of the intense $C_2H_n^+$ (n = 0–3) fragments expected upon C_2H_4 reionization.[3,26] As observed[4b] for **e**, **f**, and **g**, the experimental data are consistent (Figure 1) with isomerization of **a**, **b**, and **d** to **e**, dissociation to $CH_3^\bullet$ + $^\bullet CHO$ ($\sum\Delta H_f$ = 191 kJ mol^{-1}) and $CH_3CO^\cdot$ + $^\cdot H$ ($\sum\Delta H_f$ = 194 kJ mol^{-1}), and further dissociation to CO. A similar sequence has been suggested by Benson[6b] for the thermal decomposition of oxirane, with **b** → **e** as the rate-determining step (experimental activation energy, 238 kJ mol^{-1}). Isomer c can form $HCO^\bullet$ + $^\cdot CH_3$ by direct O–C bond cleavage (Figure 1). These postulates are completely supported by MS/MS/MS experiments. After collisional activation of the neutrals from $\mathbf{d}^{\cdot+}$, the recovered $C_2H_4O^{\bullet+}$ ions ($^+NCR^+$ spectrum, Figure 6) are subjected to CAD; the spectrum thus produced from $\mathbf{d}^{\bullet+}$ (Figure 9A) is identical within experimental error with the CAD spectrum of the original $\mathbf{d}^{\cdot+}$ precursors (Figure 9B) and different from the CAD spectrum of pure $\mathbf{a}^{\cdot+}$ ions (Figure 9C), consistent (Figure 1) with high isomerization barriers for **d** (as well as for its cation $\mathbf{d}^{\cdot+}$, vide supra).

Similarly for the isomerization of **b**, the corresponding CAD spectrum of recovered $C_2H_4O^{\cdot+}$ from $^+NCR^+$ of $\mathbf{b}^{\bullet+}$, is compared in Figure 10 with reference spectra of pure $\mathbf{b}^{\bullet+}$, $\mathbf{d}^{\bullet+}$, $\mathbf{e}^{\cdot+}$, and $\mathbf{f}^{\bullet+}$ cations measured under the same conditions. The much lower abundances of 30^+, 31^+, and 44^{2+} in the CAD spectrum of the recovered cations, versus those from $\mathbf{b}^{\cdot+}$, indicates that neutral **b** has been extensively isomerized by collisional activation but not to **d**, which is also consistent with the large m/z 24–27 peaks. Similarly, [27^+]:[26^+] and [30^+]:[31^+] indicate that $\mathbf{f}^{\bullet+}$ is not a major component; the data of Figure 10 are best reconciled as representing a mixture of 20% $\mathbf{b}^{\bullet+}$ and 80% $\mathbf{e}^{\cdot+}$. Thus the barrier for **b** → **d** is considerably higher than that for **b** → **e** (Figure 1), the only significant disagreement with Benson's proposed mechanism,[6b] but supporting theoretical predictions.[11a]

Under multiple collision conditions that lead to CO formation from **a**, no $C_2H_4O^{\cdot-}$ is observed in the $^+NCR^-$, Hg/benzene, spectrum of $\mathbf{a}^{\cdot+}$, showing a much higher activation energy for the H migration **a** → c than for the ring closure **a** → **d**. The MS/MS/MS data for the collisional activation of isomer **a** (Figure 8) show less isomerization for this diradical, with **d** favored over **e** (approximate values 60% $\mathbf{a}^{\cdot+}$, 30% $\mathbf{d}^{\bullet+}$, and 10% $\mathbf{e}^{\cdot+}$), consistent with the transition state for **a** → **d** lying well below that for **d** → **b**. Consequently, C–C ring opening in oxirane requires less energy than C–O bond rupture (Figure 1).

Conclusions

These neutralization–reionization experiments clearly show that the ring-opened oxirane isomers **a** and **b** and the carbene **c**, key intermediates on the C_2H_4O energy surface, represent stable structures. Product abundances from their fragmentation and isomerization reactions, monitored in NCR/CAD (MS/MS/MS) experiments, establish the relative order of activation energy values for the potential energy profile of Figure 1, clarifying predictions of molecular orbital theory[9] and oxirane pyrolysis studies.[6] $^+NR^{+,-}$ spectra have also provided the first direct evidence that cation $\mathbf{b}^{\cdot+}$ and the anions $\mathbf{b}^{\bullet-}$, $\mathbf{c}^{\bullet-}$, and $\mathbf{g}^{\bullet-}$ represent stable structures.

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Oscillatory Oxidation of Benzaldehyde by Air. 1. Experimental Observations[†]

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Abstract: In 90% aqueous acetic acid at 70 °C, the oxidation of benzaldehyde to benzoic acid by air is catalyzed by a mixture of cobalt(II) and bromide. Jensen has shown that the concentration of cobalt(III) undergoes major oscillations during this reaction. Consistent with these prior observations, we find that the rate of formation of cobalt(III) increases exponentially until at about 10^{-5} M s^{-1} it becomes comparable to the maximum rate at which O_2 can be transported from atmosphere to solution. A virtually discontinuous change of behavior then causes the concentration of cobalt(III) to decrease at about 10^{-4} M s^{-1}; the rate of this decrease is almost constant and independent of [Co^{III}] until most of this species has been consumed. We have examined most of the subsystems that we could prepare and study independently. Among other observations, we find that increasing acidity increases the rate at which bromide catalyzes the oxidation of benzaldehyde by cobalt(III). We also find that free Br_2 is formed and can be entrained by gas flow. We propose a detailed molecular mechanism for the oscillations that seems to be consistent with most of what we know about the behavior of the subsystems, and we have initiated modeling computations with encouraging results. We also suggest additional experiments and computations that could further test the validity of our proposed mechanism.

I. Introduction

In 1983, Jensen[2] reported oscillatory behavior during the air oxidation of benzaldehyde in aqueous acetic acid catalyzed by a combination of cobaltous and bromide ions. Both electrode potentials and visual observation indicated that the dominant oxidation state of cobalt underwent major repetitive changes with a period of a few minutes.

Roelofs, Wasserman, Jensen, and Nader[3] (RWJN) subsequently proposed a mechanism of 11 steps that did indeed generate oscillations during computer simulations.

Roelofs, Wasserman, and Jensen[4] (RWJ) have since published a more detailed study of the same system and have proposed an

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[†] This paper is No. 87 in the series Chemical Oscillations and Instabilities. No. 86: Noyes, R. M. *J. Phys. Chem.* **1990**, *94*, 4404–4412.

(1) Based in part on the Ph.D. thesis of Zhi Yuan, University Oregon, August 1987. Copies are available on microfilm/microfiche or on paper from UMI Dissertation Information Service, 300 North Zeeb Road, Ann Arbor, MI 48106, or call (800) 521-3042. Order No. DA8800562.

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expanded mechanism of 21 steps that models the oscillations still more successfully.

Additional studies by one of us led to a thesis[1] that contained a somewhat different mechanism involving only 9 steps that also generated oscillations consistent in many ways with observations.

We have now carried out further experimental studies that show that none of the previous mechanisms[1-4] is tenable in detail. The present paper summarizes our studies of the behavior of the total system and of the various component systems that can be studied independently. Work done previously has also been summarized briefly so that we can present in one place a listing of the relevant experimental facts as they are now known. We also propose a detailed molecular mechanism that we believe to be consistent with almost all that is now known. Computations to simulate the experimental behavior will be reported subsequently.

II. Experimental Section

A. Materials. The solvent for our studies was 90/10 w/w AcOH/H_2O. It was prepared by diluting reagent-grade glacial acetic acid with triply distilled water.

The inorganic materials used as reagents were $Co(OAc)_2 \cdot 4H_2O$, NaBr, Br_2, NaOAc, and aqueous $HClO_4$; all were of analytical grade and were used without purification.

The organic reactants were reagent grade benzaldehyde (PhCHO), benzoyl bromide (PhCOBr), and dibenzoyl peroxide ($(PhCO_2)_2$). Opened bottles of benzaldehyde tended to develop perbenzoic acid and eventually benzoic acid on standing; small bottles were purchased from the manufacturer and were discarded if they developed a yellow color.

Perbenzoic acid ($PhCO_3H$) was prepared by the action of sodium methoxide on dibenzoyl peroxide by the method of Braun[5] as modified by Kolthoff et al.[6] The sodium salt was extracted into water, acidified, extracted into benzene, and crystallized by evaporation of solvent. Qualitative NMR indicated the only significant impurity was benzoic acid ($PhCO_2H$), which is inert to the reactions of interest to us. The concentration of peracid in a solution was determined by iodometric titration.

Solutions of cobalt(III) acetate were prepared from cobalt(II) acetate by the action of ozone generated in a Welsbach ozonator or by oxidation with perbenzoic acid. The resulting solution was bubbled with argon for at least 30 min and used without delay. When the ozonizer was not available, some solutions of mixed cobalt species were prepared electrolytically with platinum electrodes. The concentration of Co^{III} could be calculated from the Co^{II} originally taken, be titrated iodometrically, or be measured spectrophotometrically as described in section VI.A. The different methods gave consistent results whenever they could be compared appropriately.

B. Equipment. Most of the spectrophotometric measurements reported here were made with a Hewlett-Packard HP 8452 diode array spectrophotometer connected to a Vectra CS computer.

Potentiometric measurements were made with a platinum electrode, an Orion bromide ion selective electrode, or a Cole-Parmer Lazar 166 dissolved oxygen probe to monitor $[Co^{III}/Co^{II}]$, $[Br^-]$, and $[O_2(sol)]$, respectively. A conventional Ag/AgCl electrode was used for reference. We did not generally attempt to interpret potentiometric measurements quantitatively.

The substrate benzaldehyde could be followed in a deuterated solvent by taking an aliquot and integrating the area of the NMR signal for the aldehydic proton.

