spin orbital coupling is influenced by conditions 1 and 3, with respect to both the internal and external heavy atom effects.[8] Since few data existed to verify condition[9] 2, we undertook the investigation of the monobromonaphthonorbornenes. Quite surprisingly, we did not find a direct relation between the distance of the heavy atom from the chromophoric naphthalene and the degree of singlet–triplet state mixing. As mentioned above, we considered this as good evidence for other mechanisms[7a,b] in addition to spin orbital coupling, such as spin vibronic coupling and photochemistry. The results also made it necessary to invoke a special role to the back lobe of the carbon–bromine bond in electronic state mixing. The data on the dibromonaphthonorbornenes reported in this paper further serve to emphasize the complex mechanisms involved in the heavy atom effect, especially those governing radiationless deactivation of the triplet state.

(8) See ref 6, Chapters 7 and 8.

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Nicholas J. Turro,* George Kavarnos, Victor Fung
A. L. Lyons, Jr., Theron Cole, Jr.
Department of Chemistry, Columbia University
New York, New York 10027

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Oscillations in Chemical Systems. I. Detailed Mechanism in a System Showing Temporal Oscillations

Sir:

Belousov[1] first observed temporal oscillations in a sulfuric acid solution containing bromate and cerium ions and malonic acid. Figure 1 presents the simultaneous behavior in such a system of electrodes sensitive to bromide ion activity and to cerium(IV)/cerium(III) ratio. Studies by several investigators[2-4] have obtained additional information but have not elucidated the mechanism. We now present a detailed mechanism supported by quantitative information about the elementary processes involved. No attempt is made here to explain the spatial oscillations observed[5,6] in the same system.

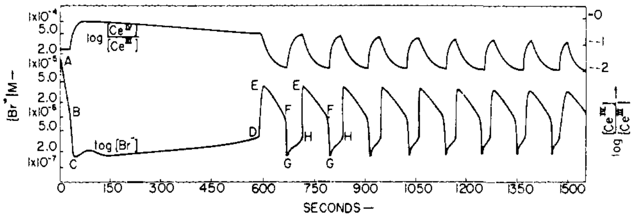

Figure 1. Potentiometric traces at room temperature of log [Br⁻] and of log [Ce(IV)]/[Ce(III)] for a stirred solution in which the initial concentrations were $[CH_2(COOH)_2] = 0.032\ M$, $[KBrO_3] = 0.063\ M$, $[KBr] = 1.5 \times 10^{-5}\ M$, $[Ce(NH_4)_2(NO_3)_5] = 0.001\ M$, and $[H_2SO_4] = 0.8\ M$.

In an acid solution of bromate and malonic acid containing sufficient bromide ion, the sequence (R3) + (R2) + 3(R1) + 3(R8) results in net process A. Let

$$BrO_3^- + Br^- + 2H^+ \longrightarrow HBrO_2 + HOBr \qquad (R3)$$

$$HBrO_2 + Br^- + H^+ \longrightarrow 2HOBr \qquad (R2)$$

$$HOBr + Br^- + H^+ \longrightarrow Br_2 + H_2O \qquad (R1)$$

$$Br_2 + CH_2(COOH)_2 \longrightarrow BrCH(COOH)_2 + Br^- + H^+ \qquad (R8)$$

$$BrO_3^- + 2Br^- + 3CH_2(COOH)_2 + 3H^+ \longrightarrow 3BrCH(COOH)_2 + 3H_2O \qquad (A)$$

rate constant subscripts correspond to R numbers. We have confirmed the observation of Bray and Liebhafsky[7] that at 25° $k_3 = 2.1\ M^{-3}\ sec^{-1}$. If the free energy of formation of BrO_2^- calculated by Lee and Lister[8] is used to estimate the free energy of $HBrO_2$ and combined with the kinetics reported by Betts and MacKenzie[9] for the decomposition of HOBr, then $k_2 = 4 \times 10^9\ M^{-2}\ sec^{-1}$. Eigen and Kustin[10] observed $k_1 = 1.6 \times 10^{10}\ M^{-2}\ sec^{-1}$. The rate of (R8) is controlled by the acid-catalyzed enolization of malonic acid, which is usually sufficient to remove bromine as rapidly as it is formed in our system.

