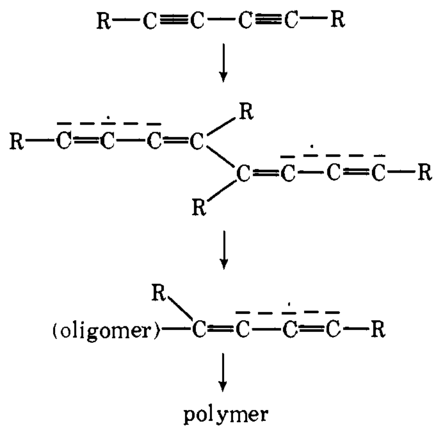
Scheme I



27° of biradical X must occur before polymerization is complete. In comparison, the proton couplings found for the $S = \frac{1}{2}$ intermediate in PTS[20] are larger (7.5 vs. 16 G), indicating that either the spin density on C^4 is smaller for X than that for the intermediate in PTS or a difference occurs in the orientation of the side group. Furthermore, it may be possible that the other radical pair observed (peak A′ in Figure 1) may have a different spin distribution and a different configuration than biradical X, and may be the much more favored biradical for polymerization.

In conclusion we have observed that biradical X is an initiator in the solid-state polymerization of TCDU crystal. Combining the results of this study with those found previously for PTS,[20] it is suggested that polymerization proceeds according to Scheme I. From these studies it appear that the solid-state polymerization of diacetylene compounds at low X-ray dosage proceeds principally according to a radical mechanism rather than a carbene mechanism. A radical mechanism is also in good agreement with the findings of Chance and co-workers.[10]

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A Heterogeneous Chemical Oscillator. The Belousov-Zhabotinskii-Type Reaction of Oxalic Acid

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Abstract: A new type of oscillating reaction, the heterogeneous Belousov-Zhabotinskii reaction of oxalic acid, is described. Periodic CO_2 and Br_2 evolution was measured with the aid of flame ionization and coulometric detectors. The stoichiometry of the reaction was determined and a radical mechanism was proposed based on experiments with acrylamide as a radical scavenger. A possible connection with the mechanism of the original Belousov reaction is mentioned.

Introduction

The so-called Belousov-Zhabotinskii (BZ) reaction, the cerium ion catalyzed oscillatory oxidation of several organic compounds by bromate in aqueous sulfuric acid media, is the most studied chemical oscillator.[1-10]

Field, Körös, and Noyes (FKN) developed a detailed theory for the phenomenon especially when the organic component is malonic acid.[1] The essential features of their mechanism are summarized in steps FKN1-FKN5.[2]

$$\mathrm{BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr} \tag{FKN1}$$

$$\mathrm{HBrO_2 + Br^- + H^+ \rightarrow 2HOBr} \tag{FKN2}$$

$$\mathrm{BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2\cdot + H_2O} \tag{FKN3a}$$

$$\mathrm{Ce^{3+} + BrO_2\cdot + H^+ \rightarrow Ce^{4+} + HBrO_2} \tag{FKN3b}$$

$$\mathrm{2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+} \tag{FKN4}$$

$$\mathrm{HOBr} + \text{organic matter} \rightarrow \text{bromoorganic compounds} \tag{FKN5a}$$

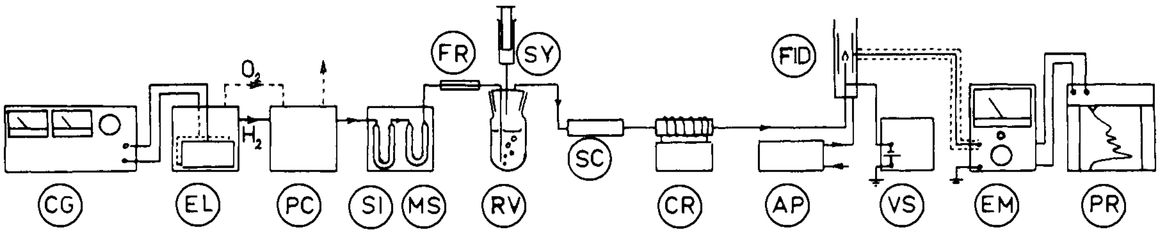

Figure 1. Experimental apparatus used for monitoring oscillatory evolution of CO_2. See text for description of the various components.

$$nCe^{4+} + \text{brominated and unbrominated organic compounds} \rightarrow nCe^{3+} + Br^- + \text{oxidized products} \qquad \text{(FKN5b)}$$

Jwo and Noyes[3] made an extended experimental study on reaction FKN5b when the "organic matter" was malonic acid and found it to be extremely complex. Moreover, it was shown recently that, besides CO_2, CO is also a gaseous product of the oscillating reaction with malonic acid.[4].