III. Classification of the System

A. Major Reactants and Products. The substrate benzaldehyde is particularly useful for this study because only one bond to one carbon atom is involved in all of the organic chemistry that occurs. We shall use Bz to refer to the C_6H_5CO group. RWJ[4] report that for this substrate the overall chemical change in the oscillatory system can be described virtually quantitatively by process T. This reaction provides the change of free energy that drives all of the chemistry, and any overall mechanism must generate this simple stoichiometry.

$$2PhCHO(BzH) + O_2(g) \rightarrow 2PhCO_2H(BzOH) \qquad (T)$$

B. Primary and Secondary Intermediates. Of course many intermediate species are formed and destroyed during the accomplishment of process T. We designate as primary the species $O_2(sol)$, Co(II), Co(III), Br^-, Br_2, $PhCO_3H(BzOOH)$, $(PhCO_2)_2(BzOOBz)$, PhCOBr(BzBr), H_2O, and H^+. These species can be prepared and added to the system independently, and many can be followed at least semiquantitatively during processes that may be components of the oscillatory mechanism.

We designate as secondary the species $PhCO^\bullet(Bz^\bullet)$, $PhCO_2^\bullet(BzO^\bullet)$, $PhCO_3^\bullet(BzOO^\bullet)$, $Br^\bullet$, and HOBr. All except HOBr are free radicals. Although at least many of these species must be present sometimes during the oscillations, they cannot be prepared independently nor followed quantitatively by techniques presently available to us.

This classification of intermediates does not attempt to distinguish the various possible mononuclear and polynuclear complexes of Co^{II} and Co^{III} nor species in rapid protolytic equilibria with each other. It also relies on the assumption that the aldehydic C–H bond in benzaldehyde is the only site where any chemistry will occur under the relatively mild conditions of the reaction. Even with these simplifications, the material below shows that it is a very complicated undertaking to sort out the information that is of potential relevance for determining the mechanism of the oscillations!

C. Oxidants and Reductants. It is also useful to classify the various species as oxidants or reductants. Species that can act as oxidants are (in decreasing power) O_2, Co^{III}, and Br_2. Species that can act as reductants are (in increasing power) Co^{II}, Br^-, and BzH. Categories I to III then constitute the types of overall processes that may take place in the system.

$$O_2 + (Co^{II},Br^-,BzH) \rightarrow (Co^{III},Br_2,BzOH,H_2O) \qquad (I)$$

$$Co^{III} + (Br^-,BzH) \rightarrow (Co^{II},Br_2,BzOH) \qquad (II)$$

$$Br_2 + BzH \rightarrow Br^- + BzOH \qquad (III)$$

D. Component Stoichiometric Processes. Overall process T can be generated by at least one combination of component stoichiometric processes. Such a process is a balanced equation with use of some of the reactant, product, and intermediate species defined above. If each of the selected component processes is multiplied by a proper positive coefficient, all contributions from intermediate species will cancel and the stoichiometry of process T will be recovered. Not every component process as written needs to proceed with a decrease of free energy, but the combination to generate process T does so proceed. We shall use an E designation for each of the component stoichiometric processes discussed below.

E. Pseudoelementary Processes. At the level of complete understanding, any chemical mechanism will consist of a number of elementary processes. Each such process involves one, two, or at most three species on the left side, and the number on the right side will be similarly limited. Stoichiometry and kinetics will be identical, and the process will take place by passage over a single potential energy barrier. The net direction of passage will be determined strictly by the free energies of the individual species at the time of interest.

In order to make a mechanistic description tractable, it is convenient to define pseudoelementary processes that recognize that the reactants and products may each be in rapid equilibrium with several other species and that there may be more than one barrier provided that the path over each barrier leads from the same pool of reactants to the same pool of products. The overall rate is the total flux over all such barriers. We shall use a P designation for each of the pseudoelementary processes invoked below.

IV. Behavior of the Total System

Most observations of oscillations were made in 90% aqueous acetic acid at 70 °C. The concentration of benzaldehyde was about 0.75 M, and the cocatalysts $Co(OAc)_2$ and NaBr were at concentrations a few times 0.01 and 0.001 M, respectively. A slow stream of air oxidized the benzaldehyde to benzoic acid.

Oscillations in such a system take place with a period of a few minutes and can be followed visually by noting the color changes

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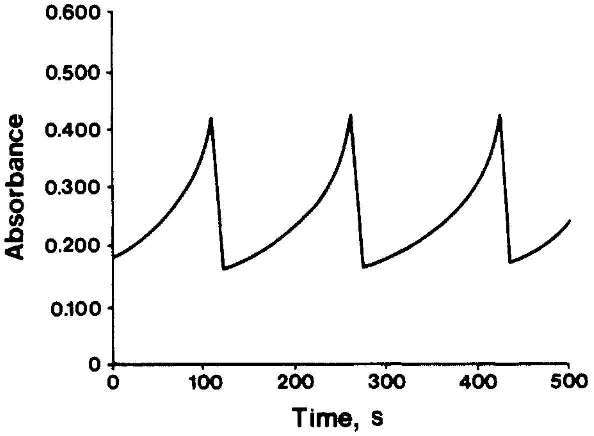

Figure 1. Typical oscillating system. Absorbance is at 800 nm of a system at 70 °C and initially containing $[Co^{II}]_0 = 0.02$ M, $[BzH]_0 = 0.75$ M, $[Br^-]_0 = 0.005$ M. The flow of air was about 100 bubbles per min.

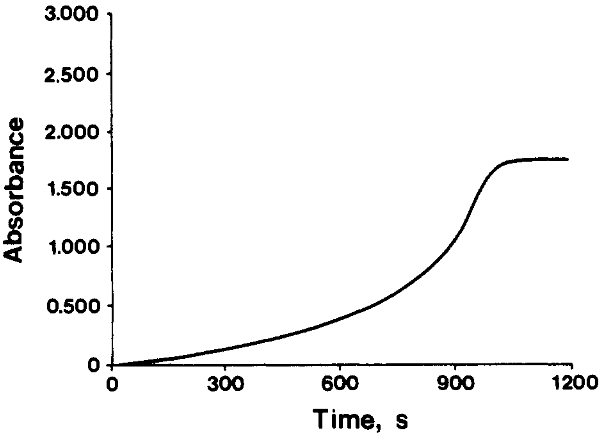

Figure 2. Absorbance at 700 nm of a system at 70 °C and initially containing $[Co^{II}]_0 = 0.02$ M and $[BzH]_0 = 0.75$ M and subject to a flow of air similar to that in Figure 1.

during alternating preponderance of Co^{II} and Co^{III} species. Most studies reported previously[1-4] were conducted potentiometrically with a platinum electrode. Interpretation of such measurements is somewhat unsure because both Co^{III} and Br_2 behave as oxidizing species against such an electrode. We found that spectrophotometric measurements could be interpreted with less ambiguity. Most of such observations were made with a Hewlett-Packard HP8452 diode array spectrophotometer connected to a Vectra CS computer.

Figure 1 illustrates the behavior of a typical system at a wavelength where most of the absorbance is due to Co^{III} while a little is due to bromide complexes of Co^{II}. Note that the concentration of Co^{III} rises at an increasing rate until it reaches a sharp maximum and then drops very rapidly by a process that appears to be zero order in the species producing the absorbance.

The potential of an electrode specific to bromide ion also oscillates at the same frequency but at a much smaller amplitude of only about 2 mV. In one experiment with $[Co^{II}]_0 = 0.02$ M and $[Br^-]_0 = 0.004$ M, the activity of Br^- was reduced about 7% when $[Co^{III}]$ was near its maximum.

The concentration of dissolved oxygen also undergoes coupled oscillations and at times becomes undetectably low. This behavior has been reported by RWJN,[3] who report that during oscillations even the maximum concentration of O_2 is only about 25% of saturation.

The behavior in Figure 1 must ultimately be explained. In sections V–VII below we present information on various subsystems categorized according to the most powerful oxidant present. Then in section VIII we report additional observations on systems containing all four of the components necessary to attain oscillations. A mechanistic explanation is developed in section IX.

V. Subsystems in Category I

Subsystems in category I contain the oxidant O_2 or one of the peroxidic species BzOOH or BzOOBz derived from it. They also contain no more than two of the reducing species BzH, $Co(OAc)_2$, and NaBr. We have studied as many different subsystems as we could.

A. Transport of O_2. Transport of oxygen between gas and solution takes place by reversible process P1.

$$O_2(g) \rightleftarrows O_2(sol) \qquad (P1)$$

The kinetics of this process can be written as

$$d[O_2]/dt = k_{P1}(1 - [O_2]/K_{P1}) \qquad (1)$$

We estimate very roughly from handbook values that 90% HOAc saturated with air at 70 °C will satisfy eq 2. RWJ[4] make

$$[O_2]_{sat} = 10^{-4}\ M = K_{P1} \qquad (2)$$

a somewhat greater estimate of this value. The present level of understanding of the chemistry of the total system does not justify an accurate determination of this solubility.

The value of k_{P1} depends upon the rate of gas flow. A method of estimation is suggested by noting that the rate of consumption of benzaldehyde during oscillations is often zero order in BzH until reaction is almost complete. Such behavior requires that absorption of oxygen is rate determining for process T and that on average $[O_2] \ll K_{P1}$. In one experiment 0.75 M initial BzH decayed to almost zero in about 2 h, corresponding to a rate of process T of about 5×10^{-5} M s^{-1}. The details are presented in the thesis of Yuan.[1] Flow rates in most of our subsequent experiments were somewhat less, and our model computations have used the equation

$$k_{P1} = 2 \times 10^{-5}\ M\ s^{-1} \qquad (3)$$

RWJ used a somewhat different experimental setup but found about the same rate of transport for their flow conditions.

B. Reduction of O_2 by BzH. Although process T is strongly favored by thermodynamics, it would probably take days for significant reaction to occur in the absence of catalysts. The direct reaction can be ignored during efforts to understand the mechanism of the oscillations.

C. Reaction of O_2 with Co^{II}. Solutions of $Co(OAc)_2$ seem to be indefinitely inert to change during contact with air. We have not explored whether this inertness is due to kinetic or to thermodynamic reasons. However, potentials for aqueous solutions suggest that the inertness of Co^{II} is probably associated with a true thermodynamic stability.

D. Reduction of O_2 by Br^-. Solutions of NaBr are thermodynamically unstable to oxidation by air under the conditions of the oscillating reaction. However, at least a day will be required before the solution takes on significant coloration due to elementary Br_2.

