The Light-Perturbed Ru-Catalyzed Belousov−Zhabotinsky Reaction: Evidence for Photochemically Produced Bromous Acid and Bromide Ions by Phase Response Analysis

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Phase response analysis of light-perturbed closed and aging Ru-catalyzed Belousov−Zhabotinsky (BZ) reactions with malonic, methyl-, ethyl-, butyl-, and phenylmalonic acids as organic substrates suggests two major responses of the light-perturbed Ru-catalyzed BZ system. One is the photoproduction of bromous acid ($HBrO_2$) in the beginning of the reaction when little bromoorganic species are present, while another response is the photoproduction of bromide ions in the presence of bromomalonic acid or bromomalonic acid derivatives. From this analysis the light-induced production of bromide ions directly from bromate can be excluded. The experimentally observed phase response curves agree well with calculations performed with the Oregonator model. An oxidative quenching mechanism for the photoproduction of bromide is suggested. Interestingly, during illumination of the Ru(II)/MA subsystem, i.e., in the absence of BrMA and bromate, the oxidative quenching does also occur.

Introduction

After the work of Vavilin et al.[1] had been published in 1968, photochemical modulations of temporal oscillations as well as spatial wave phenomena were observed by several authors.[2−21] The work by Demas and Diemente[3] introduced the fluorescent tris(2,2′-bipyridine)ruthenium(II) complex, $Ru(bpy)_3^{2+}$, as a catalyst to the Belousov−Zhabotinsky (BZ) reaction, and the photochemistry of Ru-catalyzed BZ systems were studied by many researchers.[6−10] Agladze et al.[17] studied the phase resetting of the light-perturbed malonic acid Ru-catalyzed BZ reaction and observed phase-delays.

Several authors have investigated the role of bromide ions in the Ru-catalyzed BZ reaction. According to Yamaguchi et al.,[22] bromomalonic acid (BrMA) is a source of photochemically produced bromide ions, while Mori et al.[23] studied the photoinduced bifurcation of the BZ reaction in a continuous-stirred tank reactor in the presence of BrMA. Kádár et al.[24] stress the importance of two separate processes that are induced on the irradiation of the Ru-catalyzed BZ system: the photochemical production of bromide ion from BrMA and the photochemical production of $HBrO_2$ from bromate ion in the absence of BrMA. Recent findings by Matsumura-Inoue et al.[25] showed that MA and BrMA contribute differently to the phase resetting of a BZ system in a CSTR when treated by light pulses.

The Ru-catalyzed minimal bromate oscillator studied by Kaminaga and Hanazaki[26] was found to exhibit various dynamic responses to pulsed light perturbations. Kaminaga and Hanazaki stress, in accordance with the suggestion by Kádár et al.,[24] the importance of the photoproduction of $HBrO_2$ and the induction of its autocatalytic production. Accordingly, no evidence of photoproduced bromide ions in the minimal bromate oscillator was found. Furthermore, numerical calculations[26] based on the Noyes−Field−Thompson mechanism,[27] which is the autocatalytic subset of the Field−Körös−Noyes[28] (FKN) mechanism of the BZ reaction, supported the proposed features.

Kuhnert et al.[6] explained the photoproduction of bromide ion by the interaction between the photoexcited $*Ru(bpy)_3^{2+}$ and bromate:

$$6*Ru(bpy)_3^{2+} + BrO_3^- + 6H^+ \rightarrow$$
$$6Ru(bpy)_3^{3+} + Br^- + 3H_2O \quad (1)$$
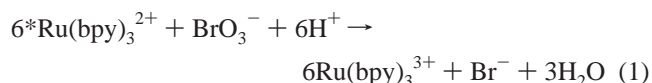
which according to Jingui et al.[10] might be thermodynamically allowed. As found by Hanazaki and co-workers,[11,14,19] light has a profound accelerating effect on the autocatalytic oxidation of $Ru(bpy)_3^{2+}$ by bromate ions,[26] where $HBrO_2$ also plays, according to these authors an important role in the bromide ion production:

$$*Ru(bpy)_3^{2+} + 3Ru(bpy)_3^{2+} + HBrO_2 + 3H^+ \rightarrow$$
$$4Ru(bpy)_3^{3+} + Br^- + 2H_2O \quad (2)$$
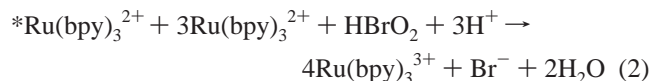
Agladze et al.[17] suggest two general routes for the production of photogenerated bromide ions. The first route involves the reaction scheme proposed by Sekiguchi et al.[29]

$$*Ru(bpy)_3^{2+} + Ru(bpy)_3^{2+} + BrO_3^- + 3H^+ \rightarrow$$
$$2Ru(bpy)_3^{3+} + HBrO_2 + H_2O \quad (3)$$
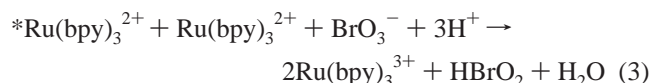
and the subsequent oxidation of BrMA by $Ru(bpy)_3^{3+}$ as the second route:

$$4Ru(bpy)_3^{3+} + BrMA + 2H_2O \rightarrow$$
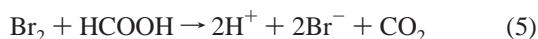$$4 Ru(bpy)_3^{2+} + HCOOH + 2CO_2 + Br^- + 5H^+ \quad (4)$$
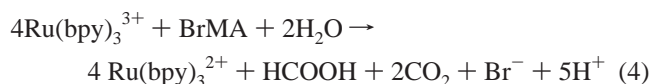
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with

$$Br_2 + HCOOH \rightarrow 2H^+ + 2Br^- + CO_2 \qquad (5)$$

On the other hand, Reddy et al.[18] stress the important role of molecular oxygen for the release of bromide ions.

Since the explanations of the authors cited above differ to some extent, and since phase response analysis is an interesting tool to analyze chemical oscillators, we decided to study the light-induced phase resetting in a closed and aging Ru-catalyzed BZ reaction in more detail. In this paper, we show that during the early stages of the reaction, when only little or no bromomalonic acid (BrMA) has been built up, light perturbations lead to phase response curves which are consistent with the photoproduction of $HBrO_2$. Later in the reaction, when BrMA is present, phase response curves indicate the photoproduction of bromide ions, with increasing phase delays as BrMA accumulates during the process. From these results we conclude that bromate ion alone cannot be a major source of photoproduced bromide ion as described by eq 1. However, another implication of our study is that in the presence of BrMA, photoproduced $HBrO_2$ may lead to the formation of bromide ion when bromo-organic compounds are present.
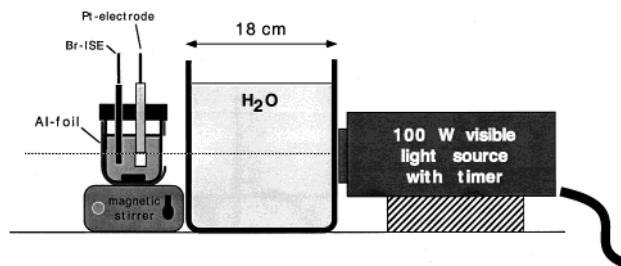
Experimental Section

Materials and Methods. All experiments were performed in a closed stirred thermostated glass reactor (Metrohm, Switzerland) at 20 °C. The reactor was wrapped with Al foil to avoid disturbances by ambient light. The reaction solution was stirred at 500 rpm using a magnetic stirrer. The oscillations were followed by means of a Pt electrode and a bromide-ion-selective electrode (Br-ISE, both Metrohm). The potential was measured against a double-junction Ag/AgCl reference electrode (Metrohm, sleeve type) using a saturated KCl solution as the inner electrode and a 1 M sulfuric acid solution (the reaction medium) as the outer electrolyte. The potentials were registered on a 2-channel YEW type 3066 pen recorder (Yokogawa, Japan).