Later on Field and Noyes[5] presented a skeletonized version of the FKN mechanism, the "Oregonator" model, summarized in the steps

$$A + Y \rightarrow X \qquad \text{(O1)}$$

$$X + Y \rightarrow P \qquad \text{(O2)}$$

$$B + X \rightarrow 2X + Z \qquad \text{(O3)}$$

$$2X \rightarrow Q \qquad \text{(O4)}$$

$$Z \rightarrow fY \qquad \text{(O5)}$$

where $A \equiv B \equiv BrO_3^-$, $X \equiv HBrO_2$, $Y \equiv Br^-$, $Z \equiv Ce^{4+}$, and P and Q are products of no further interest. They pointed out numerically that the kinetic model above exhibits a limit cycle type oscillation behavior for certain values of the rate constants k_{O1}-k_{O4} and fixing the concentrations of $[BrO_3^-] = 0.06$ M and of $[H^+] = 0.8$ M they stated that the oscillating behavior was "determined solely by two parameters k_{O5} and f"[2]

It is clear now that in the FKN mechanism and in the Oregonator model as well the oxidation of organic species by Ce^{4+} with formation of bromide ion is a key process; however, it is rather complicated if the organic substrate is malonic acid. Thus it would be desirable to find an organic substrate for which the mechanistic possibilities are more limited.

In the literature a lot of organic compounds are mentioned as appropriate substrates of the BZ reaction. Kasparek and Bruice[6] reported that the conditions employed with malonic, citric, and maleic acids to provide an oscillatory appearance of Ce(IV) failed to do so with oxalic acid. Beck and Vâradi[7] pointed out that the presence of an "active" methylene group is not a necessary condition of the oscillating reactions involving dicarboxylic acids. They observed oscillations with acetylenedicarboxylic acid. Stroot and Janjic[8] and Farage, Stroot, and Janjic[9] list some aliphatic and cyclic ketone compounds, including acetone itself, that exhibit oscillations.

Looking for a simple substrate it was found in our laboratory that the oxalic acid produces a heterogeneous-type BZ reaction. Periodic CO_2 and Br_2 evolution was measured depending on the rate of the removal of the produced Br_2. We have determined the stoichiometry of the reaction and proposed a radical mechanism involving Br_2 based on experiments with acrylamide as a radical scavenger.

Experimental Section

Materials. All the applied chemicals were of reagent grade supplied by Reanal and were used without further purification. Three solutions were frequently used: A, B, and C. Concentrations follow: solution A, $[(COOH)_2] = 4 \times 10^{-2}$ M, $[H_2SO_4] = 1.5$ M; solution B, $[KBrO_3] = 8 \times 10^{-2}$ M, $[Ce(SO_4)_2] = 2 \times 10^{-3}$ M, $[H_2SO_4] = 1.5$ M; solution C, $[KBrO_3] = 1.6 \times 10^{-1}$ M, $[Ce(SO_4)_2] = 2 \times 10^{-3}$ M, $[H_2SO_4] = 1.5$ M.

Analysis of Products. Two gaseous products were measured: CO_2 and Br_2.

Description of the CO_2 Measuring Apparatus (Figure 1). In all experiments H_2 was applied as a carrier gas for removing the gaseous products of the oscillating reaction. The electrolytic H_2 production could be controlled by an electric current generator.CG (HIKI TR 9120) within the range of 1-10 A. The electrolyzing cell EL was made of Perspex containing nickel electrodes and KOH electrolyte. An automatic mercury-filled pressure controller PC equilibrated the electrolyte levels of the diaphragm-separated O_2 and H_2 elevating half cells. The organic vapor traces coming from the Perspex cell were removed by a molecular sieve column MS. The water vapor was fixed by silica gel SI previously. The "bubbling frequency" and the sizes of the H_2 bubbles were stabilized by a fixed restrictor FR inserted just before the glass reaction vessel RV of 5-cm^3 volume where the oscillating reaction takes place. With the aid of a plastic syringe SY a 0-2 cm^3 solution of acidic bromate and Ce^{4+} B or C could be introduced at the start of the experiment into the reaction vessel containing 0-3 cm^3 of the solution A.

The experiments were carried out at room temperature (24 ± 2 °C). A selective scrubber for bromine SC containing a glass filter paper roll (Whatman GF-C) wetted by aqueous acrylamide solution removed any gaseous bromine stripped from the oscillating mixture. After the scrubber the H_2 carrier gas was introduced into a catalytic reactor CR with alumina-supported nickel as catalyst where the CO_2 content of the carrier was converted to CH_4. At last the gas stream entered into a flame ionization detector FID where an ionization current proportional to the methane content of the H_2 carrier was produced. The ionization current of the FID was measured by a Keithley 610-B electrometer EM and displayed with a Radelkis OH-814/1 potentiometric recorder PR. The applied voltage between the collector electrode and the jet of the FID was 200 V provided by a stabilized voltage source VS. An air pump AP produced a stabilized air flow (600 cm^3/min) for a diffusion-type flame. All the flexible gas junctions were made of polypropylene tubing; the scrubber, the catalytic reactor, and other tubings were made of glass.