E. Reduction of O_2 by BzH + Co^{II}. Each of the species BzH, Co^{II}, and Br^- is individually inert to reaction with air under the conditions of interest. However, mixtures of two or more of these species may induce rapid reduction of atmospheric oxygen! The most dramatic effect of two simultaneous species is attained with BzH + Co^{II}.

Figure 2 shows the behavior of a system containing these two species and subject to a stream of air. The autocatalytic increase in absorbance is very similar to that observed in Figure 1 which had Br^- also, but instead of oscillating as in Figure 1, the system in Filure 2 terminates the autocatalysis by suddenly attaining a steady state corresponding to virtually complete oxidation of Co^{II} to Co^{III}.

The more Co^{II} that is present initially, the longer is the induction period, defined as the time until the inflection point of a plot like Figure 2 of absorbance against time. In one set of experiments, the induction period increased from 100 to 1200 s as $[Co^{II}]_0$ increased from 0.01 to 0.04 M.

The behavior in Figure 2 is the consequence of component stoichiometric processes E1 and E2. Of course process E2 is identical with process T, and this component process of Figure 2 is the total net change for one cycle of Figure 1.

$$O_2(g) + 4Co^{II} + 4H^+ \rightarrow 4Co^{III} + 2H_2O \qquad \text{(E1)}$$

$$O_2(g) + 2BzH \rightarrow 2BzOH \qquad \text{(E2)}$$

The overall reaction per oxygen consumed is given by

$$O_2(g) + 4fCo^{II} + 4fH^+ + 2(1-f)BzH \rightarrow 4fCo^{III} + 2fH_2O + 2(1-f)BzOH \qquad \text{(E3)}$$

We estimate without formal justification that the stoichiometric factor f is about 0.5.

The growth of absorbance in Figure 2 can be fitted approximately by the equation

$$dA/dt = k_A A \qquad (4)$$

For the entire period between 0 and 990 s, Figure 2 is best fitted by $k_A = 0.0021$ s^{-1} with a standard deviation of 7.7%. For the interval between 300 and 900 s, the fit is much better, and it is $k_A = 0.0029$ s^{-1} with a standard deviation of 1.6%.

If the flow of air was stopped after the steady state had been attained, the absorbance in the composition of Figure 2 decayed with a first-order rate constant of about 0.0045 s^{-1} corresponding to a half-life of about 150 s. For systems that also contained bromide, the rate of decay was approximately proportional to $[Br^-]^2$. The implications of these observations will be discussed further in section VI.B–D below.

F. Formation of BzOOH. All investigators have agreed that process E3 involves perbenzoic acid, BzOOH, as an intermediate. They also agree that its formation is initiated by process P2 followed by process P3 or P4.

$$O_2(sol) + Bz^\bullet \rightarrow BzOO^\bullet \qquad \text{(P2)}$$

$$BzOO^\bullet + BzH \rightarrow BzOOH + Bz^\bullet \qquad \text{(P3)}$$

$$BzOO^\bullet + Co^{II} + H^+ \rightarrow BzOOH + Co^{III} \qquad \text{(P4)}$$

The alternative stoichiometries of processes E4 and E5 are generated by the indicated sequences.

$$O_2(g) + BzH \rightarrow BzOOH \qquad \text{(E4)}$$

$$\text{(E4)} \equiv \text{(P1)} + \text{(P2)} + \text{(P3)}$$

$$O_2(g) + Co^{II} + H^+ + Bz^\bullet \rightarrow BzOOH + Co^{III} \qquad \text{(E5)}$$

$$\text{(E5)} \equiv \text{(P1)} + \text{(P2)} + \text{(P4)}$$

The rates of processes E4 and E5 are presumably directly proportional to $[Bz^\bullet]$, which is very low in solutions that contain only BzH. This low radical concentration explains the inertness reported in section B above.

Experience with other organic peroxy radicals suggests that P2 is virtually irreversible and diffusion controlled. For our modeling, we use eq 5.

$$k_{P2} = 10^9 \text{ M}^{-1} \text{ s}^{-1} \qquad (5)$$

G. Reduction of BzOOH by Co^{II} in the Absence of BzH. We studied the reduction by $Co(OAc)_2$ of BzOOH prepared as described above.[5,6] The reaction was carried out at room temperature under an atmosphere of argon, and the initial composition contained at least 2 mol of Co^{II} per mol of BzOOH. The details are presented in the thesis of Yuan.[1] The reaction is rapid, and the stoichiometry to be expected is that of process E6.

$$BzOOH + 2Co^{II} + 2H^+ \rightarrow BzOH + 2Co^{III} + H_2O \qquad \text{(E6)}$$

That stoichiometry was approached only when the initial concentration of Co^{II} was at least 20 times that of BzOOH. When the initial dropped to only a little above 2, the amount of Co^{III} produced was about three-quarters of that predicted by process E6. We interpret the deficiency to indicate that Co^{II} is in competition with some species for an intermediate and that the Co^{II} does not react quantitatively unless it is in sufficient excess. In a system undergoing oscillations, $[Co^{II}]$ should be large enough that the stoichiometry of process E6 would be obeyed almost exactly.

A plausible mechanism for process E6 involves steps P4 to P7.

$$BzOOH + Co^{II} + H^+ \rightarrow BzO^\bullet + Co^{III} + H_2O \qquad \text{(P5)}$$

$$BzO^\bullet + BzOOH \rightarrow BzOH + BzOO^\bullet \qquad \text{(P6)}$$

$$2BzOO^\bullet \rightarrow BzOOBz + O_2 \qquad \text{(P7)}$$

The sequence of steps P5, P6, P4 generates process E6, and the competition of step P4 with step P7 can explain the stoichiometric deficiency we observed at low concentrations of Co^{II}. Whether or not the same stoichiometric deficiency would also occur at the higher temperature used for the oscillations, the basic mechanism should be about the same.

The kinetics of process E6 are controversial. Jones[7] studied the oxidation of Co^{II} by *m*-chloroperbenzoic acid in 95% acetic acid and claimed the rate of the process corresponding to process E6 would be described by eq 6.

$$2d[Co^{III}]/dt = k_J[BzOOH][Co^{II}]^2 \qquad (6)$$

RWJ[4] did not attempt quantitative measurements but extrapolated the Jones data to conclude that $k_J = 2 \times 10^6$ M^{-2} s^{-1} for unsubstituted peracid in 90% solvent at 70 °C.

Before we were aware of the Jones and RWJ studies, we measured initial rates for the first few seconds and obtained data that could be fitted reasonably well by eq 7. Measurements

$$d[Co^{III}]/dt = k_Y[BzOOH][Co^{II}] \qquad (7)$$

between 10 and 50 °C were extrapolated to 70 °C to give $k_Y = 614$ M^{-1} s^{-1}. The two expressions give identical rates when $[Co^{II}] = 6 \times 10^{-4}$ M, which is within a factor of 2 of the concentration we used at the highest temperature studied. More extensive measurements could certainly resolve the discrepancy between the kinetics claimed by the two groups and could also provide a more accurate rate constant.

H. Reduction of O_2 by Co^{II} in the Presence of BzH. Neither the mechanism of process E6 nor the stoichiometry that generates it provides any explanation for the prominent autocatalysis in Figure 2, which shows the behavior of the same reactants. The stoichiometry of process E6 was obtained in a system containing considerable BzOOH, while in Figure 2 this species was in very low concentration compared to BzH. In such a system P8 competes very efficiently with step P6.

$$BzO^\bullet + BzH \rightarrow BzOH + Bz^\bullet \qquad \text{(P8)}$$

If step P8 is more important than step P6 in the oscillating system, process E6 should be replaced by process E7.

$$BzOOH + Co^{II} + H^+ + BzH \rightarrow BzOH + Co^{III} + H_2O + Bz^\bullet \qquad \text{(E7)}$$

$$\text{(E7)} \equiv \text{(P5)} + \text{(P8)}$$

If process E7 is combined with the stoichiometries of processes E4 and E5, we obtain processes E8 and E9, respectively.

$$O_2(g) + Co^{II} + H^+ + 2BzH \rightarrow BzOH + Co^{III} + H_2O + Bz^\bullet \qquad \text{(E8)}$$

$$\text{(E8)} \equiv \text{(E4)} + \text{(E7)} \equiv \text{(P1)} + \text{(P2)} + \text{(P3)} + \text{(P5)} + \text{(P8)}$$

$$O_2(g) + 2Co^{II} + 2H^+ + BzH \rightarrow BzOH + 2Co^{III} + H_2O \qquad \text{(E9)}$$

$$\text{(E9)} \equiv \text{(E5)} + \text{(E7)} \equiv \text{(P1)} + \text{(P2)} + \text{(P4)} + \text{(P5)} + \text{(P8)}$$

The total stoichiometry describing reactions in Figure 2 will be the sum of that from parallel processes E8 and E9. The stoichiometry of process E9 is that of process E3 if $f = 0.5$ and results precisely from the indicated sequence. The prominent autocatalysis in Figure 2 is caused by process E8. That autocatalysis increases $[Co^{III}]$ by first-order kinetics, rising to a final

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(8) March, J. *Advanced Organic Chemistry*, 3rd ed.; J. Wiley: New York, 1985; p 990.

concentration of about 10^{-2} M attained by a rate of a few times 10^{-5} M s^{-1}.

Although the concentrations of Co^{III} and of $Bz^{\bullet}$ both increase exponentially, at all times $[Co^{III}] \gg [Bz^{\bullet}]$. This difference may arise because $Bz^{\bullet}$ is consumed by process P2 as rapidly as it is formed. It may also arise because step P4 is much faster than step P3 even though step P3 and the resulting process E8 are responsible for the autocatalysis in Figure 2. This competition between steps P3 and P4 may be at least partly responsible for the effect of Co^{II} on the induction period described in section E above. Oxidation of BzH to $Bz^{\bullet}$ may also contribute to the autocatalysis; that reaction is discussed in sections VI.B and VI.D below.

