

Influence of Visible Light and Malonic Acid Derivatives on the Autocatalytic Oxidation of Ru(II) by Bromate Ions

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The influence of visible light on the autocatalytic oxidation of Ru(II) by bromate ions has been investigated. The inflection time (IT) was measured in darkness, at constant illumination, or as a function of the length of a perturbing light pulse. Measurements were performed without organic substrate, as well as in the presence of the malonic acid derivatives HOOC–CHR–COOH (RMA), with R being H, methyl-, ethyl-, *n*-butyl-, or the benzyl-group. The presence of RMA influences the length of the inflection time in darkness and for light-perturbed conditions. In the presence of benzylmalonic acid (BzMA), small amplitude oscillations are observed in darkness at the end of the autocatalytic oxidation of Ru(II). The most pregnant effects of RMA are observed by malonic acid (MA). At constant illumination, the inflection time is found to increase with increasing MA concentration and small-amplitude oscillations can even be observed in the preexponential phase of the Ru(II) oxidation. Model calculations based on a modified Noyes–Field–Thompson mechanism are in accordance with experimental observations. The calculations suggest that the small-amplitude oscillations observed in the BzMA and MA systems are due to second-order organic radical recombination.

Introduction

During recent years, an increasing number of studies have dealt with light-sensitive oscillatory chemical reactions. Busse and Hess¹ found that chemical waves can be initiated by use of ultraviolet (UV) light in a ferroin-catalyzed Belousov–Zhabotinsky (BZ) reaction. As soon as in 1968, Zhabotinsky and co-workers^{2,3} described that in cerium-catalyzed BZ systems, oscillations can be modified or even stopped by UV irradiation. Gaspar et al.⁴ described significant changes in the amplitude and frequency of oscillations induced by visible light in ruthenium- and ferroin-catalyzed BZ systems. Sharma and Noyes⁵ reported effects of light also in the Bray–Liebhafsky (BL) oscillatory reaction, and De Kepper and co-workers^{6,7} found similar effects in the Briggs–Rauscher (BR) reaction. Quite recently, it was found that light induces oscillations in the H₂O₂–Fe(CN)₆^{4–} system in a continuously stirred tank reactor (CSTR).^{8,9}

As far as Ru(II)-catalyzed BZ systems are concerned, light works both as an inhibitor and promotor of temporal^{4,10–16} and spatial^{17–22} oscillations. The work dealing with the influence of light on the Ru(II)-catalyzed BZ systems can be divided into two groups. The first group deals with the inorganic subset of the BZ reaction (the autocatalytic oxidation of Ru(II) by bromate), and the second one is focused on the reduction of Ru(III) with the organic substrate (malonic acid or bromomalonic acid). The main attention in both cases has been paid to the photoinhibition of oscillations because of photoproduced bromide ions which are known to inhibit the oxidation of the reduced form of the catalyst by bromate, in accordance with

the Field–Körös–Noyes (FKN) mechanism.²³ According to Kádár et al.,²⁴ irradiation of the Ru(II)-catalyzed BZ system gives rise to two separate processes: (1) the photochemical production of bromide ion from bromomalonic acid (BrMA) and (2) the photochemical production of bromous acid (HBrO₂) from bromate ion.

Since the cited papers differ in their interpretation about the role of the “inorganic subset” of the Ru(II)-catalyzed BZ systems, we devoted our attention to the study of the autocatalytic oxidation of the Ru(II) ions by bromate in detail. In subsequence to our previous work,²⁵ the main goal of this work was to study the effect of light on the autocatalytic oxidation of Ru(II) by bromate in the absence as well as in the presence of malonic acid derivatives.

Materials and Methods

Sulfuric acid, NaBrO₃ (both Merck), malonic acid (MA), and its derivatives methylmalonic acid (MeMA), ethylmalonic acid (EtMA), *n*-butylmalonic acid (BuMA), and benzylmalonic acid (BzMA) were of commercial analytical quality (all Fluka, Aldrich). Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate, Ru(bpy)₃Cl₂·6H₂O, (Aldrich) was used without further purification. Ru(phen)₃(ClO₄)₂ was prepared at Prof. Matsumura's laboratory, Department of Chemistry, Nara University of Education, Japan.²⁶ 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 prepared by mixing initial reagent solutions in the following order: sulfuric acid, NaBrO₃, organic acid (if applied), and finally the catalyst. 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, Metrohm). The potentials were measured against a double-junction Ag/AgCl reference electrode (Metrohm, sleeve type) using a saturated

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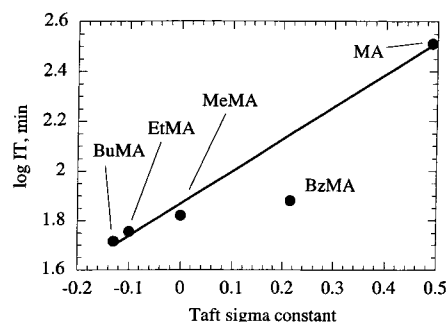