All commercial chemicals were of analytical grade and used without further purification. Alkaline $NaBrO_2$ solutions were prepared by the method of Lee and Lister,[30] and BrMA was synthesized and twice recrystallized as described earlier.[31] When not otherwise stated, the standard initial concentrations of our BZ systems were 1 M sulfuric acid, 0.3 M organic substrate, 0.1 M sodium bromate, and 5×10^{-4} M $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (Aldrich, USA). From results of earlier studies,[32] we do not expect significant differences in the oscillatory behaviors when $Ru(bpy)_3Cl_2 \cdot 6H_2O$ or chloride-free Ru(II) salts are used.

Chemical perturbations were applied by adding perturbant solution into the reaction mixture. Pulse perturbations of white light were applied by means of a 100 W photosynthetic halogen lamp (Hansatech, USA). In order to avoid a warming-up of the reaction solution during illumination, the light passed through a large glass vessel which contained distilled water (Figure 1). The light beam entered the reactor through a window in the Al foil (Figure 1). The photon irradiance (fluence rate) inside the (empty) reactor was measured to 380 ($\pm$5) μmol m^{-2} s^{-1}, which was checked repeatedly to ensure that the same light intensity was applied in the different experiments.

Definition of Phase Shift. In previous experimental and theoretical studies of BZ phase response curves we have used the Pt electrode's response to determine period lengths and phase shifts.[33-35] The period length P_0 of an unperturbed oscillation is defined to be the time difference between two successive

Figure 1. Experimental setup. Reaction volume is 30 mL with the following standard initial concentrations: 1 M sulfuric acid, 0.3 M organic substrate, 0.1 M sodium bromate, and 5×10^{-4} M $Ru(bpy)_3$-$Cl_2 \cdot 6H_2O$.

maxima of the oxidized form of the catalyst ($M^{(n+1)+}$). Let $t_n = 0$ define the time of the nth maximum in the concentration of $M^{(n+1)+}$, while $t_{n+1} = P_0$ defines the succeeding one. The time interval between $t_n = 0$ and $t_{n+1} = P_0$ is referred to as one cycle. If a perturbation is applied during this cycle, the subsequent $M^{(n+1)+}$ maximum will appear at t_{app} which is generally different from P_0. The normalized *phase shift* $\Delta\Phi$ is then defined[33-35] to be

$$\Delta\Phi = (t_{app} - P_0)/P_0 \qquad (7)$$

When $t_{app} > P_0$ the $M^{(n+1)+}$ spike appears later than the unperturbed $M^{(n+1)+}$ maximum and the effect of the perturbation is a *delay* of the pulse. The phase shift is then *positive*. On the other hand, when the $M^{(n+1)+}$ maximum is earlier than P_0, we have an *advance* and the phase shift is *negative*. The sign and magnitude of $\Delta\Phi$ will depend on t_{per} the time between 0 and P_0, at which the perturbing pulse occurred. In the figures t_{per}/P_0 is called the *phase of perturbation*. A *phase response curve* (PRC) is a plot of $\Delta\Phi$ against t_{per}/P_0.

Results and Discussion

The Ru-catalyzed MA BZ reaction as studied here shows no induction period, i.e., oscillations start immediately. However, this is not a general feature of the system, as for other BZ systems (lower initial Ru(II) concentration or another organic substrate, as for example methylmalonic acid (MeMA)) an induction period is normally observed.[32]

When in the malonic acid system, light-perturbations were applied directly after the onset of oscillations (i.e., directly after mixing of the initial reagents), the phase response curves (Figure 2a) were similar to that of $HBrO_2$-perturbed BZ systems (Figure 2c).[35] Typical is the linear relationship between negative phase shifts (phase advances) and the phase of perturbation ("excitable branch")[33] which describes an immediate excitation to the oxidized state by the perturbation and indicates the removal of bromide ions.