Description of the Br_2 Measuring Apparatus (Figure 2). The carrier H_2 was generated in the same way as before. The gas stream leaving the reaction vessel was bubbled through a high column (~10 cm) of 0.5 M KBr solution where the Br_2 content of the H_2 carrier was absorbed. A constant flow (2 cm^3/min) of the KBr solution was supplied by a peristaltic pump PP from a reservoir RE to the absorber AB. The bubble-free KBr solution containing the absorbed Br_2 flowed through a coulometric cell CC where an electric current proportional to the Br_2 concentration could be measured. The polarizing voltage was 0.9 V. The electrodes were made of Pt wire. The electric potential difference caused by the current of the coulometric cell on a resistor of 100 Ω was displayed with a Radelkis OH-814/1 potentiometric recorder PR.

Description of the Electrolytic CO_2 and Br_2 Generating Cells. Calibration. An electrolytic gas-generating cell containing platinum electrodes could be inserted into the H_2 carrier gas stream just before the reaction vessel. Thus a carrier with known concentration of CO_2 or Br_2 could be applied for calibration and for other experiments. The calibrating anodic reactions were

$$(COOH)_2 \rightarrow 2CO_2 + 2H^+ + 2e^- \qquad \text{(C1)}$$

and

$$2Br^- \rightarrow Br_2 + 2e^- \qquad \text{(C2)}$$

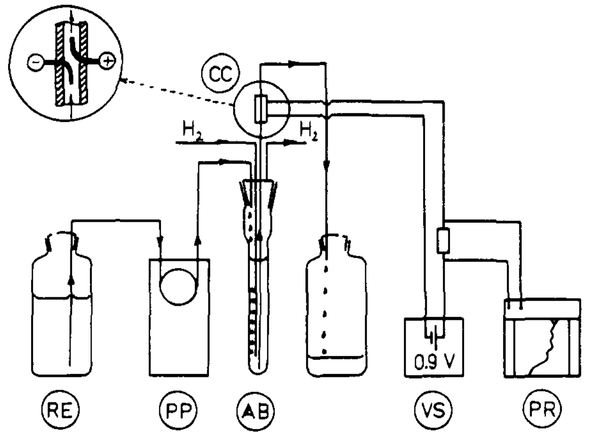

Figure 2. Experimental arrangement for detection of Br_2 evolved in the oscillating reaction. See text for description of the various components.

The gas-generating cell contained 10 cm^3 of 0.5 M oxalic acid or 0.5 M KBr solution, respectively. The sulfuric acid concentration was 1 M in both cases. An electronic current generator served as a constant current source.

Another possibility to calibrate the CO_2 and Br_2 measuring systems was to use chemical reactions generating known amount of gases. We used the following reactions:

$$(COOH)_2 + 2Ce^{4+} \rightarrow 2CO_2 + 2H^+ + 2Ce^{3+} \qquad (C3)$$

$$6H^+ + BrO_3^- + 5Br^- \rightarrow 3Br_2 + 3H_2O \qquad (C4)$$

applying a tenfold excess of Ce^{4+} and Br^- compared to $(COOH)_2$ and to BrO_3^-, respectively. Naturally calibration was possible by a known amount of gases or their aqueous solutions introduced physically into the systems, e.g., by a syringe, but the accuracy and the precision were not as good as in the previous procedures.

The sensitivity of the CO_2 measuring system was 0.103 μC/μmol CO_2 if the carrier H_2 was generated by an electric current of 4 A. The sensitivity of the Br_2 measuring system was 1.56 mC/μmol Br_2.

Results

Existence of Oscillations. The most important qualitative result of our experiments is that the oxalic acid can produce an oscillating CO_2 evolution in a Belousov-type reaction if the gaseous products are removed by a constant flow of H_2 carrier gas. As an illustration Figure 3 depicts the results of an early experiment. The reaction vessel contained 3 cm^3 of solution A and 1 cm^3 of solution C was added at the start of the experiment. The H_2 generating current was 4 A. Here Br_2 scrubber was not applied because a poisoning effect of Br_2 on the nickel catalyst (see Figure 5) was disclosed later. Nineteen maxima were registered. Potentiometric, spectrophotometric, and thermometric measurements with stirred solutions but without the application of a carrier gas failed to show oscillations.

Products of Reaction. Two gaseous products were found: CO_2 and Br_2. The CO content was measured applying the procedure described in ref 4 and it was under the detection limit (less than 0.1% of the CO_2).

