the transfer barrier and the deuterium isotope effect is less than 3, slowly approaching its high-temperature limit of 1.12. The Arrhenius activation energy deviates slightly from E^{I} , due to properties of the vibrational partition functions, the behavior of which can be simply understood on the basis of eq 7-10.

In closing, it is our belief that the rate constants calculated for $E^{\dagger} = 15.4$ kcal/mol by summation of RRKM data including tunneling, represented by the appropriate solid curves in Figures 1-5, provide realistic estimates of the true values. We would suggest the highest degree of caution for the data in the regimes of very low energy and temperature where tunneling is dominant, due primarily to the arbitrariness in the choice of mathematical form of the potential function. Although this choice influences the quantitative data, our qualitative conclusions should retain their validity regardless of potential.

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Kinetics of Chemical Waves in the Acidic Bromate–Malonic Acid–Ru(bpy)₃²⁺ System in Comparison with the Ferroin System

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Propagation of trigger waves was investigated in the acidic bromate-malonic $acid-Ru(bpy)_3^{2+}$ system. In excitable but not oscillatory solutions the concentration dependence of wave velocity v follows the equation $v = 2(k_{\rm R1}D_{\rm x})^{1/2}([{\rm H}_2{\rm SO}_4][{\rm NaBrO}_3])^{1/2}$ $-v_0$. Concentration and temperature dependence of wave velocity coincide quantitatively with the corresponding results from BZ systems containing ferroin as catalyst. In solutions with coexisting phase and trigger waves the trigger wave velocities follow the empirical law $v \sim [H_2SO_4]^{1.26} [NaBrO_3]^{1.68}$.

Introduction

Chemical waves are waves of concentration impulses travelling at constant velocity due to interaction of feedback steps with diffusion. Such waves and structures are observed in "active media" in several chemical, physical, and biological systems, e.g., heterogeneous catalytic reactions, combustion or migration of populations.1

The first demonstration of wave propagation in autocatalytical chemical systems was performed by Luther² 80 years ago. Significant progress in the study of chemical waves has been achieved during the past 15 years, in which the Belousov–Zhabotinsky (BZ) reaction and its modifications have been employed for such experiments. The malonic acid-bromate-ferroin system³⁻¹⁹ was

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investigated most thoroughly and the relation between the kinetics of its autocatalytic step and the trigger wave velocity was clarified.²⁰ Although oscillations²¹⁻²⁶ and wave propagation²⁷⁻²⁹ are known in BZ systems replacing ferroin by $Ru(bpy)_3^{2+}$, in literature there are no quantitative data given about wave propagation in the Ru(II)-catalyzed system. In the present paper we want to report such data and compare them with the corresponding results from ferroin systems.

Experimental Section

Solutions were prepared with triply distilled water. Malonic acid, sulfuric acid, 2,2'-bipyridine, and KBr were of commercial reagent grade and used without further purification. NaBrO₃ was three times recrystallized. Preparation of Ru(bpy)₃SO₄·8H₂O was carried out according to ref 30.

Kinetic measurements of the autocatalytic oxidation of Ru- $(bpy)_3^{2+}$ by bromate were performed by following the light absorption at $\lambda = 460 \text{ nm} (\epsilon_{Ru(II)} = 13400 \text{ M}^{-1} \text{ cm}^{-1}, \epsilon_{Ru(III)} = 400$

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Figure 1. Oxidation of Ru(bpy)₃²⁺ by bromate. Kinetic plot of Ru- $(bpy)_3^{3+}$ concentration at T = 25 °C. Initial concentrations: 5×10^{-5} $M Ru(bpy)_3^{2+}$. (a) 0.1 M H₂SO₄, 10⁻² M NaBrO₃; (b) 0.5 M H₂SO₄, 5×10^{-3} M NaBrO₃.

M⁻¹ cm⁻¹) using a Spekol-10 spectrometer (Carl Zeiss Jena). The vigorously stirred reaction volume was 20 mL.

Velocity of wave propagation was measured in thin layers (~ 1 mm) of reaction mixture in a thermostated petri dish. The system was photographed at definite times and the distance of bands from a fixed reference point was taken down from each photograph. The trigger waves were initiated manually by means of a silver wire.

Results

Kinetic Constants of the Autocatalytic Process. For the acidity region in question for trigger wave experiments (0.05-0.6 M H_2SO_4) we have studied the oxidation of $Ru(bpy)_3^{2+}$ by an excess of bromate separately without malonic acid. In comparison to the oxidation of ferroin^{19,31} following differences were noted:

(a) The Ru(II) complex is stable against dissociation in sulfuric acid solution.

(b) Long induction periods occur ($\tau_{ind} > 10\tau_{ox}$) even in the absence of initially given bromide.

