a mass flowmeter,[9] an iodide-selective electrode,[7] and a spectrophotometer. The preferred reaction vessel, which was used in the present work, is of fused glass where it touches the reaction mixture. It has flat parallel sides, 4.5 cm apart, through which one spectrophotometer beam passes, and semicylindrical ends, a geometry found by Woodson to minimize disturbance of the light beam by oxygen bubbles. The reaction vessel, set in the spectrophotometer, is covered by a black box, through the top of which pass conduits (also shielded against light) for the necessary services. Reaction temperature, which

nominally is 50° but subject to pulses[8] during oscillatory decomposition, is maintained by circulating water. On occasion, a gas buret replaces the flowmeter.

Reaction is begun by the rapid addition of H_2O_2, preheated when advisable, to the rest of the magnetically stirred reaction mixture at 50° to make the final reaction volume 143 ml. Initial uncertainties, possible oxygen losses included, deriving from the manner of mixing, and the onset of gas evolution have been minimized. In the experiments reported here, iodine was generated by the prior addition of iodide in known amount to the reaction system.

Results

The figures contain the three kinds of simultaneous chart recordings, photographically reduced to ensure fidelity, for experiment W-27 and the concentration recordings for experiment W-24. Figure 1 also contains the $[H_2O_2]$ curve calculated according to reaction 11 by use of the gas-buret readings. Tables I and II summarize the more significant results of numerical analyses of the figures.

The footnotes make the tables almost self-explanatory. Net rates (R's) that are identified by subscripts representing substances will later be set equal to combinations of rates from the skeleton mechanism that have numerical subscripts identifying reactions. Other subscripts identify *maximum* and *minimum* values. The rates in rows 12 and 13, Table I, and in rows 10 and 11, Table II, were calculated from the slopes of lines drawn on the original charts. The uncertainty in these rates increases with the slopes of the lines, an extreme example being $(-R_{I_2})_{max}$ for pulse 0; here the two values could have been made to agree by redrawing the slopes. The (R_{O_2}) values were obtained from the recorded curves by correcting them for the "VdP effect," as described in Table II, footnote h. How this changes the shape of the oxygen pulse is shown by the broken-lined peak for pulse 1 in Figure 1.

Figures 1 and 2 speak well for the experimental method. All instrumental response appears to be effectively instantaneous. These results are among the best ever obtained. Iodide concentrations as computed from the original charts seem reliable to better than 2%. Iodine concentrations simi-

Table II. Analysis of Experiment W-27 (Duplicate of W-24 with Mass Flowmeter Replacing Gas Buret)

Row	Data									
1	Number of pulse	0	1	2	3	4	5	6	7	8
					Concentration Data					
2	t (min) at $[I^-]_{min}{}^a$	0	8.0	15.8	24.2	32.8	41.9	51.2	60.7	70.5
3	$[H_2O_2]^a$	0.112	0.098	0.095	0.092	0.089	0.085	0.082	0.079	0.076
4[b]	$10^8[I^-]_{min}$	0.9	5.4	5.0	4.5	4.2	3.9	3.6	3.3	3.0
5[c]	$10^4[I_2]_{max}$	15	3.0	3.0	2.9	2.8	2.7	2.6	2.5	2.4
6[b]	$10^8[I^-]_{max}$		24	23	22	20	19	18	17	16
7[c]	$10^4[I_2]_{min}$	2.3	2.2	2.1	2.1	2.0	1.9	1.8	1.7	1.6
8	$[I^-]_{max}/[I^-]_{min}$		4.4	4.6	4.9	4.8	4.9	5.0	5.2	5.3
9	$[I_2]_{max}/[I_2]_{min}$		1.4	1.4	1.4	1.4	1.4	1.4	1.5	1.5
					Measured Rates					
10[d]	$10^5(+R_{I_2})_{max}$		1.63	1.55	1.36	1.28	1.30	1.11	1.14	1.19
11[d]	$10^5(-R_{I_2})_{max}$	1500	44	48	42	47	38	42	49	36
12[d,e]	$10^5(R_{O_2})_{max}$	180	101	82	64	63	65	54	58	43
13[d,e]	$10^5(R_{O_2})_{min}$		20.0	13.2	12.3	13.5	11.9	11.3	10.6	11.3
14	$(R_{O_2})_{max}/(R_{O_2})_{min}$		5.1	6.2	5.2	4.7	5.5	4.8	5.5	3.8
					Calculated Data					
15[f]	$10^7[HIO]_{max}$	120	4.0	4.3	4.6	4.8	5.0	5.1	5.5	5.8
16[g]	$10^7[HIO]$ at $(R_{O_2})_{min}$		0.66	0.66	0.68	0.72	0.72	0.72	0.72	0.72
17	[HIO] ratio		6.1	6.5	6.8	6.7	6.9	7.1	7.6	8.1
18[h]	$10^5 R_5$ for row 15	870	25.5	26.6	27.5	27.8	27.6	27.2	28.2	28.7
19[h]	$10^5 R_5$ for row 16		4.2	4.1	4.1	4.2	4.0	3.8	3.7	3.6
20[i]	$10^5 R_{10}$ for rows 15 and 16	2.4	2.1	2.0	2.0	1.9	1.8	1.7	1.7	1.6
21[j]	F for row 12		0.72	0.65	0.53	0.52	0.55	0.46	0.48	0.53
22[k]	F for row 13		0.69	0.54	0.50	0.55	0.51	0.51	0.49	0.54

Average Temporal Relationships for Pulses 1–8

23	$t[I^-]_{min} = t[I_2]_{max}$
24	$= t[R_{O_2}]_{max} - 0.4$ min
25	$= t[I_2]_{min} - 0.6$ min
26	$= t[I^-]_{max} + 2.6$ min
27	$= t(R_{O_2})_{min} + 1.3$ min