Figure 1. The logarithm of inflection time of the oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ by bromate as a function of the Taft sigma constants for the different R-substituted malonic acids RMA. The Taft sigma constants σ_R^* and inflection times (in parentheses) for the malonic acid substituents are $\sigma_{\text{Bu}}^* = -0.13$ (31 min); $\sigma_{\text{Et}}^* = -0.10$ (57 min); $\sigma_{\text{Me}}^* = 0.00$ (66.2 min); $\sigma_{\text{Bz}}^* = +0.215$ (76 min); $\sigma_{\text{H}}^* = +0.49$ (325 min). Initial concentrations: 1 M H_2SO_4 , 5×10^{-4} M $\text{Ru}(\text{bpy})_3^{2+}$, 5×10^{-2} M NaBrO_3 , and 0.01 M RMA. Solid line shows linear regression without including the data of BzMA.

KCl solution as the inner electrolyte and a 1 M sulfuric acid solution (the reaction medium) as the outer electrolyte. The potentials of the Pt-electrode and the Br-ISE provide measures of the $\log\{[\text{Ru(III)}]/[\text{Ru(II)}]\}$ and $\log[\text{Br}^-]$ concentrations, respectively. The potentials were registered on a two-channel YEW type 3066 pen recorder (Yokogawa, Japan).

Illumination by white light was carried out by means of a 100-W photosynthetic halogen lamp (Hansatech, USA). To avoid a warming-up of the reaction solution during illumination, the light passed a large glass vessel which contained distilled water. The light beam entered the reactor through a window in the Al-foil. The photon irradiance (fluence rate) inside the (empty) reactor was measured to $380 (\pm 5) \mu\text{mol m}^{-2} \text{s}^{-1}$, which was checked repeatedly to ensure that the same light intensity was applied in the different experiments. For details of the experimental setup, see ref 27.

Integration of the rate equations from the reaction kinetic model were performed with a double-precision version of LSODE.²⁸

To quantify the autocatalytic oxidation of Ru(II) ions by bromate, we determine (both in the experiments and in the model calculations) the reaction's inflection time (IT), that is, the elapsed time between mixing of the reagents and the inflection point of the sigmoidal autocatalytic $[\text{Ru(III)}]$ curve. The inflection point is the time point where the production rate of Ru(III) ions is at a maximum.

Experimental Results

Influence of Substituted Malonic Acid Derivatives on Inflection Time in Non-Illuminated Systems. As in our previous work on the Ce(III) oxidation by bromate,²⁵ we observe also in the nonilluminated $\text{Ru}(\text{bpy})_3^{2+}$ system a systematic change of the inflection time (IT) in the presence of various R-substituted malonic acids RMA. Plotting the logarithm of IT as a function of the Taft sigma constant²⁹ of the substituent R, σ_R^* , gives a straight line (Figure 1). Such a linear Taft plot indicates that the oxidation of the alkyl-substituted malonic acids by bromate probably follows the same mechanism. In addition, the Taft plot also allows to estimate the inflection times for other alkyl-substituted malonic acids on the basis of their σ_R^* values. In accordance with previous results on Ce(III)-bromate systems,²⁵ an exception in the linear IT- σ_R^* relationship is BzMA: in this case, a significant lower IT value is observed. The oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ ions by bromate in the presence

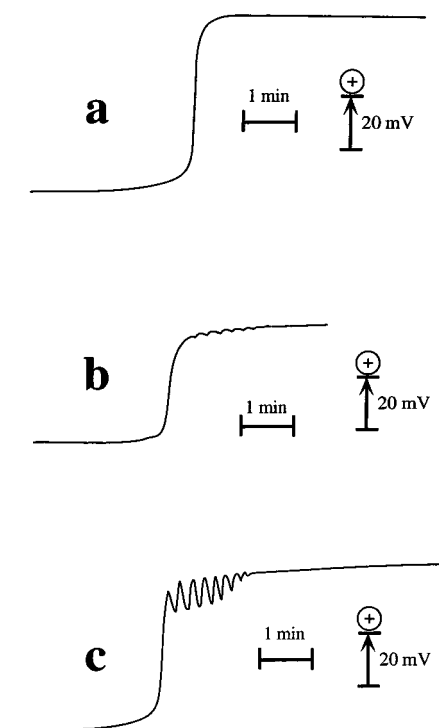


Figure 2. The oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ by bromate in the presence of BzMA without illumination. $[\text{H}_2\text{SO}_4] = 1$ M, $[\text{Ru}(\text{bpy})_3\text{Cl}_2] = 5 \times 10^{-4}$ M, $[\text{NaBrO}_3] = 5 \times 10^{-2}$ M. (a) $[\text{BzMA}] = 5 \times 10^{-3}$ M, (b) $[\text{BzMA}] = 1 \times 10^{-2}$ M, (c) $[\text{BzMA}] = 2 \times 10^{-2}$ M. For values of inflection times, see Table 1.