Simultaneous CO_2 and Br_2 measurement was possible if the carrier gas leaving the bromine absorber column was introduced into the CO_2 measuring system. In this case the sensitivity of the CO_2 detection was reduced to 0.082 μC/μmol CO_2 because a 20% loss occurred due to the CO_2 dissolved in the KBr stream. The result of the experiment is depicted in Figure 4. Solution B (1 cm^3) was added to 2 cm^3 of solution A establishing the initial concentrations indicated below the diagram.

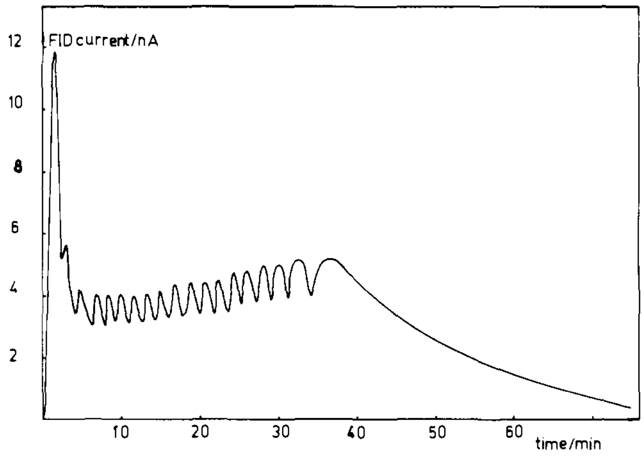

Figure 3. Oscillatory CO_2 evolution from oxalic acid. Initial concentrations: $[(COOH)_2] = 3 \times 10^{-2}$ M, $[KBrO_3] = 4 \times 10^{-2}$ M, $[Ce(SO_4)_2] = 5 \times 10^{-4}$ M, $[H_2SO_4] = 1.5$ M.

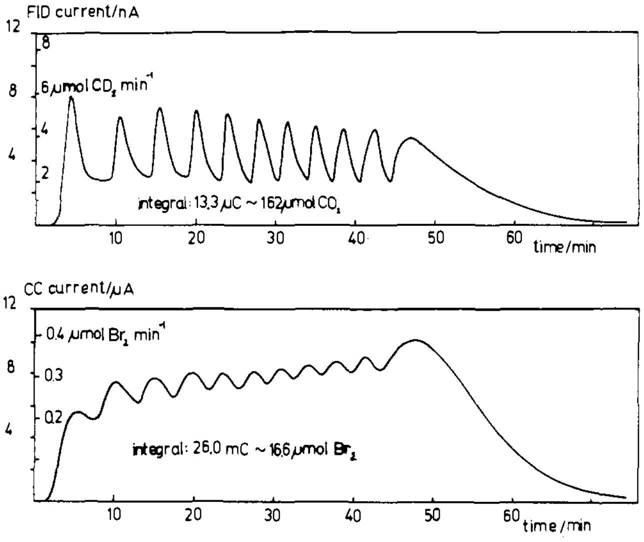

Figure 4. Simultaneous CO_2 and Br_2 evolution from an oscillating reaction mixture. Initial concentrations: $[(COOH)_2] = 2.66 \times 10^{-2}$ M, $[KBrO_3] = 2.66 \times 10^{-2}$ M, $[Ce(SO_4)_2] = 6.66 \times 10^{-4}$ M, $[H_2SO_4] = 1.5$ M. H_2 generating current: 4 A.

It has to be mentioned that the electric current in the coulometric and in the flame ionization detector is proportional to the component flows in the detectors and these component flows show their production rate in the chemical reactor some seconds or some minutes before. This time lag of the two systems was determined in a separate experiment (when the systems were calibrated by chemical reactions) and a synchronization of the curves was made based on those data.

Another problem is that we can regard the component flows to be real production rates only as an approximation because the system transforms the "sharper" production rate-time curves to "smoother" component flow-time curves if the time constants of the system are not much smaller than the period of the oscillations. Calculations are in progress to convert the component flow-time curves to reaction rate (gas production rate)-time curves regarding the time constants of the systems. Nevertheless it can be seen from the present experimental curves that the CO_2 and the Br_2 evolution take place with the same frequency and approximately in the same phase. (In fact we found that the bromine evolution reaches its maximum a little bit earlier than carbon dioxide evolution does, but to measure that difference exactly the above-mentioned transformation of the curves is needed.)