[a] Table I, footnote b. [b] Table I, footnote d. [c] Table I, footnote e. [d] Table I, footnote f. [e] Obtained from recorded output of mass flowmeter by use of eq 7, ref 9. [f] Calculated by use of $[H^+]$, $[I_2]_{max}$, $[I^-]_{min}$, and 41.2×10^{-13}, the value from ref 12 for the equilibrium constant of reaction 1 at 50°. Equilibrium may not be established, and the values of $[I_2]$ and $[I^-]$ may not coexist. But, no other calculation is possible, and this one does approximate the maximum [HIO] possible in the system. [g] Calculated as in preceding footnote with $[I_2]$ and $[I^-]$ values from original charts for time at which $(R_{O_2})_{min}$ occurred. [h] Calculated by use of $[H_2O_2]$, [HIO], and 6.5×10^3, which is the value from ref 10 for the specific rate at 50° of reaction 3. [i] Calculated from the rate law of reaction 10 at 50°, which is $-d[IO_3^-]/dt = 2.6 \times 10^{-4}[IO_3^-][H_2O_2] + 129 \times 10^{-4}[H^+][IO_3^-][H_2O_2]$ according to ref 4. [j] $F = [(R_{O_2})_{max} - R_5 - R_{10}]/(R_{O_2})_{max}$. F here is the fraction of $(R_{O_2})_{max}$ attributed to reaction 8. [k] F here is for $(R_{O_2})_{min}$. See preceding footnote.

larly obtained seem reliable to at least 0.1×10^{-4} M. As is to be expected, values of $(R_{O_2})_{max}$ and $(R_{O_2})_{min}$ are considerably less reliable than the recorded mass-flowmeter curves.

At 461 nm, the wavelength used for recording $[I_2]$, the beam intensity at the detector, has been reduced to less than 1% of its initial value[24] in the case of pulse 0. This makes the optically established $[I_2]$ at $t = 0$, the maximum ordinate in Figure 2, less certain than the stoichiometric value, which appears in the tables.

Concentration of H₂O₂. As reaction 11 drives the reaction system, the change of $[H_2O_2]$ with t is of prime importance. Initial unreproducibilities[5] at high $[H_2O_2]$ often have counterparts in oscillatory systems. As $[H_2O_2]$ decreases, oxygen pulses are the first to disappear. During pulse 0 (the induction period), 1.2×10^{-3} M iodine disappears between $t = 0$ and $t[I^-]_{min}$, the time of minimum iodide concentration in pulse 1. What happens to this iodine is not certainly known: it could be oxidized by H_2O_2 to $H_2I_2O_3$, HIO_2, or IO_3^-. Nor are the concentrations of all iodine species known for $t = 0$. As a compromise remedy for this situation, the values of $[H_2O_2]$ taken from the curve in Figure 1 after $t = 0$ were arbitrarily reduced by 0.004 M, which is two-thirds the peroxide required to oxidize 1.2×10^{-3} M iodine to IO_3^-. The resulting values of $[H_2O_2]$ appear in row 2, Table I.

Mass flowmeter experiments such as W-27 present an additional problem. The VdP effect complicates integration of the oxygen curves. The following alternative method of determining $[H_2O_2]$ in such experiments is simple and promises to be useful.

For oscillatory decomposition, $[I^-]_{min}$ values make the best reference points. They can be precisely located, and it seems plausible that the individual concentrations of iodine species change insignificantly from one value of $t[I^-]_{min}$ to the next. The corresponding change in $[H_2O_2]$ may therefore be calculated according to reaction 11. Also, at these times row 9, Table I, shows that $[I_2]_{max}$ and $[H_2O_2]$ are proportional. Reasonably good proportionality of this kind was found in 1928 for *smooth* decomposition (ref 4, p 911). It is an important characteristic of the reaction system, and its kinetic significance will appear below. Here we use it to calculate $[H_2O_2]$ for pulses after the first in experiment W-27, the value $[I_2]_{max}/[H_2O_2]$ being taken as $3.1 \times 10^{-4}/0.098$ for the first pulse. Values of (H_2O_2) in row 3, Table II, were calculated thus.