(c) At lower acidities ($\approx 0.1 \text{ M H}_2\text{SO}_4$), the Ru(III) concentration curves show in the autocatalytic phase a sigmoid shape (Figure 1a) whereas at higher acidities ($\gtrsim 0.35 \text{ M H}_2 \text{SO}_4$) they tend to the shape of the corresponding ferroin curves having an abrupt finish of the reaction (Figure 1b). As rate-limiting step of the autocatalytic reaction there is considered the synproportionation reaction R1 which is strongly reversible. R1 is followed

$$HBrO_3 + HBrO_2 + H^+ \xrightarrow{} 2BrO_2 + H_2O + H^+ (R1)$$

by the fast oxidation step R2 which is considered to be irreversible

$$BrO_2 + H^{\dagger} + Ru(II) \longrightarrow Ru(III) + HBrO_2$$
 (R2)

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Figure 2. Dependence of kinetic constants k_{R1} obtained via oxidation of ferroin and $Ru(bpy)_3^{2+}$ by bromate on sulfuric acid concentration. The number beside each point indicates the initial bromate concentration (M) taken for the experiment. Initial catalyst concentration was throughout 5×10^{-5} M. T = 25 °C. Calculations of constants k_{R1} were carried out by using H_2SO_4 concentration instead of h_0 acidity function which is almost identical with [H⁺] for the low acidity region.

for catalysts with low redox potential couples. Assuming that R2 proceeds much faster than the backward reaction R-1, (R1 + $2 \times R2$) represents an irreversible feedback cycle leading to an exponentially increasing Ru(III) concentration as long as the disproportionation reaction R3 can be neglected for small auto-

$$2HBrO_2 \longrightarrow HBrO_3 + HOBr$$
 (R3)

catalyst concentrations. Detailed conditions for this behavior are given in ref 31 and 19.

The sigmoid shape of the Ru(III) concentration curves at lower acidities may be due to the fact that the potential of the Ru-(II)/Ru(III) couple (1.262 V in 0.11 M H_2SO_4)³² comes close to the value of 1.33 V of the BrO2•/HBrO2 couple³³ and R2 then becomes reversible. Furthermore, the assumption of R2 being much faster than R-1 may become invalid and the autocatalytic process then proceeds at partial equilibrium.

With $[H_2SO_4] \gtrsim 0.35$ M, we obtain Ru(III) concentration curves having almost throughout exponential shapes, thus allowing us to separate k_{R1} values from exponents α as performed in ref 19. The rate constants so obtained are given in Figure 2 to be compared with values k_{R1} determined by means of the ferroin system.¹⁹ Obviously, constants k_{R1} do not depend on initial bromate concentration, nor on the specific nature of the catalyst, and only weakly on acidity. The average of the Ru(II) values is

$$k_{\rm R1} = 43.3 \pm 2.5 \ {\rm M}^{-2} \ {\rm s}^{-1}$$
 (1)

From measurements of k_{R1} at 0.36 M H₂SO₄ and 10⁻² M NaBrO₃ between 19.5 and 47.8 °C we obtained an energy of activation of

$$E_{\rm a} = 58.0 \pm 3.3 \text{ kJ mol}^{-1}$$
 (2)

being in agreement with the value of $E_a = 60.1 \pm 3.6 \text{ kJ mol}^{-1}$ obtained by means of ferroin oxidation.¹⁹

Velocity of Waves Depending on Concentrations and Temperatures. The procedure of carrying out experiments was similar to that of ref 19. The sulfuric acid, NaBrO₃, malonic acid, and KBr solutions were mixed together in the given sequence. A part of the malonic acid was brominated by free bromine liberated by the bromide-bromate reaction. After the free bromine had disappeared $Ru(bpy)_3^{2+}$ solution was added and the mixture was poured into the petri dish. Figure 3 shows data plots of wave

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Figure 3. Typical plots of distances vs. time for traveling waves from one leading center initiated by a silver wire. T = 25 °C. The average velocity is 5.70 mm min⁻¹. Initial concentrations: 1.95×10^{-1} M H₂SO₄, $3.1 \times$ 10^{-1} M NaBrO₃, 4.5×10^{-2} M MA, 1.05×10^{-1} M BMA, 3.2×10^{-3} M Ru(bpy) $_{3}^{2+}$.

TABLE I: Representative Concentrations of Solutions Exhibiting Wave Trains Used in This Paper

concn range/M	
0.075-0.445	
0.145-0.640	
0.045-0.330	
0.105	
0.001-0.005	
	concn range/M 0.075-0.445 0.145-0.640 0.045-0.330 0.105 0.001-0.005

^{*a*} MA = $CH_2(COOH)_2$, BMA = BrCH(COOH)_2.

positions against time for a typical run. Linearity of these plots indicates that velocities of the waves are constant. Standard deviations of average velocities in one set of concentrations were usually about 10%.