I. Reduction of BzOOH by Br^-. Reduction of perbenzoic acid by bromide should obey the stoichiometry of process E10.

$$BzOOH + 2Br^- + 2H^+ \rightarrow BzOH + Br_2 + H_2O \qquad (E10)$$

We confirmed this stoichiometry spectrophotometrically at room temperature with $\epsilon = 120$ M^{-1} cm^{-1} at 395.5 nm. We also obtained good linear plots of $\ln \{[Br^-]/[BzOOH]\}$ against time. That linearity could be defined by eq 8, and the slope could be used to calculate k_{E10}.

$$d[Br_2]/dt = k_{E10}[BzOOH][Br^-] \qquad (8)$$

Measurements betwen 10 and 50 °C were extrapolated to 70 °C to give $k_{E10} = 120$ M^{-1} s^{-1}. Comparison with k_Y in eq 7 indicates that at this temperature when $[Co^{II}] = 0.02$ M and $[Br^-] = 0.004$ M, then BzOOH is consumed about 13 times as fast by (E8) + (E9) as by (E10).

The most plausible mechanism for reaction E10 is a pair of nucleophilic displacements by bromide ion in processes P9 and P10.

$$BzOOH + Br^- + H^+ \rightarrow BzOH + HOBr \qquad (P9)$$

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \qquad (P10)$$

These two steps generate the stoichiometry of process E10, and step P9 is rate determining. Because process E10 retains paired electrons throughout while processes E8 and E9 involve free radicals, the intermediate species in the two-component stoichiometric processes probably do not interact with each other.

J. Reduction of BzOOH by BzH. Thermodynamics suggests that the Bayer-Villiger reaction[8] E11 should be strongly favored.

$$BzOOH + BzH \rightarrow 2BzOH \qquad (E11)$$

However, we conducted a number of experiments with *m*-chloroperbenzoic acid, cobalt(II), and benzaldehyde, adding reactants in different orders. We concluded that peracid oxidizes cobalt(II) rapidly and quantitatively while benzaldehyde does not compete to divert the oxidant to other paths. Therefore, the processes in sections H and I will consume BzOOH much more rapidly than will process E11.

K. Reduction of BzOOBz by Co^{II} and by Br^-. Dibenzoyl peroxide, BzOOBz, might conceivably be formed by disproportionation of $BzOO^{\bullet}$ radicals by process P7 and might then oxidize some of the reducing species by process E12 or E13.

$$BzOOBz + 2Co^{II} + 2H^+ \rightarrow 2BzOH + 2Co^{III} \qquad (E12)$$

$$BzOOBz + 2Br^- + 2H^+ \rightarrow 2BzOH + Br_2 \qquad (E13)$$

We found by direct test that process E12 was much too slow to be of significance in our system. Process E13 did proceed at a significant rate but much slower than the corresponding reaction of I^-. We estimate that a BzOOBz molecule if formed would survive about 2 min at 70 °C in the presence of 0.004 M Br^-. Therefore, peroxidic species will not build up in the system, but most chemical reaction will pass through BzOOH rather than through BzOOBz.

VI. Subsystems in Category II

Subsystems in category II contain the oxidant Co^{III}; they may also contain one or both of the reducing species BzH and NaBr.

A. Characterization of Co^{III} Solutions. Cobalt(III) solutions have been studied in solvents ranging from the acetate in dehydrated acetic acid to the perchlorate in pure water. There does not seem to be any way in which the different species claimed to be present in some of these systems can be rendered mutually consistent.

We are only aware of two cryoscopic studies, both in glacial acetic acid which is alleged to contain about 0.1% water. Koubek and Edwards[9] oxidized Co^{II} with peracetic acid and obtained a molecular weight consistent with that of $Co_2(OH)_2(OAc)_4$. Lande, Falk, and Kochi[10] used ozone as oxidant and obtained a molecular weight consistent with $Co_2(OH)_2(OAc)_4(HOAc)$. They also obtained good agreement with Beer's law from 4×10^{-3} to 1.05 M, indicating either a monomeric cobalt species or a very stable dimer.

Hendriks et al.[11] applied Stokes law to ion migration rates in a range of solvent compositions and interpreted the radii as consistent with that of monomeric species.

We used a solvent that was 10% water by weight corresponding to a mole fraction of 27% water. The cryoscopic evidence for dimeric species in almost anhydrous medium is not necessarily applicable to our work.

Extensive studies of cobalt(III) reactions were carried out by Jones.[7] Although most of his observations were in 95% aqueous acetic acid, they seem to be relevant to the studies by RWJ and by us in 90% acid. Jones reports that when cobalt(II) is oxidized by peracid, the first species which forms is an "active" apple-green dimer designated Co^{IIIa}. This active species then rearranges rapidly to a "stable" olive-green dimer designated Co^{IIIs} which reacts much more slowly with reducing agents like Br^-. RWJ say the rearrangement takes only 1 s at 70 °C. Jones also reports a "complexed" species designated Co^{IIIc} and thought to contain two Co^{III} and one Co^{II}. The rearrangement of Co^{IIIs} to Co^{IIIc} requires days at ambient temperature, and RWJ neglect it in their model for oscillations. Although Jones considers these obviously different species to be dimers or trimers, he does not provide spectral justification for his stoichiometric assignments. He also notes that these species react as oxidants with kinetics which are almost invariably first order in total Co^{III}.

We prepared solutions of Co^{III} by oxidation of Co^{II} by O_3 and by BzOOH and by electrolysis with platinum electrodes. Spectral and kinetic measurements indicated that all three methods of preparation produced the same species.

The spectral studies were made at the absorbance maximum of 620 nm. At 25 °C, we obtained excellent Beer's law plots from 2×10^{-4} to 2×10^{-2} M and computed $\epsilon = 167$ M^{-1} cm^{-1} with a scatter of less than 2%, although we saw minor spectral variations at other wavelengths in the more concentrated solutions. We measured ϵ between 10 and 50 °C and found a 4% range of values with no trend with temperature. We therefore used the 167 value to evaluate our kinetic measurements at 70 °C. RWJ report $\epsilon = 150$ M^{-1} cm^{-1} at 70 °C. The deviation of 10% is a little larger than our scatter would suggest, but we do not consider it to be serious.

The kinetic evidence was based on the oxidation of Br^- that took place at the same rate with aged electrolytic samples or with samples prepared in situ by addition of BzOOH. We also note that during oscillations like those in Figure 1 the rate of decay of Co^{III} is similar if not identical with that in solutions of BzH + Br^- + Co^{III} in which the Co^{III} has been prepared by electrolysis.

We were obviously examining the species called Co^{IIIs} by Jones.[7] If it is indeed a dimer, either the dissociation constant is less than 10^{-5} M or Co^{III} ions absorb identically at 620 nm whether they are in monomeric or dimeric form. The excellent linearity and

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(9) Koubek, E.; Edwards, J. O. *J. Inorg. Nucl. Chem.* **1963**, *25*, 1401–1408.

(10) Lande, S. S.; Falk, C. D.; Kochi, J. K. *J. Inorg. Nucl. Chem.* **1971**, *33*, 4101–4109.

(11) Hendriks, C. F.; van Beek, H. C. A.; Heertjes, P. M. *Ind. Eng. Chem. Prod. Res. Dev.* **1979**, *18*, 43–46.

(12) Hendriks, C. F.; van Beek, H. C. A.; Heertjes, P. M. *Ind. Eng. Chem. Prod. Res. Dev.* **1978**, *17*, 260–264.

zero intercepts of our Beer's law plots and our first-order kinetics encourage us to regard this species as a monomer. Because d^6 species like Co^{3+} may be very sluggish in substitution reactions, it is even conceivable that the differernt ions observed by Jones are all monomers. Of course our data are equally consistent with a very stable dimer reacting by first-order kinetics as postulated by RWJ. Very few of the mechanistic proposals in this paper will be seriously affected by which assumption is made.

B. Reduction of Co^{III} by BzH. Process E14 is about the only overall chemical change to be expected if oxygen and peroxides are excluded and if there are no bromine compounds.

$$2Co^{III} + BzH + H_2O \rightarrow 2Co^{II} + BzOH + 2H^+ \quad (E14)$$

The anticipated kinetics are given by eq 9.

$$-d[Co^{III}]/dt = k_{E14}[BzH][Co^{III}] \quad (9)$$

Hendriks et al.[12] report precisely these kinetics with $k_{E14} = 3.5 \times 10^{-5}\ M^{-1}\ s^{-1}$ in glacial acetic acid at 25 °C. RWJ[4] note that Co^{III} can also oxidize acetic acid slowly. For 0.75 M BzH in 90% AcOH at 70 °C, they report a rate equivalent to $k_{E14} = 1.8 \times 10^{-3}\ M^{-1}\ s^{-1}$. In 1987, two rough runs in solutions purged with argon indicated $k_{E14} = 1.5 \times 10^{-4}\ M^{-1}\ s^{-1}$ for the same conditions. In 1989, a value of $k_{E14} = 7 \times 10^{-3}\ M^{-1}\ s^{-1}$ was obtained for a solution purged with argon and initially containing about 10^{-3} M Co^{III} in 0.75 M BzH at 70 °C. The rate was only about half as great when more Co^{III} was added to the spent solution. Almost identical rates were obtained with solutions that also contained 0.001 M of the radical scavenger butylated hydroxy toluene, BHT (2,6-di-*tert*-butyl-4-methylphenol).

These rather scattered kinetic studies show that some factor was out of control even with no oxygen or bromide present. However, we note the comparability of most of the values of k_{E14} with the value of k_A describing the increase in absorbance in Figure 2 and with the decrease of absorbance in a system like Figure 2 after the flow of air has been cut off. Most of the variations of these different rate constants are not greater than about a factor of 2. All of these rates are much less than those in the presence of bromide reported in section D below.