TABLE 1: Inflection Time as a Function of Initial BzMA Concentration^a

$10^2 \times [\text{BzMA}], \text{M}$	inflection time, min
0.5	36.9
1.0	36.4
2.0	35.7

^a 1 M H_2SO_4 , 5×10^{-4} M $\text{Ru}(\text{bpy})_3\text{Cl}_2$, 5×10^{-2} M NaBrO_3 .

of BzMA is remarkable also in another way: after the inflection time, at high Ru(III) concentrations, we observe the occurrence of small-amplitude oscillations (Figure 2). In the presence of BzMA, the inflection time (IT) decreases slightly with increasing BzMA concentrations (Table 1).

Inflection Time in Illuminated Systems. If we apply different light pulses on the inorganic $\text{Ru}(\text{bpy})_3\text{Cl}_2$ -bromate reaction system, we observe a remarkable influence of light on the inflection time. With increasing length of the light pulse, the value of the inflection time (IT) decreases (Figure 3). We measured the same dependence also for the oxidation of $\text{Ru}(\text{phen})_3(\text{ClO}_2)_2$ ions by bromate to get results with a similar system (Figure 4). If we plot the reciprocal value of inflection time, which corresponds to the value of the averaged rate constant of autocatalysis (see Appendix), as a function of the length of light pulse, we obtain a sigmoidal curve. In the absence of organic substrate, the "most efficient" light pulse has a duration of about 15–20 s corresponding to the inflection point in the graph (Figure 5a).

The relationship between inflection time and light-pulse length is also influenced by the type of organic substrate present. Excluding MA for the moment, we see that going from MeMA to EtMA, the inflection time increases but decreases again for BuMA approaching the values of a system without organic substrate (Figure 5b). If we plot $1/\text{IT}$ as a function of the length of the perturbing light pulse, we get a sigmoidal curve indicating

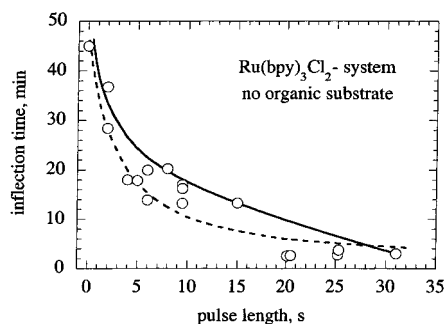


Figure 3. Inflection time as function of the length of light pulse in the absence of organic substrate. $[\text{H}_2\text{SO}_4] = 1 \text{ M}$, $[\text{Ru}(\text{bpy})_3\text{Cl}_2] = 5 \times 10^{-4} \text{ M}$, $[\text{NaBrO}_3] = 5 \times 10^{-2} \text{ M}$, $T = 20^\circ\text{C}$. Solid line: model computations using simple autocatalysis; dashed line: use of extended NFT mechanism, $k_{36} = 3.2 \times 10^{-5} \text{ s}^{-1}$, $k_{37} = 2.05 \text{ M}^{-3} \text{ s}^{-1}$.

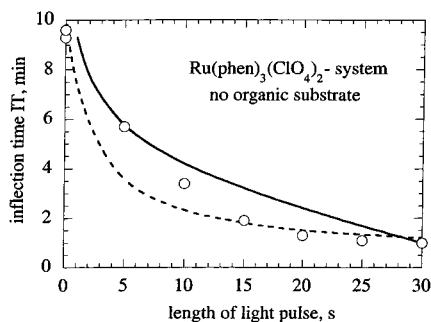


Figure 4. Effect of light pulses on the oxidation of $\text{Ru}(\text{phen})_3(\text{ClO}_4)_2$ by bromate. $[\text{H}_2\text{SO}_4] = 1 \text{ M}$, $[\text{Ru}(\text{phen})_3(\text{ClO}_4)_2] = 5 \times 10^{-4} \text{ M}$, $[\text{NaBrO}_3] = 5 \times 10^{-2} \text{ M}$, $T = 20^\circ\text{C}$. Solid line: model computations using simple autocatalysis; dashed line: use of extended NFT mechanism, $k_{36} = 3.2 \times 10^{-5} \text{ s}^{-1}$, $k_{37} = 2.05 \text{ M}^{-3} \text{ s}^{-1}$, but $[\text{Cl}^-]_0 = 0.2 \text{ mM}$ instead of 1 mM .

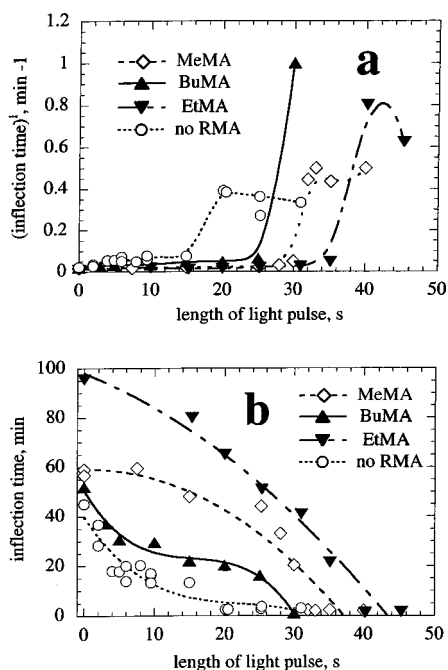


Figure 5. Inverse of inflection time (a) and inflection time (b) as a function of the length of light pulse in the presence of malonic acid derivatives. Initial concentration of reactants as in Figure 3, $[\text{RMA}] = 0.01 \text{ M}$, $T = 20^\circ\text{C}$.

the effectiveness of the light pulse on the autocatalysis specific to the present substrate (Figure 5a).