Quite differently is the phase resetting behavior when light perturbations are applied 100−120 min after mixing of initial reagents (Figure 2b). Now light-perturbations result only in delays (positive phase shifts) indicating a release of bromide ions during the pulse. For comparison, Figure 2d shows a typical PRC for the Br^--perturbed BZ reaction.

When MeMA is used instead of MA, an induction period of about 70 min is observed. However, after the onset of oscillations, light causes only delays and the observed PRC is very similar to those of Figures 2b,d. As a rule, in the MeMA system we get almost straight-line PRCs (Figure 3a) and the slope increases linearly with pulse length (Figure 3b). Quite similar

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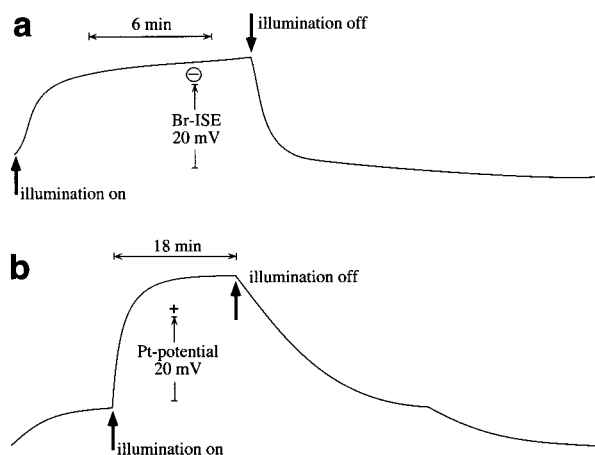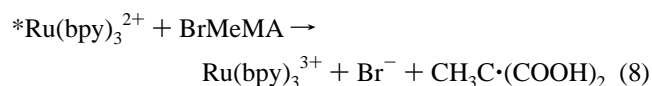*J. Phys. Chem. A, Vol. 104, No. 46, 2000* **10785**
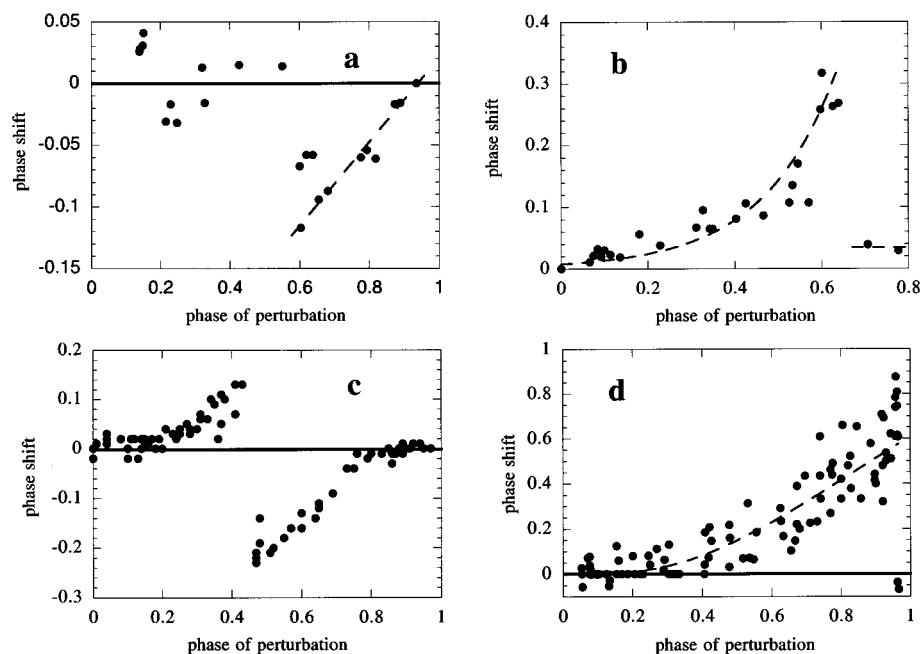
Figure 2. Comparison of phase response curves: (a) 5 s light pulse applied immediately after mixing of initial reagents and start of oscillations; (b) Same light pulse as in a, but 120 min after mixing of initial reagents; (c) 1.2 μM $HBrO_2$ as perturbant in a Ce-catalyzed system;[35] (d) 1 mM Br^- ion as perturbant applied immediately after mixing of initial reagents.
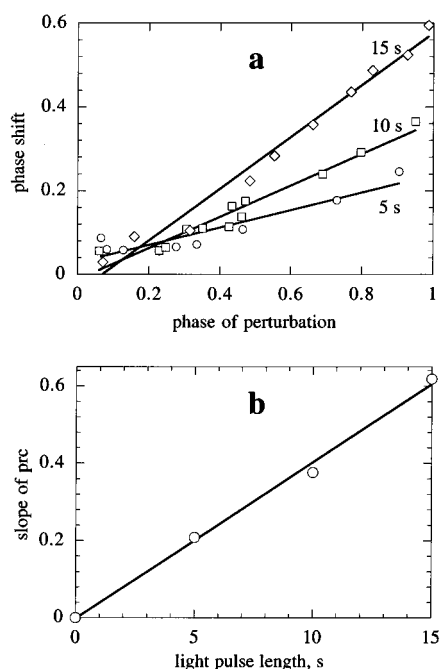
Figure 3. (a) Phase response curves of a light-perturbed Ru-catalyzed methylmalonic acid BZ reaction with pulse lengths of 5, 10, and 15 s. (c) Linear relationship between slopes of phase response curves (prc) in a and the applied light pulse lengths.