The concentration ranges of employed compositions are presented in Table I; each composition is calculated for the time when free bromine initially generated completely reacted with malonic acid. The result is an orange (reduced) solution that is in most cases marginally stable with respect to temporal oscillations--other situations will be discussed below-but will still propagate bluish fluorescent (oxidizing) bands once they have been initiated. Each of the components of the solution was varied over a considerable concentration range while the other components were left constant. The results of these measurements are plotted in Figures 4-6. The velocity of wave propagation is independent of the concentration of malonic acid, this is in accordance to the results in ferroin systems.^{9,13} With increasing concentration of $Ru(bpy)_3^{2+}$ the velocity is slightly growing. In this point there is a difference to the ferroin systems in ref 9 and 13, where the velocity of wave propagation was clearly independent from the catalyst concentration.

Figure 6 demonstrates the dependence of velocity v on the value $C = ([H_2SO_4][NaBrO_3])^{1/2}$. There we can distinguish between two regions: at low concentrational values $C (C \leq 0.28 \text{ M})$ the system is excitable but not oscillatory, but for higher values of C the system exhibits spontaneous oscillations. For the excitable region we can confirm the result from ref 9, 13, and 18 for the ferroin system: the proportionality of wave velocity to C. The best two-parameter line through the points in Figure 6 is

$$v/(\text{mm min}^{-1}) = -(1.2 \pm 0.8) + (27.5 \pm 3.8)C/M$$
 (3)

$$v/(\text{mm min}^{-1}) = (22.0 \pm 0.74)C/M$$
 (4)

The parameter values in eq 3 are in excellent agreement with the corresponding parameters from ferroin systems (see Table II).

•

In the oscillatory domain ($C \gtrsim 0.28$ M) a more complex dependence was found for v. In that region spontaneous occurrence



Figure 4. Velocity of wave propagation vs. initial concentrations of malonic acid. T = 25 °C. Other initial concentrations: 2.55×10^{-1} $\rm H_2SO_4,~3.1~\times~10^{-1}~M~NaBrO_3,~1.05~\times~10^{-1}~M~BMA,~3.2~\times~10^{-3}~M$ $Ru(bpy)_3^{2+}$



Figure 5. Velocity of wave propagation vs. initial concentrations of $Ru(bpy)_{3}^{2+}$, T = 25 °C. Other initial concentrations: 1.35×10^{-1} M H_2SO_4 , 3.1 × 10⁻¹ M NaBrO₃, 4.5 × 10⁻² M MA, 1.05 × 10⁻¹ M BMA.



Figure 6. Velocity of wave propagation vs. $([H_2SO_4][NaBrO_3])^{1/2}$. T = 25 °C. Initial concentrations of other species: 4.5×10^{-2} M MA, 1.05 $\times 10^{-1}$ M BMA, 3.2×10^{-3} M Ru(bpy)₃²⁺. Concentration ranges: (×) $(0.75-4.45) \times 10^{-1}$ M H₂SO₄ with 3.1 × 10⁻¹ M NaBrO₃, and (0) $(1.45-6.4) \times 10^{-1}$ M NaBrO₃ with 1.35×10^{-1} M H₂SO₄.

of phase waves was observed which were coexistent with bands of trigger waves. This oscillatory state establishes in the Ru(II) catalyzed system already at lower C values compared with the ferroin system. This difference can be due to the stability of the ruthenium complex against dissociation and its consecutive side reactions. A precipitation of brominated dissociation products as in the ferroin system¹³ no longer takes place. Furthermore, uncomplexed ferrous ions from ferroin dissociation reduce bromate to Br₂ and Br⁻ leading to an inhibition of spontaneous oscillations.

Trigger waves in the oscillatory domain also propagate with constant velocity. Diagrams of front positions vs. time similar to Figure 3 were obtained. Deviations from velocity constancy

TABLE II: Comparison of Kinetic Values between Ferroin and Ru(bpy)₃²⁺ Systems

	ferroin	$Ru(bpy)_3^{2+}$
v ^d /(mm min ⁻¹)	-0.8 + 27.9C° (25 °C) (9) ^f -0.999 + 27.33C (25 °C) (13) -3.2 + 28.3C (18 °C) (18)	-1.2 + 27.5C (25 °C) ^b
$\bar{k}_{R1}^{e}/(M^{-2} s^{-1})$	$45.3 \pm 2.0^{\circ}$	43.3 ± 2.5^{c}
activation energy $E_a^{\text{autocat}}/(\text{kJ mol}^{-1})$ $E_a^{\text{wave}}/(\text{kJ mol}^{-1})$	$60.1 \pm 3.6 (19)$ $34.9 \pm 1.2 (19)$ 34.0 (18)	58.0 ± 3.3^{b} 37.6 ± 3.2^{b}