Extraordinary Influence of Malonic Acid. As it is seen from the Taft plot (Figure 1), MA has a large influence on the

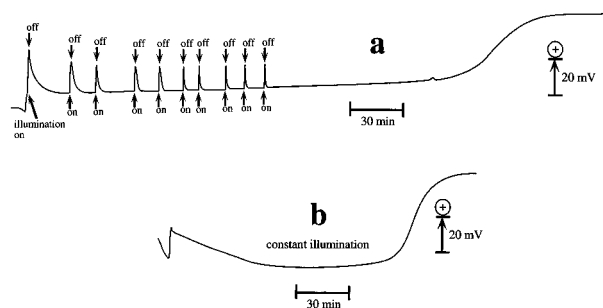


Figure 6. Effect of 30-s light pulses or constant illumination on the autocatalysis in the presence of MA. $[\text{MA}] = 0.01 \text{ M}$, initial concentrations of reactants as in Figure 3; (a) Ten 30-s light-pulses; (b) constant illumination.

inflection time already in darkness. In addition, MA has also an extraordinary influence on the effect of light on the autocatalytic oxidation of $\text{Ru}(\text{II})$ by bromate (Figure 6). In the presence of MA, even several 1-min (subcritical) light pulses do not cause a start of the autocatalysis (which in absence of MA is normally observed). After each light pulse, the system returns rapidly to the reduced steady state. The amplitude and the width of these excursions diminish with time. The potential of the Br-ISE indicates a decrease of the bromide ions' concentration whenever the light pulse is applied and a "photoconsumption" of bromide is observed under these conditions (data not shown). For example, if 10 1-min light pulses are applied, the inflection time decreases from 325 min (without light) to 265 min (Figure 6a).

If continuous illumination is applied, the inflection time decreases from 325 min without light (or from the value of 265 min when 10 1-min light pulses are applied) to 144 min (Figure 6b). In addition, the slope of the tangent in the inflection point increases about twice. Interestingly, decreasing the initial MA concentration between 0.002 to 0.0075 M leads at constant illumination first to the onset of oscillations followed by the start of the autocatalytic oxidation of $\text{Ru}(\text{II})$. By the time the autocatalysis is started, the oscillations have stopped (Figure 7). For example, when the initial concentration of MA is 50% decreased (to 0.005 M), constant illumination will first lead to oscillations followed by the nonoscillatory autocatalysis with an inflection time of 60.6 min. The same system, that is, the same composition with the same initial concentrations of its components, but without any light perturbation, does not exhibit oscillations and the inflection time has tripled to the value of 180 min! At constant illumination, the threshold MA concentration, that is, the lowest MA concentration at which the transient oscillations are still observed, is 0.002 M (Figure 7). If the initial MA concentration is reduced below threshold MA concentration, no oscillations occur, but the presence of MA still has a remarkable effect on inflection time: at 0.001 M MA the inflection time is 31.5 min, while in the absence of MA it is 1–2 s. The dependence of inflection time on the MA concentration under constant illumination is seen in Figure 8. The inflection time increases practically linearly with increasing concentration of MA.

Influence of Chloride Ions on Inflection Time. Chloride ions increase the inflection time of the autocatalytic oxidation of various BZ catalysts. As seen in Table 2, a 1 mM initial concentration of Cl^- has already a considerable effect. This is also indicated by the larger inflection time of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (Figure 3) compared with $\text{Ru}(\text{phen})_3(\text{ClO}_4)_2$ (Figure 4).