Figure 4. (a) Influence of light on the Ru(II)−BrMA subsystem ([Ru-(II)]$_0$ = 5 × 10^{-4} M, [BrMA]$_0$ = 0.3 M). (b) Influence of light on the Ru(II)−MA subsystem, approximately 60 min after mixing. Same initial concentrations as in a.

behaviors have been found for other substituted malonic acid derivatives RMA, although the response toward light is getting weaker for larger R.
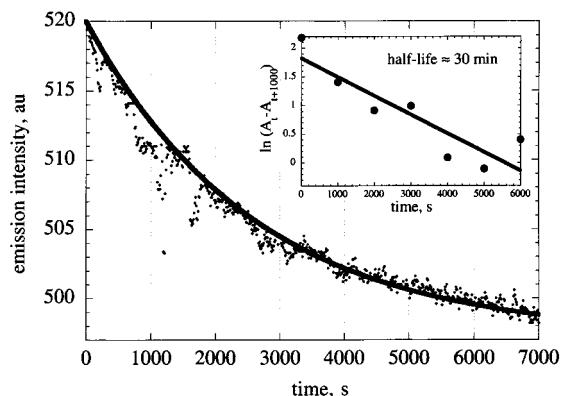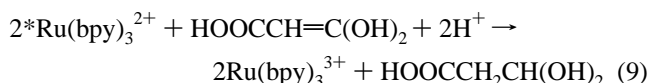
We believe that the increase of slope with increasing light pulse length (Figure 3b) may be related to an (oxidative) quenching process between the excited *Ru(bpy)$_3$$^{2+}$ and BrMe-MA (or BrMA) (in sense of a Stern−Volmer plot)

$$*Ru(bpy)_3{}^{2+} + BrMeMA \rightarrow$$
$$Ru(bpy)_3{}^{3+} + Br^- + CH_3C\cdot(COOH)_2 \quad (8)$$

The observation of Kádár et al.[24] that the BrMA−Ru(bpy)$_3$$^{2+}$ subset of the BZ reaction exhibits photoproduction of bromide ion in the absence of bromate, seems to be in accordance with such a process. Our observations with BrMA suggest (Figure 4a) that the oxidative quenching may be only partly reversible, since after a break of illumination bromide ions are not fully consumed again. In fact, if periods of light and darkness are given repeatedly, the final bromide ion steady state concentration increases during each light on/off cycles. During these illumination and darkness cycles the potential of the Pt electrode shifts to positive and negative values, correspondingly.