 ${}^{a}C = ([H_2SO_4][NaBrO_3])^{1/2}$. ^bThis work. ^cFrom Figure 1. ^dWave velocity. *Autocatalytic constant, $[H_2SO_4] \leq 0.61$ M. ^fNumbers in parentheses are reference numbers.

and transitions to phase waves with considerably higher velocities were not observed within the given compositions (see Table I). The following concentration dependence for the trigger wave velocity was found:

$$v/(\text{mm min}^{-1}) = 292([H_2SO_4]/M)^{1.26}([\text{NaBrO}_3])^{1.68}$$
 (5)

A theoretical description of this dependence cannot be given in the frame of this paper, but we want to point out the formal analogy of eq 5 with the dependence of frequency in the oscillating bromate-malonic acid-ferroin system on concentrations of bromate and sulfuric acid.³⁴ For the corresponding system containing Ru(II) as catalyst a similar formula for the frequency ν was found:35

$$\nu \sim [H_2 SO_4][NaBrO_3] \tag{6}$$

Temperature dependence of velocity of trigger waves was investigated between 15 and 40 °C by using the initial composition 2.55×10^{-1} M H₂SO₄, 3.1×10^{-1} M NaBrO₃, 4.5×10^{-2} M MA, 1.05×10^{-1} M BMA, and 3.2×10^{-3} M Ru(bpy)₃²⁺. From an Arrhenius plot of the v (T) values we obtained an energy of activation of

$$E_a = 37.6 \pm 3.2 \text{ kJ mol}^{-1}$$
 (7)

which is in satisfactory agreement with the corresponding E_a value in the ferroin system (see Table II).

Discussion

Our results on wave propagation in the Ru(II)-catalyzed BZ system support former results from ferroin systems in the excitable region^{9,13,18,19} suggesting that this phenomenon is governed by

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coupling of oxobromine chemistry with diffusion and does not depend on the specific nature of the catalyst if its redox couple has a potential value below 1.33 V.

With respect to the rate constants in oxobromine chemistry there are different opinions regarding either "lo" or "hi" sets of constants. Tyson^{20d} has shown that both classes of constants are almost equivalent in quantitative description of oscillations, bistability, and wave propagation in BZ systems. In the first two cases only the ratios of constants are relevant for modeling of experimentally observable values, leading to a difficulty to make a strong decision for one set of constants. But in the case of wave propagation, the empirically found velocity dependence $v \sim$ $[H^+]^{1/2}$ as a part of the proportionality to the value C (see Table II) can only be described by means of "lo" constants.^{20d} New experiments on Ce(III) oxidation recently presented by Field and Försterling are also leading to a "lo" set.³⁶

The empirical velocity formula from Table II (eq 3) is of the type

$$v = m_v ([H_2 SO_4] [Na BrO_3])^{1/2} - v_0$$
 (8)

The parameter m_v reads in the Kolmogorov-Fisher approach to trigger wave motion in BZ systems^{9,19,20}

$$m_{\nu} = 2(k_{\rm R1}D_{\rm x})^{1/2} \tag{9}$$

Using $k_{R1} = 43.3 \text{ M}^{-2} \text{ s}^{-1}$ from (1) and a diffusion coefficient of the autocatalyst $D_x = 1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (ref 19) we obtain from (9) a theoretical value

$$m_v^{\text{theor}} = 27.4 \text{ mm min}^{-1} \text{ M}^{-1}$$
 (10)

which is almost identical with the experimental value of $m_{\rm p} = 27.5$ \pm 3.8 mm min⁻¹ M⁻¹ given in eq 3.

The formal energy of activation of the wave process E_a^{tr} is¹⁹

$$E_{a}^{\rm tr} = (E_{a}^{\rm KI} + E_{a}^{\rm D})/2 \tag{11}$$

Using $E_a^{D} = 15.3 \pm 1.3 \text{ kJ mol}^{-1}$ for the diffusion process¹⁹ and $E_a^{R1} = 58.0 \pm 3.3 \text{ kJ mol}^{-1}$ from (2) for the autocatalytic process we obtain with (11) a theoretical value of

$$E_{\rm a}^{\rm tr(theor)} = 36.7 \pm 2.3 \text{ kJ mol}^{-1}$$
 (12)

agreeing with the experimental value $E_a^{\text{tr(expt)}} = 37.6 \pm 3.2 \text{ kJ}$ mol^{-1} given in (7).

The slight intercept $v_0 \approx 1 \text{ mm min}^{-1}$ found in the velocity equations in ferroin and Ru(II) catalyzed systems may have low statistical significance for each example, but the coincidence of the v_0 values with each other should be noted. This intercept can be interpreted as a consequence of the weak inhibiting influence of bromide as we showed in ref 19.

Registry No. Ru(bpy)₃²⁺, 15158-62-0; BrO₃, 15541-45-4; malonic acid, 141-82-2.

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