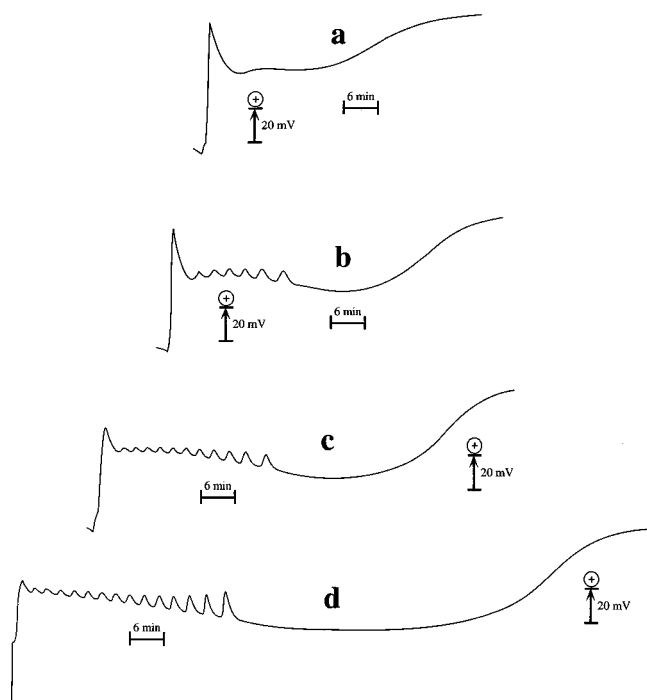


Figure 7. Transient oscillations and inflection time of autocatalysis at constant illumination in the dependence on the MA concentration. $[\text{H}_2\text{SO}_4] = 1 \text{ M}$, $[\text{Ru}(\text{bpy})_3\text{Cl}_2] = 5 \times 10^{-4} \text{ M}$, $[\text{NaBrO}_3] = 5 \times 10^{-2} \text{ M}$, $T = 20^\circ\text{C}$, (a) $[\text{MA}] = 10^{-3} \text{ M}$, (b) $[\text{MA}] = 2 \times 10^{-3} \text{ M}$, (c) $[\text{MA}] = 3 \times 10^{-3} \text{ M}$, (d) $[\text{MA}] = 7.5 \times 10^{-3} \text{ M}$.

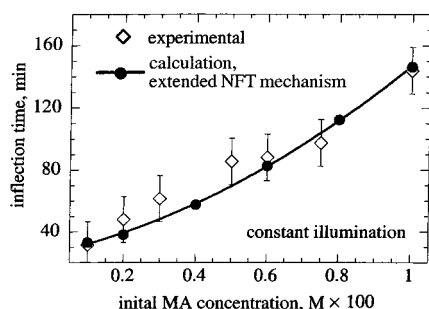


Figure 8. The dependence of inflection time on the concentration of MA at constant illumination. Initial concentrations of reactants as in Figure 3. Experimental values are means of three repetitive experiments. Values of variable rate constants used in the calculations: $k_{17} = 1.3 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$, $k_{19} = 6.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, $k_{20}[\text{O}_2] = 5.15 \times 10^9 \text{ s}^{-1}$, $k_{21} = 6.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, $k_{23} = 7.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, $k_{27} = 0 \text{ M}^{-1}\text{s}^{-1}$, $k_{36} = 1 \times 10^{-7} \text{ s}^{-1}$, $k_{37} = 0.02 \text{ M}^{-3}\text{s}^{-1}$.

TABLE 2: Inflection Times for Various Catalysts and in the Presence of Chloride Ions^a

catalyst	inflection time	inflection time (1 mM Cl^- ions added initially)
$\text{Ce}(\text{NO}_3)_3$	14 s	79 min
$\text{Fe}(\text{phen})_3\text{SO}_4$	14 s	7.5 min
$\text{Ru}(\text{phen})_3(\text{ClO}_4)_2$	9.5 min	
$\text{Ru}(\text{bpy})_3\text{Cl}_2$	45 min	

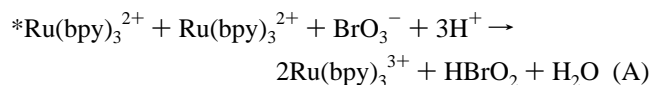
^a 1 M H_2SO_4 , $5 \times 10^{-4} \text{ M}$ catalyst, $5 \times 10^{-2} \text{ M}$ NaBrO_3 .

Model Calculations

Modeling the Influence of Light by Simple Autocatalysis.

On the basis of the results described above, we can see that a light pulse or constant illumination accelerates the autocatalytic oxidation of Ru(II) by bromate ion. As proposed by Kaminaga and Hanazaki³⁰ and Kádár et al.,²⁴ this effect is due to the

photoproduction of the autocatalytic species HBrO_2 (process A) where $^*\text{Ru}(\text{bpy})_3^{2+}$ is the photoexcited catalyst.



Also, recently performed phase-response experiments of a light-perturbed Ru-catalyzed BZ reaction supports this view.²⁷ A semiquantitative description of the influence of light pulses can already be given by considering the following simple autocatalytic reaction R1:



where B denotes the autocatalytically produced species HBrO_2 . The inflection time of process R1 will be influenced by the presence of small amounts of product B or by the presence of a (more or less slow) uncatalyzed reaction pathway leading to B. Here we assume, as indicated by process R1, that a light pulse produces a certain amount of B (HBrO_2). The longer the light pulse lasts, the more B is produced initially. Let time $t = 0$ denote the end of the light pulse with initial concentrations of A and B being $[\text{A}]_0$ and $[\text{B}]_0$, respectively. Integrating the rate equation of reaction R1 (see Appendix) leads to the following time dependence of the concentration of A

$$[\text{A}] = \frac{\Delta_0[\text{A}]_0}{[\text{A}]_0 + [\text{B}]_0 \exp(k\Delta_0 t)} \quad (1)$$

where $\Delta_0 = [\text{A}]_0 + [\text{B}]_0$. It can easily be shown that at the inflection point the concentration in A ($[\text{A}]_{\text{infl}}$) is given by

$$[\text{A}]_{\text{infl}} = \frac{\Delta_0}{2} \quad (2)$$

with the inflection time IT

$$\text{IT} = \frac{1}{k\Delta_0} \ln\left(\frac{[\text{A}]_0}{[\text{B}]_0}\right) \quad (3)$$