A plausible mechanistic interpretation is that process E14 is initiated by rate-determining step P11.

$$Co^{III} + BzH \rightarrow Co^{II} + Bz^{\bullet} + H^+ \quad (P11)$$

The further processes might be of the sort of step P12 or P13.

$$Co^{III} + Bz^{\bullet} + H_2O \rightarrow BzOH + Co^{II} + H^+ \quad (P12)$$

$$2Bz^{\bullet}\ (+H_2O) \rightarrow Bz_2\ (\text{or } BzOH + BzH) \quad (P13)$$

The value of $[Co^{III}]$ may be of the order of 0.01 M, and k_{P12} is likely to be of the order of[13] $10^6\ M^{-1}\ s^{-1}$. Then it appears unlikely that the radical concentration can be great enough for step P13 to compete with step P12 even if step P13 is diffusion controlled. However, if step P12 is the dominant step in the mechanism, the absence of radical scavenger influence on the rate seems to require that the product of reaction of $Bz^{\bullet}$ with BHT can still reduce Co^{III} by electron transfer even though it cannot propagate chains by reaction with organic molecules. We shall see in section D below that the detailed mechanism of process E11 in the absence of bromide probably is not important to the mechanism of the oscillating reaction.

C. Reduction of Co^{III} by Br^-. The stoichiometry of the overall reaction between Co^{III} and Br^- is undoubtedly given by process E15. In aqueous solution at least, this reaction would be

$$2Co^{III} + 2Br^- \rightarrow 2Co^{II} + Br_2 \quad (E15)$$

quantitative. This stoichiometry was confirmed to within 10% from the simultaneous absorbances at 396 and 660 nm for a solution that initially contained $[Co^{III}] = 0.0082$ M and $[Br^-] = 0.1$ M.

The kinetics turned out to be much more complex than this simple stoichiometry would suggest, and the rate was inhibited by the product Co^{II} in a way that indicated this species was in competition with Br^- for some intermediate. We made measurements of initial rates (to 5% completion) for a number of different compositions and found they could be fitted fairly well to eq 10 where $R = [Co^{II}]/[Br^-]$. Virtually the same rates were obtained whether the solution was saturated with air or with N_2.

$$-d[Co^{III}]/dt = k_{first}[Co^{III}] = \frac{k_1[Co^{III}][Br^-]}{1 + k_2R + k_3R^2} \quad (10)$$

At 70 °C in 90% HOAc with $[Co^{II}] = 0.02$ M and $[Br^-] = 0.005$ M, we found $k_{first}/[Br^-] = 0.87\ M^{-1}\ s^{-1}$ in excellent agreement with the value reported by RWJ[4] in similar conditions.

We were unsuccessful in efforts to develop a detailed mechanism consistent with eq 10. Only after there was insufficient time to restudy this subsystem did we realize that the rate of process E15 depends upon pH. Thus 0.021 M $HClO_4$ increased the rate by a factor of 4 to 5, suggesting that HBr reacts more rapidly with Co^{III} than does Br^-. Although process E15 as written neither consumes nor produces H^+, extents of solvolysis of Co^{II} and Co^{III} and the basicity of Br^- are all unknown. The problem is discussed further in section VIII.D below.

D. Reduction of Co^{III} by Br^- + BzH. We examined the reaction when Co^{III} was added to a solution under argon for which $[BzH]_0 = 0.75$ M and $[Br^-]_0 = 0.005$ M. Until about 80% of the Co^{III} had been consumed, it decayed with zero-order kinetics at a rate about $5 \times 10^{-4}\ M\ s^{-1}$. This rate is over ten times that of absorption of O_2 in eq 3 (section V.A); it is therefore much faster than the maximum rate of formation of Co^{III} in Figure 1 or 2. This rate is also about a hundred times that at which Co^{III} would have reacted with either BzH or Br^- alone! This remarkable synergistic effect has already been reported by RWJ.[4] Careful examination of the spectrophotometric trace showed that the apparent zero-order kinetics were actually a broad shallow maximum in a rate that first increased very slowly and then decreased.

In a comparable experiment except that $[Br^-] = 0.1$ M initially, no Br_2 could be detected spectrophotometrically at 396 nm at the end of the run. Furthermore, when Br_2 was added to the spent solution, the resulting abosrbance at 396 nm decayed slowly due to reaction of Br_2 with BzH. We conclude that even with this high concentration of Br^-, the Co^{III} is oxidizing only BzH in the overall reaction and the Br^- is not being oxidized even though it serves as a remarkably efficient catalyst.

In another pair of experiments, Co^{III} was added to solutions of composition $[BzH] = 0.75$ M, $[Co^{II}] = 0.02$ M, and $[Br^-] = 0.005$ M. The rate of consumption of Co(III) was 85 times faster in the absence of BHT than it was in the presence of this radical scavenger at 0.002 M.

In still another experiment, 0.0067 M Br^- was added to a steady state with $[Co^{III}] = 0.014$ M in the presence of air and BzH. The Co^{III} decayed almost completely and too rapidly to measure.

Finally, we established independently that Co^{III} does not react with BzBr at a significant rate.

A rationalization of these observations will be developed in section IX after the reactions of Br_2 and the effects of pH on rates have also been discussed.

VII. Subsystems in Category III

Subsystems in Category III contain no oxidizing species except Br_2, which is the weakest 2-equivalent oxidant in the system. BzH is the only 2-equivalent reductant that can be oxidized directly by Br_2. However, Br_2 can also react with a strong 1-equivalent reductant like $Bz^{\bullet}$ to form $Br^{\bullet}$ atom, which is a moderately strong oxidant.

A. Evaporation of Br_2. The element Br_2 is moderately volatile at 70 °C and should be entrained by a stream of air. We were unable to detect Br_2 in such a stream until all plastic connections were replaced with Teflon. We could then determine entrained Br_2 by collecting the evolved gas in a syringe, reacting it with phenol red in a buffered solution, and determining the resulting bromophenol blue spectrophotometrically at 590 nm[14] where we found $\epsilon = 4290\ M^{-1}\ cm^{-1}$. An average of three determinations indicated that with an air flow comparable to that in an oscillating

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(13) Asmus, K. D.; Bonifacic, M. *Landolt-Börnstein, New Series*; Fischer, H., Ed.: Springer-Verlag: Berlin, 1984; Vol. 13b, p 301.

system Br_2 evaporated from the solution with a first-order rate constant of 1.22×10^{-4} s^{-1}.

B. Reaction of Br_2 with BzH. The only plausible overall reactions of Br_2 with BzH are processes E16 and E17.

$$BzH + Br_2 \rightarrow BrC_6H_4CHO + HBr \qquad (E16)$$

$$BzH + Br_2 + H_2O \rightarrow BzOH + 2HBr \qquad (E17)$$

The product analyses of RWJ indicate that process E16 is not of significance in the oscillating system.

Process E17 does take place but rather slowly if there is no oxygen or major source of free radicals. Thus, under an atmosphere of nitrogen with [BzH] = 0.75 M, a dilute solution of Br_2 decayed with pseudo-first-order kinetics. When $[Br_2]$ was increased 30-fold from 0.33×10^{-3} to 9.6×10^{-3} M, the rate constant at 70 °C decreased from 1.7×10^{-3} to 1.0×10^{-3} s^{-1}. With $[Br^-]_0 = 0.005$ M and $[Br_2]_0 = 0.0013$ M, k was 5.3×10^{-3} s^{-1}. The rate seems to be somewhat faster in the presence of Br^-, and the reaction may involve the well-known ion Br^-_3.

The rate of process E17 also seemed to be somewhat irreproducible, consistent with a radical chain process. The most plausible mechanism for process E17 seems to be the sequence

$$Bz^\bullet + Br_2 \rightarrow BzBr + Br^\bullet \qquad (P14)$$

$$Br^\bullet + BzH \rightarrow HBr + Bz^\bullet \qquad (P15)$$

$$BzBr + H_2O \rightarrow BzOH + HBr \qquad (P16)$$

C. Hydrolysis of BzBr. Step P16 in the proposed mechanism can be tested independently. A small sample of benzoyl bromide was injected with a syringe into well-stirred solvent at 70 °C. The system was monitored with an electrode specific to bromide ion. The potential rose to a plateau within about 20 s. Variation of the logarithm of the concentration of a product is not a good way to get quantitative information about rate, but this experiment showed that process P16 is fast enough that BzBr will never accumulate in concentrations comparable to those of other bromine-containing species in the oscillating system.

VIII. Perturbations of the Total System

The total oscillatory system is prepared by passing a stream of air into a solution containing the three reducing agents BzH, Co^{II}, and Br^-. Sections V–VII describe observations on various subsystems. We also attempted to obtain information of mechanistic utility by perturbing oscillatory systems with various reactants, products, or intermediates.

A. Studies with Isotopic Oxygen. RWJ[4] report the study of an oscillator in which the air contained O^*_2, indicating labeling with O-18. They found that 45% of the product benzoic acid could be designated BzO*H, indicating that one of the two oxygens had come from the atmosphere. The other 55% was BzOH, indicating that the oxygen added to the BzH had come from the solvent.

BzOH can be formed in this system by three different paths. One path is initiated every time a $Bz^\bullet$ radical reacts with O^*_2 by step P2. According to the steps we have suggested, BzO*O*H is then invariably formed by process E4 or E5, and BzO*H ultimately results from one of the sequences discussed in section V. The most important processes are E8, E9, and E10, each of which probably generates precisely one BzO*H after each occurrence of step P2. Of the unimportant processes, process E11 produces two BzO*H for each step P2 event while process E12 may produce less than one on average. Process E13 also produces precisely one BzO*H.

If BzH is oxidized by Co^{III} according to the stoichiometry of process E14, the BzOH contains only oxygen derived from solvent whether or not the overall process is catalyzed by Br^-.

Finally, if BzH is oxidized by Br_2 according to the stoichiometry of process E17, the resulting BzOH•also contains only oxygen derived from solvent.

The isotopic studies by RWJ therefore indicate that during oscillations half or slightly less than half of the BzOH product results from sequences initiated by step P2 just as was observed by RWJ.