Mismatch between Experiments. Corresponding individual pulses in the figures are strikingly similar, and this supports the belief that the oscillatory decomposition is free of disturbing influences such as those attributable to heterogeneity. Unfortunately, numerical analysis tells another story. A significant mismatch in time is evident from a comparison of rows 2 in the tables. This mismatch carries over to concentrations and measured rates. The temporal relationships differ measurably for the two experiments. The original charts show better than the figures that the $[I^-]$
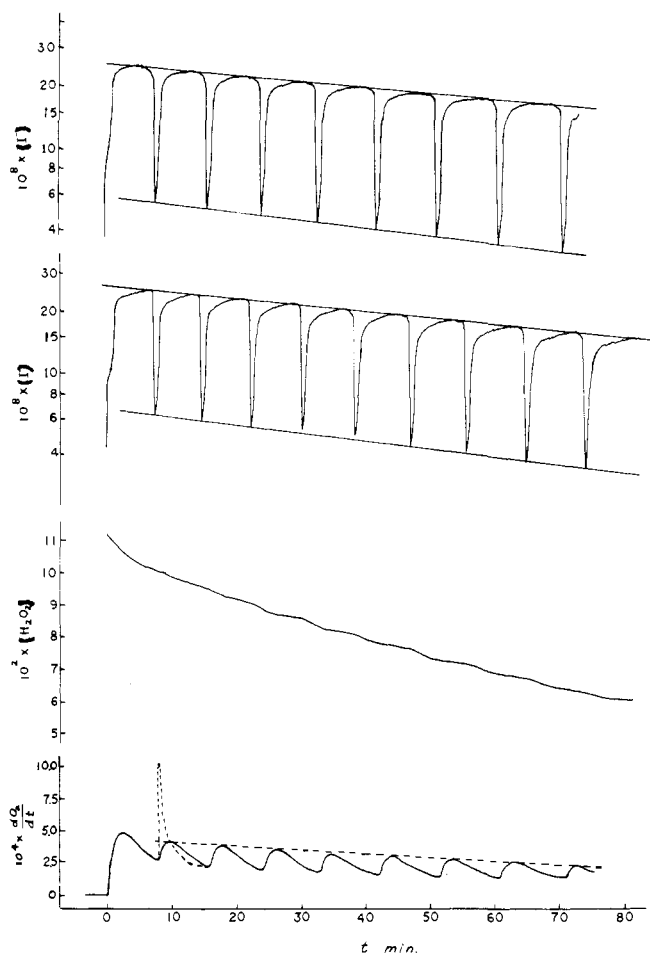
Figure 1. From the top: [I⁻] pulses from W-27; [I⁻] pulses from W-24; [H₂O₂] according to gas-buret readings from W-24. $R_{O_2} = d[O_2]/dt$ was recorded by mass flowmeter for W-27.
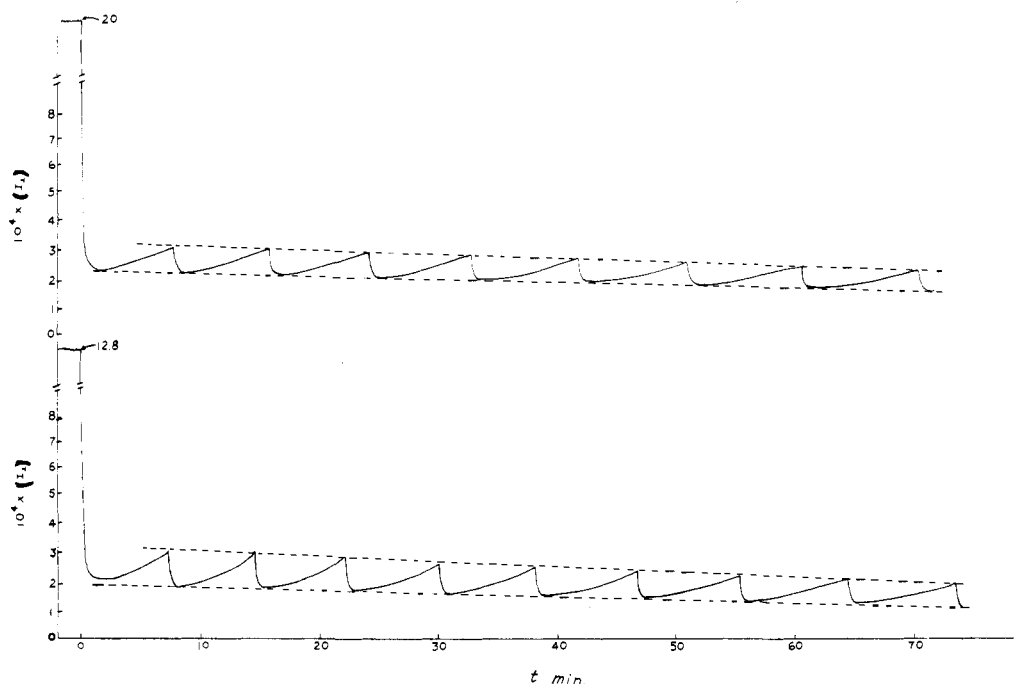
decreases; this effect, which may be only instrumental, is less pronounced in W-27. The mismatch between experiments is one reason why simultaneous recordings are needed for as many different kinds of information as can be obtained.

The tables show that numerical analysis can yield an extensive body of data showing regularities and trends that any acceptable mechanism must explain.

Discussion of Mechanism

Crude Model of Oscillatory Decomposition. The coupled, reversible reactions 1 and 2 are an essential feature of the mechanism. Each has hydrated iodine as the only reactant and they share iodide ion as a common reaction product. Conceptually, they resemble an artillery piece that can be *triggered* at t [I⁻]$_{max}$ by reaction 6 acting as a fuze to set off an explosive increase in R_{O_2} *via* reactions 5 and 8, while the system goes into *sharp recoil* until t [I⁻]$_{min}$ is reached, whereupon it *returns to battery* slowly in a complicated way to be ready for subsequent triggering at t [I⁻]$_{max}$ of the next pulse.

Oxygen Evolution. The mechanism calls for

$$R_{O_2} = R_5 + R_8 + R_{10} \tag{12}$$

Table II shows that the calculated sum $R_5 + R_{10}$ never exceeds the measured R_{O_2}, which justifies the adopted plan of isolating and studying the individual reactions considered likely to participate in the oscillatory decomposition. The fraction of R_{O_2} attributed[25] to reaction 8 appears as F in rows 21 and 22, Table II.

Oxidation of Iodine by Hydrogen Peroxide. This reaction dominates pulse 0 and the sharp-recoil portion of each succeeding pulse. A glance at Figure 2 verifies this statement, which gains further support from the measured values of $(-R_{I_2})_{max}$ in Tables I and II.

Figure 2. From the top: [I₂] pulses for W-27; [I₂] pulses for W-24.

pulses have sharper shoulders in W-24 than in W-27. In W-24, the [I⁻] pulses show a "fine structure" in the gently sloping portions that becomes more pronounced as [H₂O₂]

The rate law for this oxidation reaction[3,5,26] is

$$-d[I_2]/dt = k_{I_2}[I_2] \tag{13}$$

Table III. Calculated Rates of Iodine Formation at Two Iodide Concentrations[c]

| | Reaction[b] | | | | |
	3f	6	9	10	Sum
$10^5(+R_{I_2})$ at $[I^-] = 5 \times 10^{-8}\ M$	3.12	0.10	0.0018	1.19	4.41
$10^5(+R_{I_2})$ at $[I^-] = 25 \times 10^{-8}\ M$	15.61	2.60	0.0090	1.19	19.40

[a] $[I^-]$ values chosen to approximate $[I^-]_{min}$ and $[I^-]_{max}$. [b] Stoichiometric factors: $-d[IO_3^-]/dt = {}^1/_3\ d[I_2]/dt$ (reactions 3f and 6), $-d[I^-]/dt = 2d[I_2]/dt$ (reaction 9), $-d[IO_3^-]/dt = 2d[I_2]/dt$ (reaction 10).

in which k_{I_2} is a variable specific rate that reaches a maximum limiting value under optimum conditions.[3,5] Extrapolation of data for 0 and 25° gives 4 min^{-1} as the limiting value at 50°. At $[I_2] = 1.5 \times 10^{-3}\ M$, the (imprecise) values of $(-R_{I_2})_{max}$ for pulse 0 correspond to a k_{I_2} of 3 (Table I) and of 10 (Table II). Both values must be regarded as agreeing with 4 min^{-1}.