These numbers clearly support the kinetic inference that step R3 is rate determining for process A. When this process is taking place, the concentration of bromous acid attains a steady state given by eq 1. As is expected from the proposed mechanism, the rate of process A is independent of the presence or absence of cerium(III).

$$[HBrO_2]_A = \frac{k_3}{k_2}[BrO_3^-][H^+] = 5 \times 10^{-10}[BrO_3^-][H^+] \qquad (1)$$

When bromide ion is virtually absent, bromate ion reacts with cerium(III) and malonic acid such that the sequence 2(R5) + 4(R6) + (R4) + (R8a) results in net process B. Thompson and we[11] have pointed out that the kinetic data of Thompson[12] indicate (R5) is rate determining for this sequence, and the data of Betts and MacKenzie[13] indicate the same step is rate determining for the isotopic exchange of bromate with elementary bromine giving $k_5 = 1.2 \times 10^4\ M^{-2}\ sec^{-1}$. Then the Thompson[12] data indicate that $k_4 = 6 \times 10^7\ M^{-1}\ sec^{-1}$. Of course (R8a) is stoichiometrically equivalent to (R1) + (R8), and its rate is determined by the same enolization reaction.

$$BrO_3^- + HBrO_2 + H^+ \longrightarrow 2BrO_2\cdot + H_2O \qquad (R5)$$

$$BrO_2\cdot + Ce^{3+} + H^+ \longrightarrow HBrO_2 + Ce^{4+} \qquad (R6)$$

$$2HBrO_2 \longrightarrow BrO_3^- + HOBr + H^+ \qquad (R4)$$

$$HOBr + CH_2(COOH)_2 \longrightarrow BrCH(COOH)_2 + H_2O \qquad (R8a)$$

$$BrO_3^- + 4Ce^{3+} + CH_2(COOH)_2 + 5H^+ \longrightarrow BrCH(COOH)_2 + 4Ce^{4+} + 3H_2O \qquad (B)$$

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The sequence (R5) + 2(R6) leads to autocatalytic production of $HBrO_2$, but the second-order destruction by (R4) creates a steady state given by eq 2. Hence the

$$[HBrO_2]_B = \frac{k_5}{2k_4}[BrO_3^-][H^+] = 1 \times 10^{-4}[BrO_3^-][H^+] \quad (2)$$

concentration of bromous acid is over 10^5 times as great when process B is taking place as when process A is.

The rate of process B is proportional to $[HBrO_2]$, and the rate is related to $[Br^-]$ much as the current in a thyratron tube is related to the grid potential. Thus if the concentration of bromide ion is sufficiently great the residual rate of (B) is very small and is independent of bromide concentration, while at very low concentrations of bromide ion the rate of (B) is very much greater but is again independent of bromide concentration. When the concentration of Br^- drops below a certain critical value, the concentration of $HBrO_2$ increases autocatalytically from the value of eq 1 to that of eq 2. The transition involves the competition between (R2) and (R5), and our analysis predicts the critical concentration is given by eq 3. In terms of the

$$[Br^-]_{crit} = \frac{k_5}{k_2}[BrO_3^-] = 3 \times 10^{-6}[BrO_3^-] \quad (3)$$

numerical data reported above, the critical concentration (points B and F in Figure 1) should be 2×10^{-7} *M* for the concentrations in that run and should vary proportionately with bromate concentration; we observe a critical concentration of 1×10^{-6} *M* in Figure 1 and find the value increases linearly but less than proportionately with increasing bromate concentration.