The concentration of B after the light pulse is assumed to be proportional to the length of the HBrO_2 -producing light pulse (PL), that is,

$$[\text{B}]_0 = \alpha \times \text{PL} \quad (4)$$

We have used eq 3 to describe the influence of light-pulse lengths both for the $\text{Ru}(\text{bpy})_3\text{Cl}_2$ and the $\text{Ru}(\text{phen})_3(\text{ClO}_4)_2$ system, where α (eq 4) and the rate constant k (process R1) are considered as adjustable parameters. The solid lines in Figures 3 and 4 are the results from such a fit. We see that the simple autocatalytic model gives already a fair description of the kinetics and provides further evidence that light produces HBrO_2 in the absence of bromo-organic species.

Modeling the Influence of Light by an extended NFT Mechanism. The basic mechanism of the one-electron autocatalytic oxidation of a transition-metal ion by bromate ion has been given by Noyes, Field, and Thompson (NFT)³¹ and is an important part for the by Field–Körös and Noyes (FKN) proposed mechanism of the oscillatory Belousov–Zhabotinsky (BZ) reaction.²³ On the basis of our previous studies on the Ce-system,²⁵ we have considered the following extended NFT

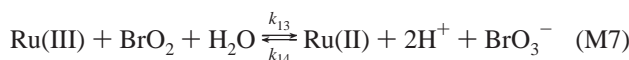
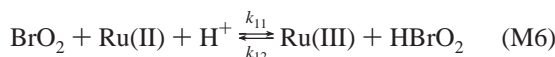
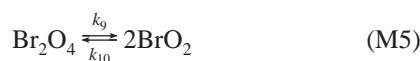
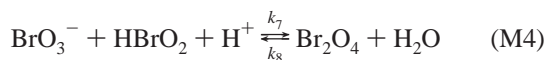
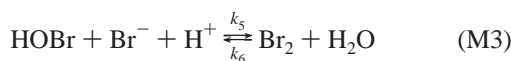
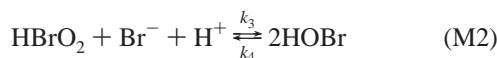
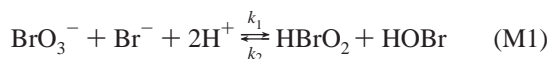
TABLE 3: Rate Constant Values in Extended NFT Model

$k_1 = 1.6 \text{ M}^{-3}\text{s}^{-1}$	$k_{15} = 3.3 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$	$k_{29} = 100 \text{ M}^{-1}\text{s}^{-1}$
$k_2 = 3.2 \text{ M}^{-1}\text{s}^{-1}$	$k_{16} = 1.8 \times 10^{-8} \text{ M}^{-2}\text{s}^{-1}$	$k_{30} = 30 \text{ M}^{-1}\text{s}^{-1}$
$k_3 = 2.5 \times 10^6 \text{ M}^{-2}\text{s}^{-1}$	k_{17} , treated as variable	$k_{31} = 0 \text{ M}^{-1}\text{s}^{-1}$
$k_4 = 2 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$	$k_{18} = 0.01 \text{ M}^{-2}\text{s}^{-1}$	$k_{32} = 7 \text{ s}^{-1}$
$k_5 = 8 \times 10^9 \text{ M}^{-2}\text{s}^{-1}$	k_{19} , treated as variable	$k_{33} = 1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$
$k_6 = 80 \text{ M}^{-1}\text{s}^{-1}$	k_{20} , treated as variable	$k_{34} = 4 \times 10^{-4} \text{ s}^{-1}$
$k_7 = 33 \text{ M}^{-2}\text{s}^{-1}$	k_{21} , treated as variable	$k_{35} = 0 \text{ M}^{-1}\text{s}^{-1}$
$k_8 = 2.2 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$	$k_{22} = 0.08 \text{ M}^{-1}\text{s}^{-1}$	k_{36} , treated as variable
$k_9 = 7.5 \times 10^4 \text{ s}^{-1}$	k_{23} , treated as variable	k_{37} , treated as variable
$k_{10} = 1.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	$k_{24} = 0 \text{ s}^{-1}$	$k_{38} = 1 \times 10^8 \text{ M}^{-2}\text{s}^{-1}$
$k_{11} = 4 \times 10^6 \text{ M}^{-2}\text{s}^{-1a}$	$k_{25} = 0 \text{ M}^{-1}\text{s}^{-1}$	$k_{39} = 1.626 \times 10^2 \text{ M}^{-2}\text{s}^{-1}$
$k_{12} = 0 \text{ M}^{-1}\text{s}^{-1}$	$k_{26} = 1 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$	$k_{40} = 1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$
$k_{13} = 0 \text{ M}^{-2}\text{s}^{-1}$	k_{27} , treated as variable	$k_{41} = 1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$
$k_{14} = 0 \text{ M}^{-3}\text{s}^{-1}$	$k_{28} = 0 \text{ s}^{-1}$	