These relationships between the oxidation reaction and the oscillatory decomposition are wholly experimental and hence independent of mechanism. In Figure 1, the $[H_2O_2]$ curve and the mass-flowmeter record show that reaction 11 proceeds to a greater extent during pulse 0 than during subsequent pulses. Row 12, Table II, confirms this. The high R_{O_2} for pulse 0 is reached shortly after the addition of H_2O_2. As reaction 11 neither produces nor consumes I_2, it is disregarded in the following discussion.

For the *absolute* (either + or −) rate of change of $[I_2]$, the mechanism prescribes

$$|R_{I_2}| = R_{1r} + R_{2r} - R_{1f} - R_{2f} \qquad (14)$$

When $-R_{I_2}$ is at its maximum limiting value, then (approximately)

$$R_{2r} = 0;\quad |R_4| = -(R_{I_2})_{max} \simeq 4(I_2)\ \text{and} \qquad (15)$$

$$R_{1r} - R_{1f} < |R_{2f}|\ \text{when}$$

$$|-(R_{I_2})| > 0\ (\text{reaction 11 disregarded!}) \qquad (16)$$

Inequality 16 arises because one I^- is formed in reaction 2f for each I^+, and some of this I^- must be disposed of *without forming iodine* in equimolar amount, which rules out reaction with HIO or I^+ for the removal of *all* the I^- produced by reaction 2f. Tables I and II show that $-R_{I_2}$ is always relatively large and reaches 1.5×10^{-2} mol/l. min) in pulse 0. The experimental data now available, if taken at face value, cannot explain I^- removal at this rate. The problem becomes more acute if reaction 11 is considered also, as it must be.

The known rate laws for the removal of I^- at 50° in this system are

$$R_{3f} = -d[IO_3^-]/dt = 30 \times 10^4[IO_3^-][I^-][H^+]^2 \qquad (17)^{11}$$

$$R_6 = -d[IO_3^-]/dt = 2 \times 10^{11}[IO_3^-][I^-]^2[H^+]^2 \qquad (18)^{27}$$

$$R_9 = -d[I^-]/dt = (4.18 + 38.9[H^+])[I^-][H_2O_2] \qquad (19)^{10,23}$$

As will be apparent from Table III, these rate laws combined cannot provide I^- removal to compare with $(-R_{I_2})_{max}$ for the later pulses (much less for pulse 0) in Tables I and II. As $[I^-]$ increases, I^- removal eventually is no longer a problem for two reasons. 1. Owing to the increase in R_{2r} at higher (I^-), k_{I_2} decreases. 2. Increasing $[I^-]$ increases the rates according to all three rate laws given above.

All I^- removal difficulties disappear if reaction 7 has a high enough specific rate. If the postulated mechanism is correct, the specific rate ratio[10] k_7/k_8 is $2.14 \times 10^5\ M^{-1}$ (possible salt effects not considered). For pulse 0, the concentration ratio $[H_2O_2]/[H^+][I^-]$ is near 5×10^7, whence

$R_7 = 4 \times 10^{-3}R_8$ (approximately). Even if all of $(R_{O_2})_{max}$ is credited to reaction 8, R_7 is too small to remove I^- rapidly enough. The situation is serious but not critical. One remedy would be to eliminate reaction 8 from the mechanism[25] and to postulate an adequately large k_7. There are other possibilities. Further discussion would be premature.

Mechanism of the Oxidation. This mechanism has been an enigma for more than half a century.[3,5,26] Although the levels of $[H^+]$, $[IO_3^-]$, and $[H_2O_2]$ affect k_{I_2}, these concentrations do not belong in the rate law, which is eq 13. The relationship of k_{I_2} to $[I^-]$, not previously published, is even more complex. At the beginning of pulse 0, I_2 *disappears* as $[I^-]$ *increases;* along the negative branch of subsequent I^- pulses, $[I_2]$ and $[I^-]$ *decrease together* until $t(I^-)_{min}$ is reached; thereupon I_2 *disappears* and $[I^-]$ *increases* until $t[I_2]_{min}$ is reached; finally, $[I_2]$ and $[I^-]$ *increase together* in all pulses until $t[I^-]_{max}$ is reached: note the temporal relationships in the tables. It has already been mentioned that k_{I_2} decreases as R_{2r} becomes appreciable. All this concentration behavior gives the impression of a complicated reaction system, of which no simple rate law can fully describe the behavior and in which reversible reactions are not at equilibrium.

Reaction 2 was put into the mechanism for these reasons. 1. As HIO *oxidizes* H_2O_2, another species closely related to I_2 was needed to *reduce* it. 2. This species had to be produced at a limiting rate in accord with eq. 13, and reaction 1f is known to be far too fast.[18,26] Emf measurements gave the first reliable quantitative value[20] for the equilibrium constant of reaction 2 at 25°; at 50°, the tentative value 3×10^{-9} was found.[12] The I^+ in reaction 2 is a hydrated cation[28] assumed to be different from protonated HIO.

Rates of Iodine Formation. Sharp recoil ends at $t[I^-]_{min}$ and iodine formation begins 0.3 or 0.6 min later (Table I or II) when $t[I_2]_{min}$ is reached. At this time, a sharp increase occurs in $(+R_{I^-})$, which is an important characteristic of the I^- pulses, being more noticeable when $[H_2O_2]$ exceeds $0.112\ M$; see Figure 1, ref 6 or Figure 3, ref 2. At this point the return to battery of the system enters its second and final phase, during which $(+R_{I_2})$ continues to increase until it reaches a maximum at $t[I^-]_{max}$ just before triggering sets off sharp recoil in the next pulse.