It is remarkable that even the sulfuric acid−Ru(bpy)$_3$$^{2+}$−RMA (R = H-, CH$_3$-, ethyl-, butyl-, benzyl-, phenyl) systems are photosensitive too! Although the potential of the Br−ISE does not change (no bromide ions are present), the potential of the Pt electrode shifts to positive values during illumination and resets back when illumination is off (Figure 4b). This does not happen when RMA is absent. In all probability, this is another case of oxidative quenching by the organic substrate. In case
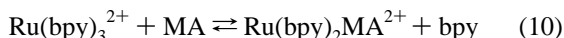
Figure 5. Emission intensity at 598 nm of a 5×10^{-5} M Ru(II) solution in 1 M sulfuric acid and in the presence of 0.3 M MA. The excitation wavelength is 452 nm. Solid line represents the obtained relaxation kinetics from a Guggenheim plot. Inset: Guggenheim plot analysis for intervals taken every 1000 s. The estimated half-life for the first-order fluorescence decay is approximately 30 min.

of MA, we can write

$$2*Ru(bpy)_3^{2+} + HOOCCH=C(OH)_2 + 2H^+ \rightarrow$$
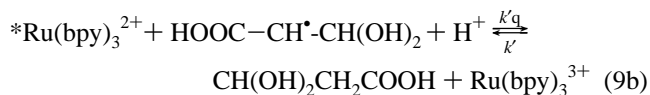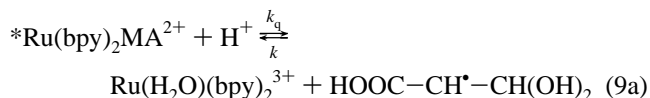$$2Ru(bpy)_3^{3+} + HOOCCH_2CH(OH)_2 \quad (9)$$

However, this photoresponse does not occur immediately after the initial reagents have been mixed. Only about 60 min after mixing of initial reagents its photosensitivity can be observed, but decreases again during the next couple of hours. We suspect that this response is due to the following slow substitution process:

$$Ru(bpy)_3^{2+} + MA \rightleftharpoons Ru(bpy)_2MA^{2+} + bpy \quad (10)$$

Although no changes in the absorption spectrum of the Ru-(bpy)$_3$$^{2+}$ in the presence of MA were detectable, a change in the Ru(II) fluorescence emission at 598 nm were observed. Guggenheim plot analysis indicates a reversible first-order half-life of approximately 30 min (Figure 5), which is the time scale when maximum light sensitivity is observed.

The oxidative quenching process (9) consists probably of the following two reversible steps:

$$*Ru(bpy)_2MA^{2+} + H^+ \underset{k}{\overset{k_q}{\rightleftharpoons}}$$
$$Ru(H_2O)(bpy)_2^{3+} + HOOC-CH^\bullet-CH(OH)_2 \quad (9a)$$

$$*Ru(bpy)_3^{2+} + HOOC-CH^\bullet-CH(OH)_2 + H^+ \underset{k'}{\overset{k'_q}{\rightleftharpoons}}$$
$$CH(OH)_2CH_2COOH + Ru(bpy)_3^{3+} \quad (9b)$$

In the absence of illumination, the reverse reactions lead only to the nonexcited Ru(II) species. The slow substitution reaction 10 will lead to that the second process (9b) cannot fully proceed, since all Ru(II) is slowly converted to Ru(bpy)$_2$MA^{2+}.

The Pt potential of the R(II)/Ru(III) redox couple is given by Nernst's equation

$$E = E^\circ + \frac{RT}{F}\ln\left(\frac{[Ru(III)]}{[Ru(II)]}\right) \quad (11)$$