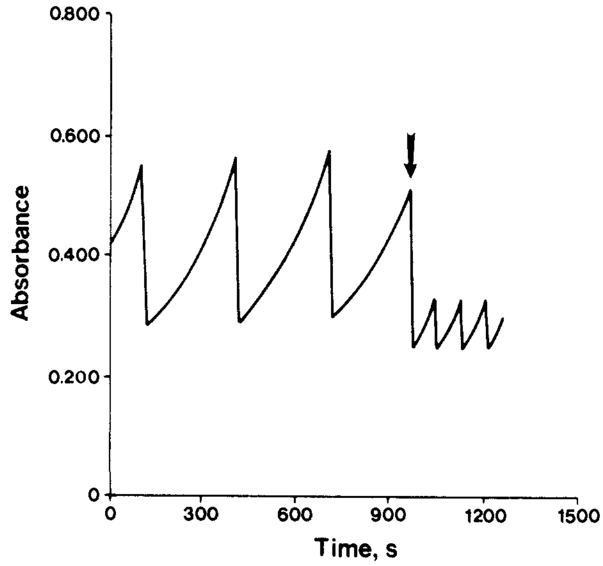

Figure 3. Absorbance at 800 nm of a system at 70 °C and initially containing $[Co^{II}]_0 = 0.04$ M, $[Br^-]_0 = 0.004$ M, and $[BzH]_0 = 0.75$ M and subject to a flow of air. At the time indicated by the arrow, enough Br_2 was added to make the system 0.0045 M in this species.

B. Effects of O_2 Flow Rate. We varied the rate of air flow semiquantitatively during some studies of oscillating systems. The maximum absorbance due to Co^{III} varied approximately as the square root of that flow rate.

If air flow was suddenly stopped while $[Co^{III}]$ was increasing, the rate of decrease of absorbance was about the same as that observed during oscillations like those in Figure 1. Therefore, the concentration of dissolved oxygen is probably very low at the time absorbance begins to decrease in Figure 1. This conclusion is consistent with the measurements with an oxygen electrode reported by RWJN[3] and in the thesis of Yuan.[1]

The rates of decrease of absorbance were about the same in systems subject to different flow rates even though the amplitudes of the oscillations were different. This behavior is consistent with the observation in Figure 1 that the decay of absorbance is a straight line zero order in $[Co^{III}]$.

C. Addition of Br_2 to the Oscillating System. We conducted a few experiments in which different amounts of Br_2 were added to an oscillating system at 70 °C initially containing $[BzH[_0 = 0.75$ M, $[Co^{II}]_0 = 0.04$ M, and $[Br^-]_0 = 0.004$ M.

Addition to make the system 0.027 M in Br_2 (more than equivalent to the Co species) immediately killed the oscillations by driving the system to a reduced state. It never oscillated again.

Figure 3 shows the result of making the system 0.0045 M in Br_2 (comparable to the concentration of Br^-). The addition was made as $[Co^{III}]$ was approaching but had not yet reached its maximum. The concentration of Co^{III} fell immediately, but oscillations continued with shorter period and smaller amplitude.

Similar additions of 0.0003 and 0.0012 M Br_2 caused delays in the times at which $[Co^{III}]$ reached its maximum, but oscillations continued with only slight reductions in period and amplitude. The potentiometric measurements in section IV indicated the activity of bromide in a similar system was reduced about 7% or 0.0004 M. If that reduction was due solely to formation of Br_2, these additions were comparable to the amount produced chemically.

All of the above observations show that additions of Br_2 can influence the subsequent behavior. However, the effects do not seem to vary significantly from what would be anticipated after additions of stoichiometrically equivalent amounts of Br^-.

Br_2 was entrained by the method of section VII.A from a similar potentially oscillatory mixture. During a 240-s period of increasing $[Co^{III}]$, the average rate of removal of Br_2 was about 3.5×10^{-9} M s^{-1}, indicating that the average $[Br_2]$ was about 2.9×10^{-5} M. This was presumably considerably less than the maximum concentration attained during oscillation. Although the concentration of dissolved Br_2 may at times become more than the 10^{-4} M concentration of O_2 at saturation, the rate of removal of Br_2 by evaporation is always much less than the 2×10^{-5} M s^{-1} rate at which O_2 can enter the solution (section V.A).

RWJ neglect any consideration of Br_2 as a significant species in their mechanism for the oscillations. Figure 3 and the other observations mentioned here indicate that it may be formed at low concentrations during the oscillations and that it may have significant effects on overall behavior.

D. Additions of Acid and Base. We carried out most of our studies under the impression that the overwhelming amount of HOAc in the solvent would establish an acidity that could not be significantly affected by the other species at concentrations less than 0.1 M. Only after we discovered the effect of acidity on reaction of Co^{III} with Br^- (section VI.C) did we realize that HOAc is subject to typical autoprotolysis equilibria with ions H_2OAc^+ and OAc^-. Then $Co(OAc)_2$ should be a strong base in this solvent. Although HBr is a strong acid in water, it is a weak acid in glacial acetic acid.[15] We do not know whether or not solvolysis of Br^- would contribute to the basicity of our solvent with 90% HOAc.

We made a few tests on an oscillatory system at 70 °C containing [BzH] = 0.75 M, $[Co^{II}] = 0.02$ M, and $[Br^-] = 0.005$ M and subject to air flow. When 0.075 M NaOAc was present initially, the absorbance due to Co^{III} went through one maximum and one minimum before it went to another maximum which then decayed slowly.

When $HClO_4$ was added to a similar system in an oxidized state, $[Co^{III}]$ decayed very rapidly and the system went to a reduced state. The effects are the opposite of what might be anticipated from the position of hydrogen ions in processes like E1.

When 0.5 M NaBr was added as a major perturbation to a similar system that contained NaOAc in an oxidized steady state, Co^{III} was reduced immediately but then the system began to oscillate. Simultaneous observations with a pH meter and a spectrophotometer showed that $[H^+]$ increased at the same time that $[Co^{III}]$ did. This effect is also contrary to the simple stoichiometric equations like E1 reported above. The observations suggest that Co^{III} is strongly acidic by solvolysis.

We did not have time to study these effects quantitatively, but it is clear that acidity is an important parameter that must be considered in any detailed mechanistic study of this system.

E. Mechanism of Co(III) Reduction in the Oscillator. Section VI.D reported on the process that has been more difficult than any other for us to explain. As reported there, Br^- at concentrations comparable to those in the oscillating system catalyzes by one to two orders of magnitude the rate of oxidation of BzH by Co^{III}. At least under the conditions reported here, the rate of this reaction of Co(III) is remarkably independent of the concentration of this species. The Br^- itself is not oxidized under these conditions. This catalyzed oxidation is strongly inhibited by the radical scavenger BHT even though the same scavenger has almost no effect on the uncatalyzed oxidation of BzH by Co(III). Most of these observations agree with those reported previously by RWJ.[4]

Over quite a range of concentrations, the rate of reduction of Co^{III} is zero order in this species. Zero-order rate usually implies that a species is not present in the transition state for the rate-determining step. A rate zero order in Co^{III} would then require that the slow step would occur before Co^{III} participated in the sequence. We have been unable to devise a chemically plausible mechanism by which BzH and Br^- reacted slowly to generate an intermediate which then reacted rapidly and irreversibly with Co^{III} by a radical mechanism to generate the stoichiometry of process E14.

An alternative hypothesis is that a reaction first order in Co^{III} generates a product that accelerates the rate autocatalytically. We can imagine that either H^+ or $Bz^•$ might behave as a species causing this sort of autocatalytic effect.

If H^+ is the autocatalytic species, we should note that a solution of $Co(OAc)_2$ is more alkaline than the pure solvent, and when Co(III) is reduced $\Delta[H^+] \approx -\Delta[Co^{III}]$. Solvolysis equilibria may also be such that $[Co^{III}]$ and $[H^+]$ are comparable in magnitude over the range of intermediate $[Co^{III}]$ values. For such a combination of circumstances, a rate of reduction porportional to $[Co^{III}][H^+]$ could generate kinetic behavior close to zero order in $[Co^{III}]$ over a considerable range of composition. A sequence that accomplished this behavior could be steps P17–P19.

$$Co^{III} + HBr \rightleftarrows CoBr^{2+} + H^+ \qquad (P17)$$

$$H^+ + BzH \rightleftarrows HBzH^+ \qquad (P18)$$

$$CoBr^{2+} + HBzH^+ \rightarrow Co^{II} + HBr + H^+ + Bz^• \qquad (P19)$$

According to this mechanism, $CoBr^{2+}$ is a bromide complex of Co^{III} and $HBzH^+$ is protonated benzaldehyde. It is easy to devise other ways to generate a transition state of stoichiometric $CoBrBzH_2^{3+}$. If step P19 is rate determining, the overall effect of this sequence is that of process E18.

$$Co^{III} + BzH \rightarrow Co^{II} + H^+ + Bz^• \qquad (E18)$$

$$(E18) \equiv (P17) + (P18) + (P19)$$

If $Bz^•$ is the autocatalytic species, steps P18 and P19 could be replaced by steps P20 and P21.

$$CoBr^{2+} + BzH \rightarrow CoBrBzH^{2+} \qquad (P20)$$

$$CoBrBzH^+ + Bz^• \rightarrow Co(II) + HBr + 2Bz^• \qquad (P21)$$

Here again, there are alternative paths to generate a transition state of stoichiometric $CoBrBz_2H^{•2+}$. If step P21 is rate determining, the effect of this sequence is also that of process E18 with

$$(E18) \equiv (P17) + (P20) + (P21)$$

The stoichiometry of process E18 is identical with that of the pseudoelementary process P11, and the rate is porportional to $[Co^{III}][Br^-][H^+]$ or to $[Co^{III}][Br^-][Bz^•]$ depending upon whether step P19 or P21, respectively, is rate determining. In either case, the ligand Br^- facilitates the transfer of an electron from BzH to Co^{III}. There is at least some precedent for electron transfers being facilitated by polarizable ligands.

IX. A Mechanism for the Oscillations

The objective of the effort described above has been to generate a detailed molecular mechanism consistent with almost all of the known experimental facts. We believe that this objective has indeed been accomplished.

A. Stages of Oscillatory Behavior. Figure 1 shows the behavior of $[Co^{III}]$ during oscillations. Those oscillations involve two different stages and almost discontinuous switches between them.