The stoichiometry is easier to establish here than during sharp recoil. Equation 14 applies. For the H_2O_2 oxidized in reaction 11, the stoichiometry is given by

$$I_2 + H_2O_2 = 2H^+ + 2I^- + O_2 \qquad (20)$$
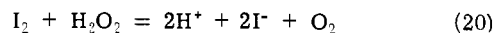
and R_{O_2} measures the rate at which this occurs. It is now permissible (as it was not during sharp recoil) to express the rates calculated from eq 17–19 as $+d(I_2)/dt$.

The kinetic situation is different also. During sharp recoil, neither reaction 1 nor reaction 2 could be considered at virtual equilibrium; now the first may certainly be so regarded, and the second at worst is not far away: in Table 1, compare rows 12 and 13; or, make the analogous comparison in Table II. The relationships in (15) and (16) no longer apply because R_{2r} is now comparable with R_{2f}. We have instead

$$R_{O_2} + (+R_{I_2}) = (+R_{I_2})_{calcd} \qquad (21)$$

Table IV. Chronology of Pulse 4, Experiment W-27

No. of Feature	Name of feature	Time, min	Artillery description	Kinetic description
1	$[I^-]_{max}$	30.2	Loaded, ready to trigger	R_6 starts to become dominant
2	$(R_{O_2})_{min}$	31.5	Fuze is burning	Reactions 1 and 2 move from equilibrium
3, 4	$[I_2]_{max}$, $[I^-]_{min}$	32.8	Fuze has triggered explosion	Reaction 2f dominates
5	$(R_{O_2})_{max}$	33.2	Explosion at peak	Reactions 5 and 8 (?) at maximum rates
6	$[I_2]_{min}$	33.4	First phase of return to battery ends	(R_{I_2}) changes sign
7	$[I^-]_{max}$	39.3	Return to battery complete, loaded for next round	$(+R_{I_2})$ at maximum

which follows from eq 20. The calculated rate in eq 21 is the sum of the rates given by eq 17-19 and the rate of reaction 10 (Table II, footnote to row 20). See Table III.

According to the temporal relationships in Table II, $t(R_{O_2})_{min}$ occurs 1.3 min after $t[I^-]_{max}$, the time when $(+R_{I_2})_{max}$ is reached. The proper value of R_{O_2} in eq 10 will thus exceed $(R_{O_2})_{min}$ if $(+R_{I_2})_{max}$ from the tables is used to test eq 21. No precise test is possible because even $(+R_{I_2})_{max}$ will be, as the tables show, always a small difference between large numbers, one of which (R_{O_2}) is never known with high precision. The known facts all support eq 21.

Fuze and Triggering. Table III shows that R_6 increases about 25-fold between $[I^-]_{min}$ and $[I^-]_{max}$. Among the three reactions annihilating I^- without forming I_2, reaction 6 accounts for 2 I^-, the others for only one.

Triggering of the sharp recoil requires, according to the mechanism, a sudden increase in $[I^+]$; reaction 6, which effectively produces 3HIO, can accomplish this. These 3HIO lower $[I^-]$ *via* reaction 1r, which increases $[I^+]$ and hence $[HIO_2]$ *via* reactions 2f and 4; the result is accelerated I^- removal *via* reaction 7. The fuze seems capable of triggering the sharp recoil.

Net Rate of Change in Iodide Concentration. The mechanism calls for

$$|R_{I^-}| = R_{1f} - R_{1r} + R_{2f} - R_{2r} + R_{3f} - R_{3r} + R_5 - R_6 - R_7 - R_9 \quad (22)$$

Owing to the iodide-removal difficulty discussed above, there will be no detailed discussion of eq 22. The following general comments are in order.

1. Among the three kinds of pulses recorded, the iodide pulses show the most striking features, all of which any acceptable mechanism must explain. Equation 22 gives promise of being able to do so.

2. $|R_{I^-}|$ may be positive or negative, but it is always small relative to the higher R values on the right of eq 22. Near the beginning of sharp recoil, $(-R_{I^-})$ is somewhere near 10^{-6} mol/(l. min). At $[I_2] = 3 \times 10^{-4}$ M, R_{1f} is somewhere near 0.6 mol/l. (min), or 6×10^5 times as great.[29] This enormous ratio may explain the observed mismatch between W-24 and W-27. An *unmeasurable* change in R_{1f} would mean a *large relative* change in $|R_{I^-}|$ at constant values of the other rates in eq 22. The reaction system would then be exceedingly sensitive to $|R_{I^-}|$. We could then have an *essentially homogeneous* reaction system inordinately sensitive to disturbance that could result from *heterogeneous influences*.

3. It seems misleading to regard $t[I^-]_{min}$ as a point of catastrophic change at which, for example, one reaction ceases or another begins. Just prior to that time in a typical pulse, $(-R_{I^-})$ is roughly 1×10^{-7} mol/(l. min); just there-

after, $(+R_{I^-})$ has about half this value. Examination of eq 22 shows that changes such as this could result from appropriate and plausible changes (+ and/or −) in rate terms on the right of the equation. For example, the sharp recoil must terminate when $[HIO]$, which increases as the recoil proceeds, has grown large enough so that the growth in R_5 can reverse the sign of R_{I^-}.

4. Even when no I^- is added, as it was here, to generate I_2, the role of the Dushman reaction

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$
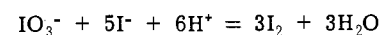
$$K_{23} = 2.54 \times 10^{43} \text{ at } 50° \quad (23)$$

is to reduce $[I^-]$ to the point[5] where reaction 4 can make possible a significant rate for reaction 11, be the decomposition smooth or oscillatory. In experiment W-27, the Dushman reaction, proceeding according to eq 17 and 18, had reduced $[I^-]$ to 2.1×10^{-8} from 2.5×10^{-3} M by the time H_2O_2 was added at $t = 0$. The equilibrium $[I^-]$ for the reaction mixture is 1.8×10^{-9} M, according to the equilibrium constant[14] given in eq 23. The significant point here is that the Dushman reaction *can*, prior to H_2O_2 addition, reduce $[I^-]$ to the low values needed for subsequent reaction, but that it *cannot* maintain these low values once such reaction has begun. Could it do so, there would be no iodide-disposal problem.