The steady state value of the total Ru(III) concentration under constant illumination can be estimated by the steady-state Ru(III)
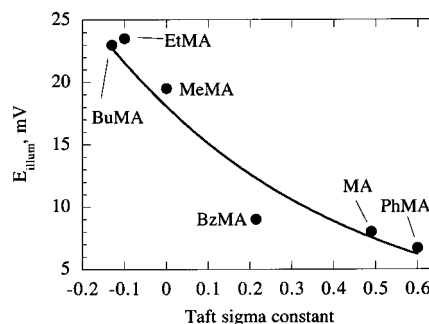
Figure 6. E_{illum} (eq 15) as a function of the Taft σ^* constant for different illuminated Ru(II)−RMA subsystems. Initial concentrations as those in Figure 4b.

values from eqs 9a and 9b:

$$[Ru(III)]_{\text{steady state}} = \left\{\frac{k_q[*Ru(bpy)_2MA^{2+}]}{k[R^\bullet]} + \frac{k_q'[R^\bullet][*Ru(bpy)_3^{2+}]}{k'[ROH]}\right\} \quad (12)$$

While $R^\bullet$ is expected to be a short-lived species present at low concentrations, ROH can be considered as stable and accumulating, such that the second term in eq 12 can be neglected. In such a case, $[Ru(III)]_{\text{steady state}}$ can be estimated as

$$[Ru(III)]_{\text{steady state}} = \frac{k_q[*Ru(bpy)_2MA^{2+}]}{k[R^\bullet]} \quad (13)$$

Because at constant illumination a certain fraction of Ru(II) will stay in the excited state, *Ru(II), we can write

$$[*Ru(II)] = \gamma[Ru(II)], \quad 1 > \gamma > 0 \quad (14)$$

Thus, under constant illumination the Pt potential can be written as

$$E_{\text{illum}} = E^\circ + \frac{RT}{F}\ln\left\{\frac{[Ru(III)]_{\text{steady state}}}{[Ru(II)]}\right\} = E^\circ + \frac{RT}{F}\ln\left\{\frac{k_q\gamma}{k[R^\bullet]}\right\} \quad (15)$$

To see whether eq 15 gives a correct trend of the potential under illumination we added 25 mM acrylamide, a radical scavenger, to the system. Also acrylonitrile[36] can be used as a radical scavenger. In accordance with a decrease in [R$^\bullet$], we observed a 5−7% increase in E_{illum}.

Because the E_{illum} determining step (9a) involves the abstraction of an electron from Ru(II)-complexed malonic acid, a systematic change in E_{illum} may be expected when R-substituted malonic acids (RMA) are used instead of MA. By using different RMA, we found that E_{illum} depends on R in a Taft-like fashion (Figure 6), which appears to reflect the substitutent effect on the quenching constant k_q and possibly also on the rate constant k.

The positive phase shifts as observed in a system in the presence of BrMA (Figure 2b, Figure 3) are consistent with photoproduced Br$^-$ ion from BrMA via photoexcited Ru(II)* as shown by Kádár et al.[24] At first sight it is not obvious that identical light pulses (with the same amount of photons) should lead to increasing positive phase shifts (delays) as BrMA concentration increases, because these light pulses should generate the same amount of bromide ion from the BrMA pool. In order to see whether the amount of BrMA has an influence
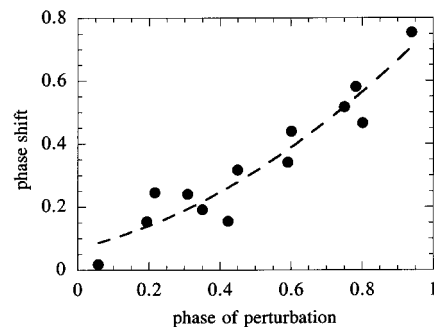
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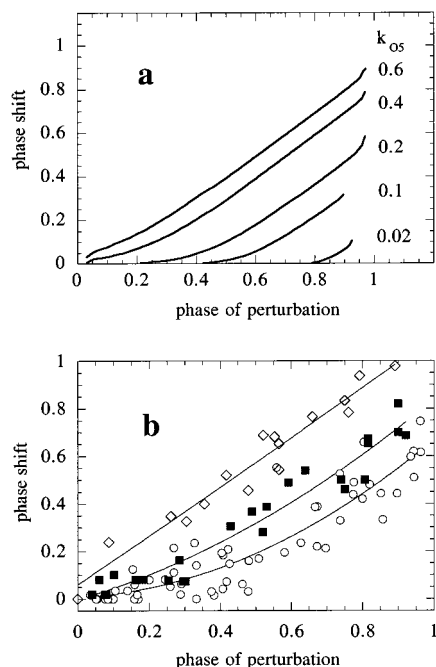
Figure 7. (a) Calculated phase shifts of the Br$^-$-perturbed (1 mM) Oregonator model with Field–Försterling parametrization and varying k_{O5}. (b) Experimental phase response curves performed in a series of Br$^-$-perturbed (1 mM) Ru-catalyzed MA BZ reactions with varying amounts of initial concentration of MA and BrMA. Open circles: 0.3 M MA; solid squares: 0.15 M MA and 0.15 M BrMA; open diamonds: 0.225 M BrMA and 0.125 M MA.