During stage α (called stage I by RWJ), $[Co^{III}]$ increases autocatalytically as Co(II) is oxidized by atmospheric oxygen. As was shown in section V.A, transport of O_2 into the solution cannot be more than a few times 10^{-5} M s^{-1}, and this rate is the maximum at which Co^{III} can be oxidized. The maximum possible concentration of Co^{III} is 0.02 M, and the value of k_A in section V.E is consistent with the interpreation that the maximum $[Co^{III}]$ in Figure 1 occurs when the rate of its formation is indeed about equal to the maximum possible rate of transport of O_2.

During stage β (called stage II by RWJ), $[Co^{III}]$ decreases very rapidly by a zero-order process. It is demonstrated in section VI.D that during this stage Br^- is catalyzing oxidation of BzH at a rate a few times 10^{-4} M s^{-1}, and a mechanistic explanation is developed in section VIII.E.

B. Mechanism during Stage α. During stage α, the stoichiometry of major chemical change can be described by process E9, but section V.I shows that process E19 also occurs to several percent of the total reaction.

$$O_2(g) + 2Co^{II} + 2H^+ + BzH \rightarrow BzOH + 2Co^{III} + H_2O \qquad (E9)$$

$$(E9) \equiv (E5) + (E7) \equiv (P1) + (P2) + (P4) + (P5) + (P8)$$

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(14) *Encyclopedia of Industrial Analysis*; Snell, F. D., Ettre, L. S., Eds.; Interscience: New York, 1969; Vol. 8, p 23.

(15) Kolthoff, I. M.; Willman, A. *J. Am. Chem. Soc.* **1934**, *56*, 1007–1013.

$$O_2(g) + 2Br^- + 2H^+ + BzH \rightarrow BzOH + Br_2 + H_2O \quad (E19)$$

$$(E19) \equiv (E4) + (E10) \equiv (P1) + (P2) + (P4) + (P9) + (P10) + (P17) + (P18) + (P19)$$

Although processes E9 and E19 are sufficient to generate virtually all of the stoichiometric change during stage α, they do not explain the autocatalytic behavior during that stage. That autocatalysis arises because [$Bz^\bullet$] and [BzOOH] increase as reaction proceeds.

One way to generate the necessary autocatalysis directly is to add a contribution from process E4 generated by a different sequence from that presented in section V.F.

$$O_2(g) + BzH \rightarrow BzOOH \quad (E4)$$

$$(E4) \equiv (E5) + (E18) \equiv (P1) + (P2) + (P4) + (P17) + (P18) + (P19)$$

A linear combination of processes E9, E19, and E4 with appropriate positive coefficients will reproduce virtually exactly the total chemical change during stage α in terms of reactants, products, and primary intermediates as defined in section III.A,B. Secondary intermediates have been neglected for reasons that will become apparent in section F below.

An alternative way to generate the necessary autocatalysis indirectly is to produce the necessary radicals from Co^{III} by process P11. Computations to be presented in a subsequent paper suggest that step P11 will be sufficient to explain the experimental observations without any need to invoke process E4 as suggested above.

C. Mechanism during Stage β. Most of the net chemical change during stage β is accomplished by the stoichiometry of process E14 with a small but significant contribution from process E17. Our more detailed computations suggest that we shall also have to invoke contributions from process E18 from section VIII.E above and going through step P19 or P21 with step P21 probably preferred.

$$2Co^{III} + BzH + H_2O \rightarrow 2Co^{II} + BzOH + 2H^+ \quad (E14)$$

$$(E14) \equiv (P12) + (P17) + (P18) + (P19)$$

$$BzH + Br_2 + H_2O \rightarrow BzOH + 2HBr \quad (E17)$$

$$(E17) \equiv (P14) + (P15) + (P16)$$

$$Co^{III} + BzH \rightarrow Co^{II} + H^+ + Bz^\bullet \quad (E18)$$

D. Dynamic Effects of Bromide Ion. The arguments presented in sections B and C have been primarily stoichiometric and have not accounted for two dynamic effects of bromide ion on the oscillations. Those effects are the different rate constants for exponential growth of absorbance in Figures 1 and 2 and the oscillations in pBr that accompany the much more dramatic oscillations in absorbance due to Co^{III}.

The solution in Figure 2 contains no bromide ion, and the absorbance grows exponentially with a half-life of about 240 s. The oscillating system in Figure 1 also exhibits approximately exponential growth in absorbance during stage α, but the half-life is only about half that in Figure 2. We believe that the difference arises because the rapid bromide-catalyzed sequence of steps P17 + P18 + P19 or steps P17 + P20 + P21 is taking place during stage α as well as during stage β. During stage α, the presence of O_2 in the solution means that overall process E19 takes place by both of the sequences suggested in section B. Once O_2 has been consumed, the solution switches to stage β and the sequence of steps P17 + P18 + P19 or steps P17 + P20 + P21 is followed by step P12 instead of by step P2. It is the competition between O_2 and Co^{III} for $Bz^\bullet$ radicals that switches the stage between α and β.

The other effect of bromide involves the potentiometric oscillations in pBr reported in the thesis of Yuan.[1] Activity of Br^- will be reduced by formation of Br_2, bromide complexes of Co^{III}, and BzBr. Probably Br_2 exerts the greatest effect, but all of these reductions will occur when [Co^{III}] is a maximum during the end of stage α and the start of stage β just as is observed experimentally.[1]

E. Processes That Form and Destroy Radicals. Except for those that contain cobalt, all of the species proposed above use only s and p orbitals to form chemical bonds. They can all be classified cleanly as molecules that have an even number of electrons or as radicals that have an odd number. Because of the laws for combination of odd and even numbers, radicals can only be formed or destroyed in pairs in any process that does not involve cobalt species.

Of all of the 21 pseudoelementary processes we have proposed, *none* produces two radicals simultaneously. Any such process would break a chemical bond without any compensating energy gain and would be too slow to be significant at these moderate temperatures. This explains why the rate of thermodynamically favored process T is negligible in the absence of catalysis by cobalt.

Only two of the pseudoelementary processes destroy two radicals simultaneously. Those are the reaction of two benzoylperoxy radicals (step P7) and of two benzoyl radicals (step P13). We do not believe that either of those processes contributes significantly to the overall mechanism.

Cobalt can change its oxidation state by only 1 equivalent, and each of the five pseudoelementary processes involving this element either creates or destroys a single radical. Those processes are essential to the overall chemical change and to the switching between stages α and β.

$$BzOO^\bullet + Co^{II} + H^+ \rightarrow BzOOH + Co^{III} \quad (P4)$$

$$BzOOH + Co^{II} + H^+ \rightarrow BzO^\bullet + Co^{III} + H_2O \quad (P5)$$

$$Co^{III} + BzH \rightarrow Co^{II} + Bz^\bullet + H^+ \quad (P11)$$

$$Co^{III} + Bz^\bullet + H_2O \rightarrow BzOH + Co^{II} + H^+ \quad (P12)$$

$$CoBr^{2+} + HBzH^+ \rightarrow Co^{II} + HBr + Bz^\bullet \quad (P17)$$

F. Mechanism of Switching between Stages α and β. If we let [$R^\bullet$] be the sum of concentrations of all radical species and let v_{Px} be the rate of process Px, we can write equations like 11 and 12 to describe rates of change of intermediate species.

$$d[Co^{III}]/dt = v_{P4} + v_{P5} - v_{P11} - v_{P12} - v_{P17} \quad (11)$$

$$d[R^\bullet]/dt = -v_{P4} + v_{P5} + v_{P11} - v_{P12} + v_{P17} - 2v_{P7} - 2v_{P13} \quad (12)$$

Although [Co^{III}] may attain values of the order of 10^{-2} M, [$R^\bullet$] is probably never more than about 10^{-7} M. Therefore, the magnitude of eq 11 is almost always several powers of 10 greater than that of eq 12. Equations 13 and 14 represent the sum and difference of eqs 11 and 12, and both are excellent approximations.

$$d[Co^{III}]/dt \approx 2(v_{P5} - v_{P12}) \quad (13)$$

$$\approx 2(v_{P4} - v_{P11} - v_{P17}) \quad (14)$$

A system in stage α will contain dissolved O_2 which scavenges $Bz^\bullet$ radicals so efficiently by process P2 that process P5 will be much faster than process P12 and [Co^{III}] will increase at an accelerating rate. Eventually [Co^{III}] will become sufficiently large and [O_2] sufficiently small that eqs 13 and 14 will change sign and the system will make an abrupt transition to stage β.

Transitions from stage β to α will take place when the solution contains more O_2 and is depleted in Co^{III}.

The rate of transport process P1 provides the delayed feedback that is necessary in any chemical oscillator. If air could be dissolved so rapidly that v_{P1} was much greater than 10^{-4} M s^{-1}, process P19 or P21 could not compete and the system would go to an oxidized steady state. If oxygen dissolved very slowly, the steady state would correspond to negligible concentrations of radicals and almost all of the cobalt would be in the reduced +2 state. Oscillations involve repeated transitions between oxidized and reduced states. Our computations have so far failed to provide any evidence for rates of oxygen transport that could generate bistability, but that possibility has not been unequivocally excluded.

X. Discussion

A. What Has Been Accomplished. Experimental study of this reaction at the University of Oregon began in 1984, and this is our first publication about that work. The material in the preceding sections illustrates the major effort that is necessary in order to understand an oscillatory chemical system! We have made at least semiquantitative kinetic measurements on about ten different subsystems that we believe are important to understanding the mechanism of the oscillating system. We have also made qualitative observations on about half a dozen other subsystems that we decided were not important enough to justify kinetic study. Detailed study of any one of the potentially important subsystems could be made the basis of a note or paper in its own right. The work reported here is often incomplete by customary kinetic standards. We have had to make judgment calls as to how detailed were the necessary studies of each subsystem. In retrospect, we wish that some of those calls had been different.

The information in sections IV–VIII contains the material that we believe is of potential importance for elucidating the mechanism of this reaction. We have not included observations that we thought were unimportant. Although our judgment may have been in error here also, we felt that more detail would make it still more difficult for a reader of this paper to grasp the important connections.