5. Usually, but not always, there was a sudden decrease in $[I^-]$ upon addition of H_2O_2 at $t = 0$. The decrease $[(\text{from } 2.1(10^{-8}) \text{ to } 0.9(10^{-8})]$ in experiment W-27 was so sharp that it coincides on the chart with the increase in $[I^-]$ characteristic of pulse 0. The sharp decrease may have resulted *via* reactions 4 and 7 from the decrease to be expected in $[I^+]$ when peroxide is added. A similar decrease in $[I^-]$ occurred in experiment W-24. Its general occurrence may depend upon how mixing takes place.

6. The low $[I^-]$ during reaction makes reaction 9 everywhere insignificant, as Table III shows. A mechanism of the H_2O_2-Br_2-Br^- type[18] is therefore impossible here.

Anatomy of a Typical Iodide Pulse. Iodide pulses have 7 significant features, the descriptions of which for a typical pulse illustrate the foregoing discussion. See Table IV. An acceptable mechanism must not contravene these features. The mechanism given above promises to meet this requirement.

Hydrogen Peroxide Relationships. Any definitive study of this reaction system must produce evidence to explain the relationships, stoichiometric and kinetic, that involve H_2O_2. Among the attendant difficulties are: uncertainties in $[H_2O_2]$, some already discussed, that derive from uncertainties in stoichiometry; the problem of iodide removal; and difficulties in matching rates and concentrations; for example, what is $[I_2]$ at $t[R_{O_2}]_{max}$? We shall disregard all

Table V. Calculations for Simplified Reaction System

Pulse of W-27	1	2	3	4	5	6	7	8
$(k_{I_2})_{max}$, min^{-1}	3.4	2.7	2.2	2.3	2.4	2.1	2.3	1.8
$10^3(k)_{max}$, min^{-1}	21	17	14	14	15	13	15	11
$10^3(k)_{max}/(k_{I_2})_{max}$	6.2	6.3	6.4	6.1	6.3	6.2	6.5	6.1

uncertainties and proceed to treat the reaction system as though it comprised only reactions 1, 2, 4, 5, and 7, letting the results speak for themselves.

Because $\Delta[H_2O_2]$ during a pulse under present conditions greatly exceeds $[I_2]_{max} - [I_2]_{min}$, pulse 0 excepted, reaction 11 will be taken to describe the reaction system. Further, in this simplified reaction system, H_2O_2 is oxidized only in reaction 5 and reduced only in reaction 4, so that $R_5 = R_4$. This means that

$$k[H_2O_2] = 2R_{O_2} = 2k_{I_2}[I_2] \qquad (24)$$

where k is the *average* specific rate in row 4, Table I, if eq 24 is applied over an entire pulse.

Most of the H_2O_2 is decomposed during sharp recoil, which makes it difficult to evaluate average values other than those of k. We shall first test eq 24 by using *maximum* values as follows.

$$(k_{I_2})_{max} = (R_{O_2})_{max}/[I_2]_{max} \qquad (25)$$

$$(k)_{max} = 2(R_{O_2})_{max}/[H_2O_2] \qquad (26)$$

The calculated results, shown in Table V, rest upon data in rows 3, 5, and 12 of Table II.

Values of $(k_{I_2})_{max}$ are in accord with the extrapolated limiting value 4 min^{-1}. The values of $10^3(k)_{max}$ are satisfactory. They do not greatly exceed the average values in row 4, Table I, because the rate of decomposition in W-27 is considerably lower than in W-24, owing to the mismatch between experiments. The good constancy of specific-rate ratios shows that eq 24 is not a bad approximation and that the tendency of $(k_{I_2})_{max}$ to decrease, which we attribute to increases in R_{2r}, is reflected, as it should be, in $(k)_{max}$. The constancy of the ratio connotes a proportionality of $[I_2]$ and $[H_2O_2]$, which is supported also by row 9, Table I, and the 1928 work on the smooth catalysis (ref 4, p 911).

There is further support for this hallmark of the reaction system. If proportionality exists, $[I_2]$ may be substituted for $[H_2O_2]$ in the integrated first-order rate equation (see footnote to row 4, Table I) without affecting the k's beyond experimental error. The substitution was made in

$$2.303 \log [3 \times 10^{-4}/[I_2]_{max}] = k(t - 14.85) \qquad (27)$$

with pulse 2 as reference, which seemed better than using pulse 1 with its identical value of $[I_2]_{max}$. The $[I_2]$ values in eq 27 must of course be taken for corresponding points on the iodine pulses. Here $[I_2]_{max}$ and $t[I^-]_{min}$ values were used, the latter to 0.01 min. The calculated values of 10^3k for all eligible pulses of experiment W-24 follow with pulse numbers for $[I_2]_{max}$ in parentheses: 8.9 (3); 9.0 (4); 7.7 (5); 6.9 (6); 7.6 (7); 7.1 (8); 7.7 (9); 7.5 (10); 7.8 (11); 7.1 (12). The agreement with row 4, Table I, is unexpectedly good, both as to absolute value and as to trend. The trends in the two sets of differently established, concordant k values resemble the trend found in 1928 by H.A.L. for the k of the smooth catalysis. For all these trends, increases in R_{2r} appear to be responsible.