on the resetting of photoproduced bromide ion in the BZ reaction, we first investigated the behavior of the bromide-ion-perturbed original Oregonator model[37] using the Field–Försterling rate constants:[38]

$$A + Y \rightarrow X + P \qquad (O1)$$

$$X + Y \rightarrow 2P \qquad (O2)$$

$$A + X \rightarrow 2X + Z \qquad (O3)$$

$$2X \rightarrow A + P \qquad (O4)$$

$$Z \rightarrow fY \qquad (O5)$$

In this minimal model of the FKN[28] mechanism, X, Y, and Z are kinetic variables, describing the species HBrO$_2$, Br$^-$, and the oxidized from of the catalyst, (Ru(III)), respectively. Variable A corresponds to a fixed amount of BrO$_3^-$, while P represents HOBr.

In order to mimic an increasing amount of BrMA by the model, we increased k_{O5}, which is the rate constant of the bromide-regeneration step O5 between BrMA ([BrMA] is incorporated into k_{O5}) and the oxidized form of the catalyst Z. By applying a bromide ion perturbing pulse of 1 mM, we indeed found an increase in positive phase shifts with increasing k_{O5} (Figure 7a). To further check these results experimentally, we applied the same bromide-ion perturbing pulse in a BZ reaction where 50 and 75% of the initial MA concentration (0.3 M) has been replaced by BrMA. As predicted by the Oregonator, we find a corresponding increase in the experimental phase shifts at higher initial concentrations of BrMA (Figure 7b). These results, together with those of Figures 2 and 3, support the conclusions by Hanazaki and co-workers[11,14,19] and those by Kádár et al.[24] that dependent on whether BrMA is absent or present, either HBrO$_2$ or Br$^-$ ions are intermediates produced

Figure 8. Phase response curve of the HBrO$_2$-perturbed Ru-catalyzed MeMA BZ system. The composition of the oscillator is as described in Figure 1. The concentration of perturbing HBrO$_2$ is estimated to be approximately 1×10^{-4} M.

in the light-perturbed Ru-catalyzed BZ reaction. A recent modification of the Oregonator model which includes BrMA as a fourth variable is aimed to describe photoinduced behaviors in Ru-catalyzed BZ systems.[39]

However, our results indicate the possibility of still an additional reaction channel. Because HBrO$_2$ may be expected to be photoproduced independently of BrMA (eq 3), the in situ formed HBrO$_2$, may, like the oxidized form of the catalyst, react with BrMA (or other bromoorganic compounds) and thus produce bromide ions. In fact, on perturbing the MeMA–Ru-catalyzed BZ reaction with NaBrO$_2$, only positive phase shifts are being observed, indicating that Br$^-$ ion may be formed from BrMeMA (Figure 8). Such a reaction may also explain the observed positive phase shifts in the NaBrO$_2$-perturbed MA oscillator (Figure 2c), which so far has not been satisfactorily described by Oregonator-type of models.[35] In order to explicitly verify a reaction channel between HBrO$_2$ and bromoorganics, we consider to study these reactions in more detail in future work.

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