Stoichiometry. The whole quantity of the gases evolved during the oscillating reaction can be determined as the time

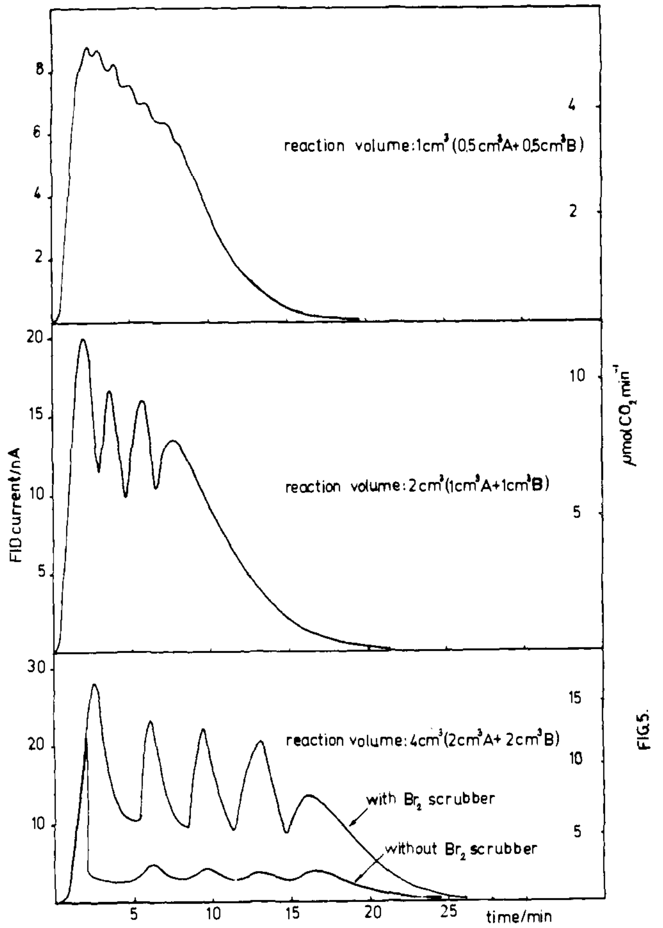

FIG.5.

Figure 5. Effect of reaction volume on the oscillating reaction at constant H_2 flow rate. H_2 generating current: 4 A. Reaction volume: as indicated in the diagrams. Initial concentrations: $[(COOH)_2] = 2 \times 10^{-2}$ M, $[KBrO_3] = 4 \times 10^{-2}$ M, $[Ce(SO_4)_2] = 10^{-3}$ M, $[H_2SO_4] = 1.5$ M.

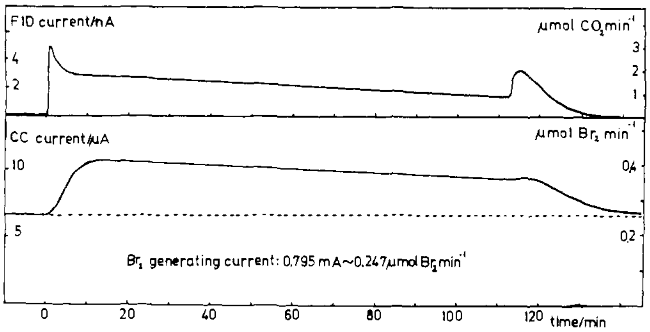

Figure 8. Effect of Br_2 introduction on the oscillating reaction. All the other parameters were the same as in the case of CO_2 introduction.

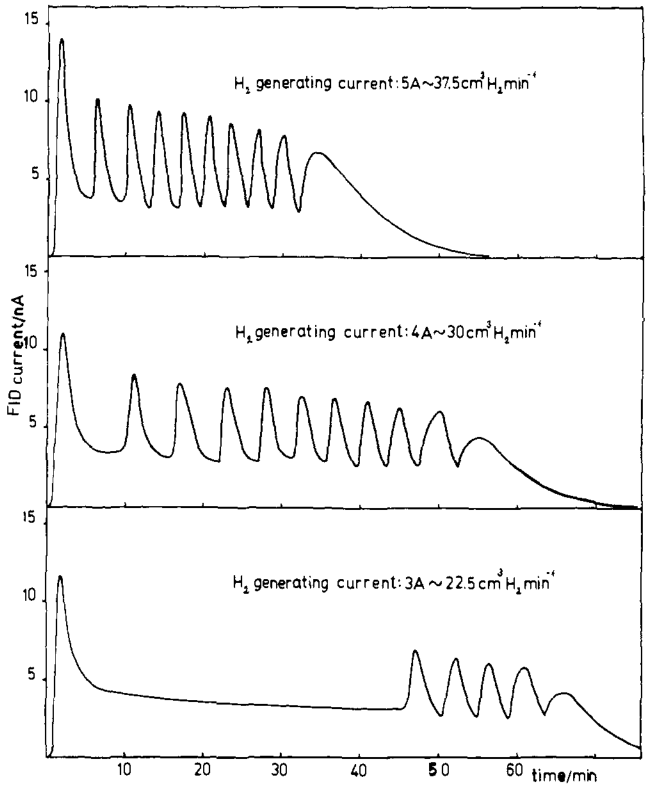

Figure 6. Effect of carrier flow rate on the oscillating reaction at constant reaction volume of 3 cm^3 (2 cm^3 A + 1 cm^3 B). H_2 generating current: as indicated in the diagram. Initial concentrations: $[(COOH)_2] = 2.66 \times 10^{-2}$ M, $[KBrO_3] = 2.66 \times 10^{-2}$ M, $[Ce(SO_4)_2] = 6.66 \times 10^{-4}$ M, $[H_2SO_4] = 1$ M.