Granted a high enough specific rate for reaction 7, the simplified mechanism (reactions 1, 2, 4, 5, and 7) seems basically correct. It ought not to oscillate. It is fundamentally different from the classic Bray-Livingston mechanism,[18] which comprises the bromine analogs of reactions 1, 5, and

9. The coupling of the reversible reactions 1 and 2 in the iodine system and the peculiar character of reaction 2 lead to the experimentally established, but wholly unexpected, proportionality of $[I_2]$ and $[H_2O_2]$ and to the decrease in k with $[H_2O_2]$, neither of which has a counterpart in the simpler bromine-bromide system.

Conclusion

The present skeleton mechanism consists of three reversible and seven irreversible reactions (13 steps in all), predominantly homogeneous but apparently sensitive in part to extraneous influences such as wall effects and free-radical reactions. The mechanism rests upon extensive work, published and unpublished, and upon a numerical analysis of results from experiments W-24 and W-27. Among problems yet unsolved are the value of k_7/k_8 and the dependence of k and k_{I_2} upon the measurable concentrations. An examination of the diverse dependences upon $[H^+]$ of the rates of the 13 steps in the mechanism illustrates the complexity of the second problem.

The mechanism must account for reaction 11 under all conditions. Two features of this reaction are illustrative. The first is the change that occurs as $[H^+]$ is lowered. When it is lowered beyond 0.004 M, then, as Table V, ref 5 shows, H_2O_2 can no longer oxidize I_2 in the absence of added IO_3^-. Reaction 11 of course proceeds until all H_2O_2 is gone. With $[H_2O_2]$ near 0.6 M and $[IO_3^-]$ near 0.1 M at $t = 0$, there is a transition from smooth to oscillatory decomposition near $t = 0$ when the initial $[H^+]$ is lowered to 0.05726 M. This transition is followed (H.A.L., 1928) by an unmistakable change to a nonoscillating mechanism. This change was established in three experiments with initial $[H^+]$ values of 0.04286 M and below. Here IO_3^- *was consumed*; $[I_2]$ *increased* to saturation; $[I^-]$ *increased* and redissolved precipitated I_2 as reaction proceeded; and, toward the end of reaction, k had the same value in all three experiments and that value was almost 10 times greater than the final k for the smooth decomposition at $[H^+] = 0.06451$ M. According to the mechanism, this change results mainly because $[HIO_2]$ is now low enough to make R_{3r} negligible and because R_9 and R_{10} have grown in relative importance owing to the first term, which is independent of $[H^+]$, in the rate laws of these reactions. Also, the oscillatory reaction was detected by gas buret in a narrow, strategically located $[H^+]$ range, this being the range *above* which reactions 4 and 3r were important and *below* which they were not. That R_{I_2} is positive in the lower $[H^+]$ range suggests an analogy to the second phase in the return to battery of the artillery model.

A second feature of reaction 11 is the transition from smooth to oscillatory decomposition in the progress of a *single run*. For such transitions, the same effects that caused the mismatch between W-24 and W-27 could well be responsible. The transitions always occur in the direction smooth → oscillatory, and they usually begin with small fluctuations in $[I^-]$. These quickly become more violent until an I^- pulse is created, whereupon oscillatory decomposition continues in normal fashion. The initiating fluctuations are more easily perceived at high $[H_2O_2]$, and their progress resembles that of a damped oscillation traversed in the direction of increasing amplitude. The following data are indicative. The first detectable fluctuation could cover a few seconds and have an amplitude near 1% of $[I^-]$, that is, about 10^{-10} M. While the fluctuation is occurring, I^- is being formed by reaction 1f (as example) at a rate above 0.2 mol/(l. min). The first detectable fluctuation in $[I^-]$ corresponds obviously to an almost infinitesimal fluctuation in R_{1f}. See eq 22. Could it be that the rates of many homo-

geneous reactions in solution are subject to such fluctuations, ordinarily undetectable and apparent here only because of the special character of the reaction system?

A significant feature of these transitions is the relation between $[I_2]$ during smooth decomposition and $[I_2]_{min}$ for the pulses following the transition. If the curve of $[I_2]$ vs. t is extended past the transition, it gives good values of $[I_2]_{min}$ for the subsequent pulses. This is reasonable; at $[I_2]_{min}$, R_{I_2} is zero (eq 14), which means that the reaction system is at its most sensitive point as regards perturbation of R_{I_2}. The amount of H_2O_2 decomposed between successive values of $[I^-]_{min}$ seems to be comparable with the amount that would have undergone smooth decomposition over the same time interval.

Further discussion, which must cover the broader implications of the present work, will be postponed until the present mechanism has been "proved."