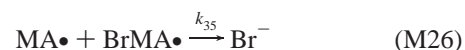
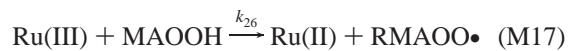
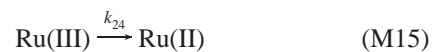
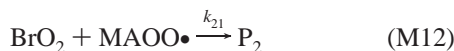
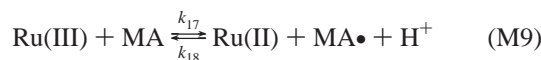
^a slightly varied in Figures 9 and 10.

mechanism using the rate constants proposed by Gao and Försterling³² for the Ru system (Table 3):

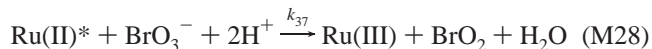
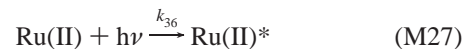
Inorganic part:



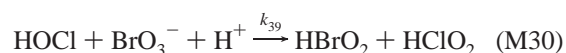
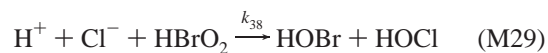
Organic part (formulated with malonic acid, MA) including influence of oxygen from atmosphere:



Influence of light:



To account for the influence of chloride ion, we also added the following four reactions suggested by Jacobs and Epstein.³³



First we reproduced and confirmed the results by Pereira and Faria,³⁴ who showed that the inflection times of the Ru(II)-bromate autocatalytic system (no organic substrate or chloride ions present) is significantly dependent even on small initial variations in HBrO₂ (data not shown). To use a consistent set of initial concentrations in our calculations (which also reflects the mixing order in our experiments), we determined the steady-state concentrations of the inorganic bromo-species for a 0.05 M BrO₃⁻ solution (in the *absence* of the catalyst) and used these values together with the initial concentrations of Ru(II) and organic substrate as the initial start concentrations for the calculations (Table 4).

Influence of Light on the Ru(II)-Oxidation with No Organic Substrate. The dashed lines in Figures 3 and 4 show the calculated influence of a light pulse with variable duration on the inflection time (with Ru(bpy)₃Cl₂ or Ru(phen)₃(ClO₄)₂ as catalysts, respectively) in the extended NFT model. However,

TABLE 4: Initial Concentrations Used in Calculations with Extended NFT Model

$[\text{BrO}_3^-]_0 = 5 \times 10^{-3} \text{ M}$	$[\text{Br}^-]_0 = 7.18 \times 10^{-15} \text{ M}$
$[\text{HBrO}_2]_0 = 2 \times 10^{-8} \text{ M}$	$[\text{HOBr}]_0 = 7.21 \times 10^{-8} \text{ M}$
$[\text{Br}_2]_0 = 5.173 \times 10^{-14} \text{ M}$	$[\text{Br}_2\text{O}_4]_0 = 2.021 \times 10^{-12} \text{ M}$
$[\text{BrO}_2]_0 = 1.041 \times 10^{-8} \text{ M}$	$[\text{Ru(II)}]_0 = 5 \times 10^{-4} \text{ M}$
$[\text{Cl}^-]_0 = 1 \times 10^{-3} \text{ M}$	$[\text{H}^+]_0 = 1.0 \text{ M}$

the calculated dashed line in Figure 4 requires a comment. While there was no problem describing the inflection time in the presence of Cl^- ions, there were difficulties to arrive at a consistent picture to model the experimental values in Figure 4. In absence of Cl^- ions, the inflection times were always very low (a few seconds) already in absence of any light and even if the rate constants k_{11} to k_{14} were subject to considerable variations. To avoid this discrepancy, we assumed that there may have been some residual Cl^- ions in the $\text{Ru(phen)}_3(\text{ClO}_4)_2$ preparation. The dashed line in Figure 4 has been calculated by using this assumption.

Modeling Small-Amplitude Oscillations in the Presence of BzMA. In the presence of BzMA, small-amplitude oscillations are observed directly *after* the oxidation of Ru(II) has occurred in darkness (Figure 2). We previously found²⁵ that small-amplitude oscillations can also be observed in simulations when the termination of organic radicals (process M14) is considered as a second-order reaction. Indeed, by changing the kinetics of process M14 from first-order to second-order, small-amplitude oscillations after the inflection point are found in the extended NFT model where the amplitude of these oscillations increases with increasing initial concentration of organic substrate (Figure 9). Although the agreement is still only qualitative in nature, our calculations point to the possibility that these oscillations are not controlled by bromide ion as those normally found in the BZ reaction³⁵ but appear to be related to second-order recombination kinetics of organic radicals. These small-amplitude oscillations are also induced/promoted when the termination of organic oxygen radicals (process M18) is considered as a second-order process (data not shown).