Several factors mitigate any possible concern over the apparent discrepancies. The less than proportional variation of critical bromide concentration with bromate concentration arises because a finite time is necessary to convert $[HBrO_2]$ from the value of eq 1 to that of eq 2, and the rate of change of $[Br^-]$ during that time is a function of $[BrO_3^-]$. The silver bromide impregnated electrode does not behave ideally below 10^{-6} *M* in static systems, and we have no assurance that the apparently ideal behavior is indeed so at the still lower concentrations in the dynamic system of Figure 1. The quantitative analysis of the various rate constants has made no attempt to correct for unknown activity coefficient effects in 1 *M* sulfuric acid. Finally, Lee and Lister[8] estimated the free energy of formation of bromide ion at 25° on the basis of a 50° extrapolation of a ratio of rate constants measured over a 20° range; if the correct value is 1.0 kcal/mol less positive than they report, k_5/k_2 would predict a critical bromide concentration in exact agreement with our observations and the thermodynamics of (R6) would be in better agreement with the requirements of our mechanism.

The above argument demonstrates that irreversible processes A and B will take place under different conditions in the same system and that a solution reacting by (A) will of necessity convert itself to one reacting by (B). If we are to explain oscillation, we must get back from (B) reaction to (A) reaction. The cerium(IV) produced in (B) reacts with the organic species by overall processes (R9) and (R10) whose kinetics have been elucidated by Kasperek and Bruice.[4] If most organic

$$6Ce^{4+} + CH_2(COOH)_2 + 2H_2O \longrightarrow 6Ce^{3+} + HCOOH + 2CO_2 + 6H^+ \quad (R9)$$

$$4Ce^{4+} + BrCH(COOH)_2 + 2H_2O \longrightarrow Br^- + 4Ce^{3+} + HCOOH + 2CO_2 + 5H^+ \quad (R10)$$

matter is unsubstituted malonic acid (as at point C of Figure 1), the system is unable to restore the high bromide concentration needed for reaction A and an extensive induction period at low bromide concentration ensues. As the concentration of bromomalonic acid increases, (R10) become increasingly more important. The bromide ion produced by (R10) is destroyed by (R2) as long as the process (R5) + 2(R6) is able to maintain the bromous acid concentration at the value of eq 2. When the rate of (R10) becomes sufficiently great, $[HBrO_2]$ drops rapidly to the value of eq 1, process B is "turned off," and $[Br^-]$ rises rapidly until the rate of production by (R10) is balanced by the rate of destruction by process A initiated by (R3). The oscillatory cycle can then begin again.

The critical bromide concentration at points D and H when cerium(IV) is present is less than the concentration at points B and F when it is not. The difference arises because (R6) is reversible and because cerium(IV) can also oxidize $BrO_2\cdot$, but these complications cannot be discussed in this brief communication.

Because cerium species are present in small concentration compared to bromate and malonic acid, they do not contribute to the stoichiometry of the overall reaction, which is given by process C. This process is the

$$3BrO_3^- + 5CH_2(COOH)_2 + 3H^+ \longrightarrow 3BrCH(COOH)_2 + 2HCOOH + 4CO_2 + 5H_2O \quad (C)$$

result of the sequence x(A) + $(3 - x)$(B) + $(2 - 2x)\cdot$(R9) + $2x$(R10), where x may have any value between zero and unity. It is the free energy change of process C that drives the overall reaction, and it is the failure of bromate ion and malonic acid to react directly with each other at a significant rate that permits the very complicated way by which the overall process is achieved. Indubitably the free energy of the system as a whole is decreasing monotonically throughout the entire process represented by Figure 1!

A longer manuscript will be presented describing our experimental observations and the detailed thermodynamics and kinetics of this fascinating system.

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(14) Also at the Physical Chemistry Laboratory, Oxford University, Oxford, England.

(15) Also at the Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary.

Richard M. Noyes,*[14] Richard J. Field, Endre Kőrös[15]
Department of Chemistry, University of Oregon
Eugene, Oregon 97403

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Photodimerization of Arylazirenes. Some Aspects of the Mechanism[1]

Sir:

Recently[2] we recorded the results of a study dealing

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(1) Photochemical Transformations of Small-Ring Heterocyclic Compounds. XXXIII. For part XXXII, see: A. Padwa and A. Battisti, *J. Amer. Chem. Soc.*, **94**, 521 (1972).

(2) A. Padwa and J. Smolanoff, *ibid.*, **93**, 548 (1971).