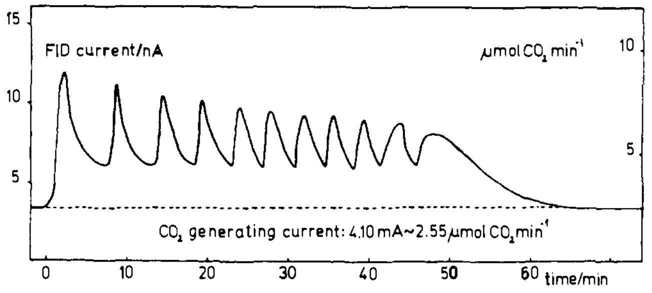

Figure 7. Effect of CO_2 introduction on the oscillating reaction. The reaction volume and the initial concentrations were as given below Figure 6. H_2 generating current: 4 A.

integral of the component flows. The areas under the curves depicted in Figure 4 are 13.3 µC for CO_2 and 26.0 mC for Br_2. Regarding the sensitivities that means 162 µmol of CO_2 and 16.6 µmol of Br_2. The original reaction mixture contained 80 µmol of oxalic acid. All these results can be explained within the experimental error by the following overall stoichiometric equation:

$$2H^+ + 2BrO_3^- + 5(COOH)_2 \rightarrow 10CO_2 + Br_2 + 6H_2O \quad (R1)$$

Effect of Reaction Volume and of Carrier Gas Velocity. As was mentioned before we could observe oscillations only when applying a carrier gas stream. Thus it seemed reasonable to examine the phenomenon at different reaction volumes and carrier gas velocities. Figure 5 depicts FID signal-time (CO_2 production rate-time) diagrams as a function of the reaction volume at constant carrier flow. In Figure 6 FID signal vs. time diagrams can be seen at different carrier velocities; in this case the reaction volume was fixed.

As Figures 5 and 6 illustrate, the reaction rate is greatly affected by the carrier flow rate-reaction volume ratio; the higher that ratio the quicker the CO_2 production.

On Figure 5 the poisoning effect of Br_2 on the nickel catalyst is also illustrated.

Effect of CO_2 and Br_2 Introduction. The most important effect of the carrier gas is the removal of the gaseous products CO_2 and Br_2. It was rather probable that Br_2 is the reaction rate controlling product. To prove that hypothesis experiments were made with H_2 carrier flows containing known concentrations of electrolytically generated CO_2 and Br_2. If the car-

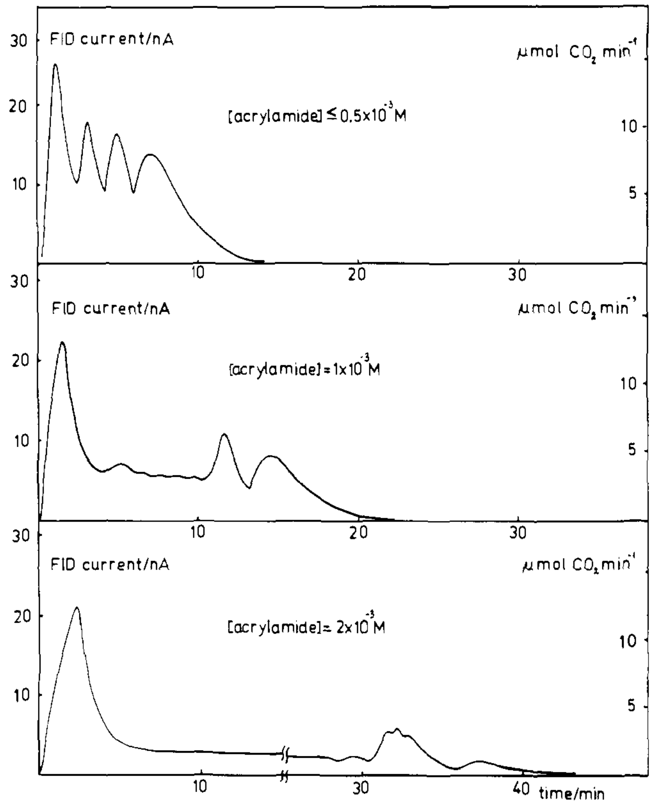

Figure 9. Effect of acrylamide on the oscillating reaction. Reaction volume: 2 cm^3 (1 cm^3 A + 1 cm^3 B) + 0.025 cm^3, or 0.05 or 0.1 cm^3 of 4 × 10^{-2} M acrylamide solution, respectively. Initial concentrations: $[(COOH)_2] = 2 \times 10^{-2}$ M, $[KBrO_3] = 4 \times 10^{-2}$ M, $[Ce(SO_4)_2] = 10^{-3}$ M, $[H_2SO_4] = 1.5$ M, [acrylamide] = as indicated in the diagrams. H_2 generating current: 4 A.

rier contained only CO_2 the Br_2 evolution-time diagram was not changed and the only change in the FID signal-time curve was that the original curve was superimposed on a higher base line (Figure 7). However, if the carrier contained Br_2 both of the diagrams changed dramatically as is shown in Figure 8.