Then in section IX we have combined our observations to generate a detailed molecular mechanism consisting of 21 pseudoelementary processes. We believe that this proposed mechanism is consistent with what is presently known about this system. We very much hope that further study will lead to minor refinement rather than to major revision of this proposed mechanism.

B. Comparison of Mechanistic Proposals. Two previous major mechanistic proposals have been developed by RWJ[4] and in a thesis by Yuan.[1] All three mechanisms agree that stage α consumes O_2 in processes initiated by step P2. During those processes, the concentrations of Co^{III}, BzOOH, and $R^\bullet$ all increase at accelerating rates which eventually become greater than that of transport process P1. The concentration of dissolved O_2 then falls to a low value and stage β is initiated. During this stage, the concentrations of Co^{III}, BzOOH, and $R^\bullet$ fall to low values before stage α is again initiated.

Although these features are common to all three mechanisms, there are also significant differences. We believe that the most important differences involve (a) the mechanism of oxidation of Co^{II} by BzOOH, (b) the nature of radical–radical reactions, and (c) the significance of Br_2 to the mechanism.

(a) RWJ propose that component process E6 takes place without any radical intermediates. The thesis reports stoichiometric discrepancies at low $[Co^{II}]$ and high [BzOOH] that seem to require radical intermediates, and the present paper proposes the alternative stoichiometry of process E7. We find this proposal more satisfactory than the RWJ mechanism which generates radicals only by reduction of Co^{III}.

(b) Neither the thesis nor the present paper attaches much importance to radical–radical reactions. It is probably useful to include processes P7 and P13 in the mechanism so that simulations will not generate implausibly large concentrations of radicals, but we do not expect either of those processes to be important during conditions under which oscillations are observed.

By contrast, RWJ invoke process R21 in their mechanism.

$$BzOO^\bullet + Bz^\bullet \rightarrow 2BzO^\bullet \qquad (R21)$$

This process would rapidly be followed by step P6 in either mechanism and would have the effect of converting $BzOO^\bullet$ to $Bz^\bullet$ once the concentration of O_2 had fallen sufficiently low. Such an effect would promote the transition from stage α to β, and it appears significant that RWJ admit they could not simulate oscillations unless step R21 was included.

However, we are disturbed by some features of unusual process R21. In the first place, this reaction between $BzOO^\bullet$ and $Bz^\bullet$ is dominant while neither reaction P7 involving $2BzOO^\bullet$ nor reaction P13 involving $2Bz^\bullet$ is ever significantly fast. Perhaps more significantly, reaction R21 between $BzOO^\bullet$ and $Bz^\bullet$ conserves the number of radicals and does not form the anticipated BzOOBz.

(c) RWJ propose that all catalysis by bromide is accomplished by complexes of Br^- with cobalt species and do not ascribe any effect to Br_2. The thesis notes that significant Br_2 must be formed by component process E10 and ascribes a major cause of the oscillations to the competition of O_2 and Br_2 for $Bz^\bullet$ radicals. Section VII.A reports entrainment by a gas stream, which confirms that Br_2 is actually present in the system.

The present paper takes an intermediate position. Br_2 must certainly be formed by process E10 and is most probably destroyed by process E17. That process is initiated by step P14 involving Br_2 and $Bz^\bullet$ just as proposed in the thesis, but subsequent rapid step P15 would prevent step P14 from causing consumption of $Bz^\bullet$ radicals. Our mechanism like that of RWJ ascribes most of the importance of Br^- to reactions of complexes of cobalt but recognizes that Br_2 is formed as an intermediate during the oscillations.

C. Present Status of Computations. Any mechanism for an oscillating chemical reaction should ultimately be tested by computations that attempt to simulate the detailed experimental behavior. This paper is already so long that it does not appear appropriate to include a major computational section also. John Guslander at the University of Oregon has already used the mechanism in section IX to develop a skeleton mechanism with three variables and five terms in the associated differential equations. That skeleton mechanism does generate oscillations with a period similar to that observed experimentally. We are now preparing a manuscript which describes that skeleton mechanism and which shows how it relates to more complicated and more detailed mechanisms based on pseudoelementary processes.

D. Proposals for Further Study. No mechanistic study of a chemical reaction can ever be considered complete. The mechanism we have developed is based on many different component systems and is so consistent with the total of information that we believe the essential causes of the oscillations are understood. We do see a number of tests that could either provide more assurance we are on the right track or else could show the direction in which more study should be directed. We have specifically identified three problems where we believe that further experimental study would be useful and perhaps important.

(1) The effects of acidity were discovered only when there was no more time for systematic study. In particular, the argument in section VIII.E uses an acidity effect involving step P19 as one of two ways to explain the zero-order kinetics during much of the bromide-catalyzed oxidation of BzH by Co^{III}. A benzoyl radical effect involving step P21 is suggested as an alternative way to explain the same behavior. The two mechanisms make different predictions about rates and kinetics which could be tested by deliberate additions of acid or base. Such tests should support no more than one of the proposals in section VIII.E and thus provide the kind of discrimination so important to developing a detailed mechanism.

It would also be desirable to find whether or not acidity is important for other processes in this system.

(2) In section V.G, we reported a clear contradiction between our observations and those of Jones[7] concerning the kinetics of oxidation of Co^{II} by BzOOH even though the two expressions generated comparable rates for the specific system of interest. It should be straightforward to resolve the discrepancy once and for all.

(3) Figure 1 shows a spectrophotometric study of $[Co^{III}]$ as a function of time in an oscillating system. The curves during stage α are strongly concave up as $[Co^{III}]$ rises to a very sharp maximum before it suddenly decreases. The same reaction was followed in the thesis by means of the potential of a platinum electrode. The observed curve for stage α was strongly concave down and exhibited a broad maximum before it began to decrease. RWJ[4] used both spectrophotometric and potentiometric techniques to follow oscillations, and Figure 1 in their paper exhibits the same difference that we found, although the curvatures in the RWJ plots are perhaps less pronounced than what we saw.

At least some of the difference in behavior arises because absorbance is a linear function of [Co^{III}] while potential is a logarithmic function. It may also be that the potential of the platinum electrode is particularly sensitive to [Br$_2$]. If that hypothesis is correct, we might be able to follow [Co^{III}] and [Br$_2$] simultaneously and thus test the predictions of our mechanism more quantitatively.

We also believe the characterization of Co^{III} solutions could be improved. However, the amount of information already accumulated about this system is so great that we believe publication at this time is warranted. A detailed molecular mechanism has been generated, and computations to test it are under way. We believe that after those computations have been carried out will be an appropriate time for further experimental study.

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Note Added in Proof. Only after this paper was being set in type did we discover the study by Reimus, Massie, and Hudson.[16] These authors studied the same reaction with the chemicals continuously introduced in a flow reactor. They simulated oscillations with a mechanism very similar to that of Roelofs, Wasserman, and Jensen[4] but with somewhat fewer steps.

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(16) Reimus, A. M.; Massie, J. M.; Hudson, J. H. *Ind. Eng. Chem. Res.* **1989**, *28*, 590–599.

Stereospecificity of the S(^3P_J) + Butene-2 Reaction and the NMR Spectra of the 1,2-Dimethylthiiranes: An Experimental and Theoretical Study

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Abstract: The gas-phase addition of S(^3P_J) atoms to *cis*- and *trans*-butene-2 has been investigated and both reactions have been shown to be 100% stereospecific, yielding the lowest excited triplet state of the 2,3-dimethylthiirane end product. The triplet thiirane has a long collisional lifetime and is capable of undergoing facile, reversible addition to the butenes causing their geometrical isomerization, while retaining its own original geometry. The cause of the gradual loss of stereospecificity in the 2,3-dimethylthiirane product with increasing conversion has been identified as this geometrical isomerization of the butene-2 substrate by the primary triplet thiirane and those produced in the secondary photolysis of the thiirane product. Ab initio SCF-MO with 6-31G* basis set and limited CI calculations predict the lowest triplet ring opened A″ state of thiirane to lie 54 kcal mol^{-1} above the ground state with a rotational energy barrier for the terminal methylene of 5.4 kcal mol^{-1}. The total computed reaction energy for the model reaction S(^{3}P) + C_2H_4 is thus approximately the same as the change in internal energy of the reaction, 58.0 kcal mol^{-1}, estimated from thermochemical data, and therefore isomerization will be slow relative to collisional deactivation. This gives a plausible account of the origin of the complete stereospecificity of triplet sulfur addition to olefins. The reaction initially proceeds in a concerted least-motion path on the lowest $^3B_1$ (C_{2v}) repulsive surface which intersects the lowest attractive $^3A''$ surface 1.9 kcal mol^{-1} above the reactant state. This intersection is identified as the transition state of the reaction for which the reported experimental activation energy is 1.6 kcal mol^{-1}. Both the $^3A''$ and the next higher lying $^3A'$ surfaces feature a significant intrinsic activation energy barrier and therefore they are effectively eliminated as adiabatic reaction surfaces. The NMR spectra of the isomerically pure *cis*- and *trans*-2,3 dimethylthiiranes have been obtained and assigned by computer simulation.

The chemistry of sulfur atoms has been systematically explored since the early 1960s, and it was soon established that both ground triplet and lowest excited singlet state sulfur atoms readily add to olefinic double bonds to give the cycloadducts, thiiranes.[1] The reactivity of $^1D_2$ sulfur atoms conforms to the general reactivity of singlet state divalent reagents in that their addition follows a stereospecific path and they are capable of insertive attack at the carbon–hydrogen bond to yield thiols. On the other hand, ^3P_J sulfur atoms do not appear to follow the pattern of reactivity established for triplet state divalent reagents since their addition to olefins is a nearly stereospecific process.[2] With *cis*-butene-2 the retention of configuration in the 2,3-dimethylthiirane product (DMT) is about 90% and with *trans*-butene-2 over 98%.

The adducts from triplet reagent additions are assumed to be initially formed in their lowest excited triplet state. This can be envisioned as a 1,3-biradical in which rotation about the C–C bond

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(1) Gunning, H. E.; Strausz, O. P. *Adv. Photochem.* **1966**, *4*, 143.

(2) Sidhu, K. S.; Lown, E. M.; Strausz, O. P.; Gunning, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 254.

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