References and Notes

(1) This paper is a memorial to William C. Bray, formerly Professor of Chemistry, University of California at Berkeley, under whose direction H.A.L. in 1927 began work aimed at explaining the oscillatory decomposition and related reactions.
(2) (a) W. C. Bray and A. L. Caulkins, *J. Amer. Chem. Soc.*, **43**, 1262 (1921); (b) *ibid.*, **53**, 44 (1931).
(3) W. C. Bray and H. A. Liebhafsky, *J. Amer. Chem. Soc.*, **53**, 38 (1931).
(4) H. A. Liebhafsky, *J. Amer. Chem. Soc.*, **53**, 896 (1931).
(5) H. A. Liebhafsky, *J. Amer. Chem. Soc.*, **53**, 2074 (1931).
(6) J. H. Woodson and H. A. Liebhafsky, *Nature (London)*, **224**, 690 (1969).
(7) J. H. Woodson and H. A. Liebhafsky, *Anal. Chem.*, **41**, 1894 (1969).
(8) I. Matsuzaki, J. H. Woodson, and H. A. Liebhafsky, *Bull. Jap. Chem. Soc.*, **43**, 3317 (1970).
(9) I. Matsuzaki, R. B. Alexander, and H. A. Liebhafsky, *Anal. Chem.*, **42**, 1690 (1970).
(10) I. Matsuzaki, R. Simic, and H. A. Liebhafsky, *Bull. Jap. Chem. Soc.*, **45**, 3367 (1972).
(11) R. Furuichi, I. Matsuzaki, R. Simic, and H. A. Liebhafsky, *Inorg. Chem.*, **11**, 952 (1972).
(12) J. D. Burger and H. A. Liebhafsky, *Anal. Chem.*, **45**, 600 (1973).
(13) R. Furuichi and H. A. Liebhafsky, *Bull. Jap. Chem. Soc.*, **46**, 2008 (1973).
(14) R. D. Spitz and H. A. Liebhafsky, *J. Electrochem. Soc.*, in press.
(15) A. D. Pethybridge and J. E. Prue, *Trans. Faraday Soc.*, **63**, 2019 (1967).
(16) W. C. Bray, *J. Amer. Chem. Soc.*, **52**, 3580 (1930).
(17) A. Skrabal, *Z. Elektrochem.*, **40**, 232 (1934).
(18) W. C. Bray and R. S. Livingston, *J. Amer. Chem. Soc.*, **45**, 1251 (1923).
(19) M. Eigen and K. Kustin, *J. Amer. Chem. Soc.*, **84**, 1355 (1962).
(20) R. P. Bell and E. Gelles, *J. Chem. Soc.*, 2734 (1951).
(21) H. A. Liebhafsky, *J. Amer. Chem. Soc.*, **54**, 3499 (1932).
(22) P. Beran and S. Bruckenstein, *J. Phys. Chem.*, **72**, 3630 (1968).
(23) H. A. Liebhafsky and A. Mohammad, *J. Amer. Chem. Soc.*, **55**, 3977 (1933).
(24) A. D. Awtrey and R. E. Connick, *J. Amer. Chem. Soc.*, **73**, 1842 (1951).
(25) An early estimate[8] that $(R_{O_2})_{max}$ and R_5 approach equality assumed R_5 to account for all the oxygen evolution in earlier experiments.[21] If R_8 is appreciable, this estimate is wrong. Also, R_{10} always contributes to $(R_{O_2})_{max}$.
(26) H. A. Liebhafsky, *Z. Phys. Chem., Abt. A*, **155**, 289 (1931).
(27) E. Abel and F. Stadler, *Z. Phys. Chem., Abt. A*, **122**, 49 (1926). Their value of the specific rate ($k_6 = 7.6 \times 10^{10}$ M^{-5} min^{-1} at 25°) has been extrapolated to 50° by use of the temperature coefficient[11] for reaction 3f. Further work is needed on reaction 6.
(28) The skeleton mechanism requires that HIO and I^+ play kinetically different roles. This point is crucial. If I^+ cannot participate in reaction 4, it must be replaced by X or by $I_2{}^*$, an activated form of iodine; and the replacement cannot conflict with the experimental facts that led to eq 13. Rather than make such an assumption, it seems better at present to take the position that the relevant evidence from other investigations does not rule out the skeleton mechanism. In support of that position, this evidence is reviewed briefly below. As I^+ is beyond doubt a hydrated species, it will be written here only as $I^+ \cdot nH_2O$. The emf measurements of Bell and Gelles[20] indicate that an equilibrium formally identical with reaction 2 exists alongside the hydrolysis equilibrium, reaction 1. Their results are supported by spectrophotometric measurements[12] that gave the tentative value $K_2 = 3 \times 10^{-9}$ at 50° for reaction 2, which is here written

$$I_2 \cdot nH_2O \rightleftharpoons$$

$$I^+ \cdot nH_2O + I^- \text{ (hydration of } I^- \text{ neglected) (1a)}$$
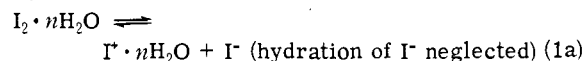
Bell and Gelles rule out Coulombic interaction as the only stabilizing force that makes the existence of $I^+ \cdot nH_2O$ possible. They assume $n = 1$, presumably because this assumption completes the electron octet around the iodine and results in a covalent bond. The $I^+ \cdot H_2O$ resulting is regarded as identical with protonated HIO. On this basis, the skeleton mechanism is in difficulty, for it is difficult to envisage simultaneously the participation of $I^+ \cdot H_2O$ in reaction 4 and of the (closely related) HIO in reaction 5. But, there is no *direct experimental evidence* that $n = 1$ or that protonated HIO actually exists. The position taken here is that n exceeds unity and that the bonds between I^+ and H_2O show considerable ionic character. Their energy is unknown, but it must be lower than that of the covalent iodine–oxygen bond in HIO. With these assumptions, the skeleton mechanism becomes viable. There is no conflict between the skeleton mechanism and the work of Eigen and Kustin; on the contrary, they support each other. Eigen and Kustin[19] interpreted their temperature-jump results at 20° to indicate an equilibrium shift involving reactions 1f and 1r. They showed that reaction 2r could not be rapid enough to explain their experimental observations. The fact[5] that reaction 2f has a specific rate of only 0.6 min^{-1} at 25° (eq 13) supports their conclusion; contrast this low value with $k_{1f} = 2.13 \times 10^3$, min^{-1}.[29] The $I_2|I^-$ electrode is well known to be highly reversible. Such behavior favors the assumption of $I^+ \cdot nH_2O$ over the assumption of $I^+ \cdot H_2O \rightleftharpoons$ HOIH$^+$ (protonated HIO) because one would expect the stronger iodine–oxygen bond in the latter species to hinder electron transfer at an electrode.
(29) Near 20°, k_{1f} is[19] 3 sec^{-1}. Reaction 1r is so rapid that its specific rate may be assumed independent of temperature. On this basis, the thermodynamic data[12] for reaction 1 yield $k_{1f} = 2.13 \times 10^3$ min^{-1} when units of time have been converted. Two further points involving reaction 1. 1. The [HIO] values in Table II are of course equilibrium values. The high value in row 15, Table II, cannot exist for long in the face of increasing $[I^-]$, which makes R_5 in row 18 unrealistically high. 2. Suppose R_{1r} exceeds R_{1f}, as it will during sharp recoil. The difference between them will be small relative to their absolute values. If so, the actual [HIO] need not significantly exceed the equilibrium value.