Effect of Acrylamide. Vâradi and Beck[10] pointed out that the periodic reaction between malonic acid, potassium bromate, and catalyst in aqueous sulfuric acid media is inhibited by molecular oxygen, hydrogen peroxide, and acrylonitrile and hence it occurs by a free-radical mechanism.

The acrylamide is also a well-known radical scavenger.[11] The series of experiments with different acrylamide concentrations in Figure 9 shows an effect which resembles the effect of Br_2 introduction.

Kinetics and Stoichiometry of Noncatalyzed Reaction. In the case of oxalic acid the uncatalyzed reaction takes place with a measurable rate. In Figure 10 the CO_2 evolution rate-time diagram of such a reaction is depicted. The stoichiometry of the uncatalyzed reaction is reported to be the same[12] as the stoichiometry of the catalyzed one found by us.

Discussion

There are two ways to explain the experimental results. One possibility is to apply the Zhabotinskii[13] FKN[1] theory of Br^- inhibition of the oxidation of Ce^{3+} by bromate. However, the source of the Br^- ions is not as clear as in the case of malonic acid. When the substrate is oxalic acid brominated products analogous to bromomalonic acid cannot exist. Naturally the reactions

$$HOBr + (COOH)_2 \rightarrow 2CO_2 + Br^- + H^+ + H_2O \quad (R2)$$

$$Br_2 + (COOH)_2 \rightarrow 2CO_2 + 2Br^- + 2H^+ \quad (R3)$$

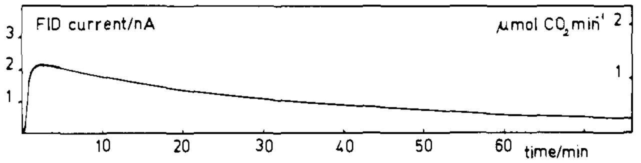

Figure 10. CO_2 evolution without Ce catalyst. Reaction volume: 2 cm^3 Initial concentrations: $[(COOH)_2] = 2 \times 10^{-2}$ M, $[KBrO_3] = 4 \times 10^{-2}$ M, $[H_2SO_4] = 1.5$ M. H_2 generating current: 4 A.

$$Br_2 + H_2O \rightarrow Br^- + H^+ + HOBr \quad (R4)$$

can provide bromide ions.

Nevertheless, according to Figure 8 there is no measurable CO_2 evolution from oxalic acid due to a bromine concentration level established by the Br_2-containing carrier gas stream. The FID signal appears only after the addition of 1 cm^3 of solution B (zero time). Calculations based on Knoller's and Hayman's[14] data also support the hypothesis that reactions R2 and R3 are too slow to be important at so low pH values.

Another possibility is to attribute a direct role to Br_2 instead of Br^- For example, a radical chain branching like

$$BrO_2\cdot + Br_2 \rightarrow Br_2O_2 + Br\cdot \quad (R5)$$

$$Br_2O_2 \rightarrow 2BrO\cdot \quad (R6)$$

can accelerate the oxidation of Ce^{3+} according to the steps

$$Ce^{3+} + Br\cdot \rightarrow Ce^{4+} + Br^- \quad (R7)$$

$$H^+ + Ce^{3+} + BrO\cdot \rightarrow Ce^{4+} + HOBr \quad (R8)$$

and deplete the original $BrO_2\cdot$ concentration at the same time due to the overall reaction

$$3H^+ + BrO_2\cdot + 3Ce^{3+} \xrightarrow{Br_2} 3Ce^{4+} + HOBr + H_2O \quad (R9)$$

Br_2 acts as a catalyst in (R9) because it regenerates in the step −R4. Br_2 can be produced in the reaction

$$2HOBr + (COOH)_2 \rightarrow 2CO_2 + H_2O + Br_2 \quad (R10)$$

The appearance of Br_2 causes a transitional acceleration of the reaction, but after consuming the $BrO_2\cdot$ content and using up the $HBrO_2$ reserve through the reaction FKN3a the process decelerates.

The Br_2 inhibits the autocatalytic regeneration of $HBrO_2$ because step R5 competes with step FKN3b. Owing to the physical removal of Br_2 the autocatalytic production of $HBrO_2$ gradually speeds up again, but there is a time delay in the formation of Br_2 because a certain amount of HOBr has to arise from $HBrO_2$ beforehand through a second-order destruction of $HBrO_2$ (FKN4) or through (R9). Thus a $HBrO_2$ reserve can accumulate and the oscillatory cycle can then begin again.

The main point in the speculations above is that the elementary bromine may play a direct role in the BZ reactions beside or instead of Br^-. Some earlier observations on the Ce^{3+}-bromate reaction may support that hypothesis. Already Vavilin and Zhabotinskii[13] observed that the induction period of the autocatalytic oxidation of Ce^{3+} by bromate was increased by addition of bromine. Barkin et al.,[15] examining the same reaction, found that the effect of bromide ions on the induction time was the same within the experimental error if bromine was added in equivalent amount to that formed by bromide. Also bubbling of inert gases through the reaction mixture caused several effects observed by Kasparek and Bruice[6] and Barkin et al.[15] and was explained by Herbo et al.[16] and by Barkin et al.[15] as an effect of Br_2 removal from the system. In the Ce^{3+}-BrO_3^- reaction no significant Br_2 production occurs according to Noyes et al.[17] The presence of an organic substrate can change that situation. For example, in the case of the original BZ reaction (substrate: malonic acid) it was demonstrated spectrophotometrically by Franck and Geiseler[18] that the concentration of Br_2 fluctuates in synchronization with the concentration of Ce^{4+}

The malonic acid and other substrates of the homogeneous BZ reaction can remove the produced Br_2 chemically. In the case of the oxalic acid reaction discussed here the bromine is swept out by a gas stream. As one of our referees pointed out to us all effects are similar. Even the mathematical description of the Br_2 removal is identical: in both cases it has the form of a pseudo-first-order chemical reaction. In this respect it is important to mention the oscillations discovered by Körös and Orbán[19,20] with phenolic and anilinic substrates in the absence of metal ion catalyst.

Finally we want to emphasize that the mechanism proposed here is by no means the only one which may account for the effects of elemental bromine in the BZ reaction. Experimental work is in progress in our laboratory to examine the role of Br^- and of Br_2 in the original BZ reaction.

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Orbital Contributions to the Nuclear Spin-Spin Coupling Constants of Molecules

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Abstract: This paper presents ab initio values for the "paramagnetic" orbital contributions J^{1b} to the spin-spin coupling constants of the molecules methane, water, hydrogen fluoride, hydrogen cyanide, hydrogen isocyanide, acetylene, ethylene, ethane, acetonitrile, and methyl isocyanide. These values are compared with those obtained from previous semiempirical studies.

I. Introduction

The isotropic nuclear spin-spin coupling constant is the sum of four experimentally indistinguishable terms: the Fermi contact term J^3, the "diamagnetic" and "paramagnetic" orbital terms (J^{1a} and J^{1b}), and the spin-dipolar term (J^2).[1] Following the pioneering treatment of J_{HD} by Ramsey,[1] most theoretical studies have concentrated on the Fermi contact term. However, recently there has been renewed interest in the orbital and dipolar terms.[2,3]

The principal theoretical method which has been used to calculate the orbital contribution is the coupled Hartree-Fock (CHF) perturbation theory.[5] It has been implemented semiempirically in the INDO approximation by Blizzard and Santry[6] and in the MINDO/3 approximation by Dewar et al.[7a] and Schulman.[7b] Another form of semiempirical theory which has been used for the orbital term is the sum-over-states perturbation theory.[8]

From a theoretical point of view ab initio values of J^{1b} in CHF perturbation theory should be more accurate than their semiempirical counterparts. We report here our results for all coupling constants in the molecules methane, water, hydrogen fluoride, hydrogen cyanide, acetylene, ethylene, ethane, acetonitrile, and methyl cyanide. A contracted Gaussian 6-31G basis set[9] was employed, the 4-31G basis giving similar results. For HCN and C_2H_2 we also used the larger contracted basis of Dunning ($10s^5 6p^3/5s^3$)[10] which gave results differing from those of the 6-31G set by about 15%. The orbital term therefore appears to be much less sensitive to the basis set than the Fermi contact term.

II. Theory

Only a brief recounting of the theory for the orbital term is necessary since the CHF method for second-order properties has been adequately discussed by Thomsen et al.[5] The contribution $J_{AB}{}^{1b}$ for the coupled nuclei A and B is obtained from the energy bilinear in the perturbations H_A and H_B, and is given in the Ramsey treatment by

$$J_{AB}{}^{1b} = (-8\beta^2\hbar^2\gamma_A\gamma_B/3h) \times \sum_m \frac{\left\langle 0 \middle| \sum_k^{2n} \mathbf{h}_A(k) \middle| m \right\rangle \cdot \left\langle m \middle| \sum_{k'}^{2n} \middle| \mathbf{h}_B(k') \middle| 0 \right\rangle}{E_m - E_0} \qquad (1)$$

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