Modeling Small-Amplitude Oscillations in the Presence of MA and Light. In a relative small window of initial MA concentrations and in the presence of light, we observed in the experiment small-amplitude oscillations *before* the main oxidation of Ru(II) occurred (Figure 7). By keeping in the model the radical recombination process M14 as a second-order reaction and increasing the rate constant value for the reaction between MA and Ru(III) (k_{17} in process M9) and slightly decreasing k_{11} , it is possible to “move” the region of small-amplitude oscillations across the inflection point (Figure 10). An increase of k_{17} reflects the higher reactivity of malonic acid toward the oxidized form of the catalyst, but the apparent need to decrease k_{11} to observe oscillations before the inflection point is less easily explained. Perhaps a lower k_{11} value is related to our previous indications²⁷ that MA appears to complex Ru(II) and that such a Ru(II)–MA complex is slightly less reactive toward BrO_2 . As indicated in Figure 10 and in qualitative agreement with the experiments, we observe in the model that small-amplitude oscillations occur only above a certain threshold in the initial MA concentration. It is interesting to observe that these small-amplitude oscillations appear to be very similar to those observed earlier in a closed ferroin-methylmalonic acid BZ reaction.³⁶

Inflection Times at Constant Illumination and Higher Malonic Acid Concentrations. At higher initial MA concentrations (and at constant illumination), no oscillations are observed and calculations were performed using a first-order MA radical

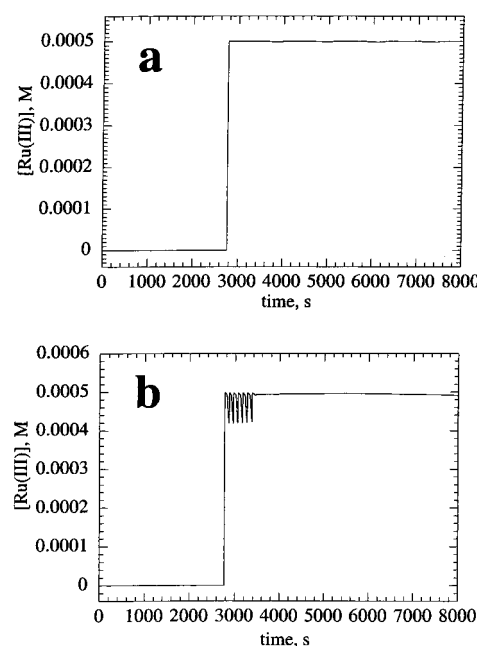


Figure 9. Observation of small-amplitude oscillations in the extended NFT model in darkness ($k_{36} = 0 \text{ s}^{-1}$, $k_{37} = 0 \text{ M}^{-3} \text{ s}^{-1}$) when organic radical recombination reaction M14 is considered second-order with respect to organic radicals. (a) $[\text{BzMA}] = 0.5 \text{ mM}$; (b) $[\text{BzMA}] = 20 \text{ mM}$. Values of variable rate constants used in the calculations: $k_{11} = 1 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$, $k_{17} = 0.2 \text{ M}^{-1} \text{ s}^{-1}$, $k_{19} = 6.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $k_{20}[\text{O}_2] = 0 \text{ s}^{-1}$, $k_{21} = 0 \text{ M}^{-1} \text{ s}^{-1}$, $k_{23} = 3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $k_{27} = 0 \text{ M}^{-1} \text{ s}^{-1}$. No oscillations are observed when reaction M14 is considered first-order with respect to organic radicals.

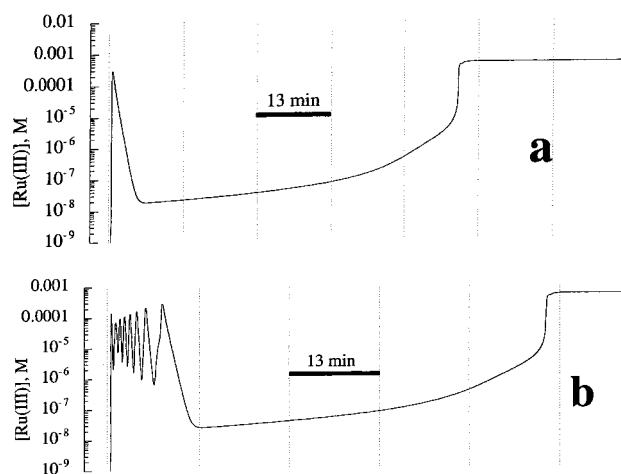


Figure 10. Observation of small-amplitude oscillations in extended NFT model under continuous light conditions ($k_{36} = 1 \times 10^{-7} \text{ s}^{-1}$, $k_{37} = 0.02 \text{ M}^{-3} \text{ s}^{-1}$). Also in this case oscillations only occur when process M14 is considered second-order with respect to organic radicals. (a) $[\text{MA}] = 1 \text{ mM}$; (b) $[\text{MA}] = 4 \text{ mM}$. Values of variable rate constants used in the calculations: $k_{11} = 1.4 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$, $k_{17} = 82 \text{ M}^{-1} \text{ s}^{-1}$, $k_{19} = 6.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $k_{20}[\text{O}_2] = 10 \text{ s}^{-1}$, $k_{21} = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, $k_{23} = 1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $k_{27} = 1 \text{ M}^{-1} \text{ s}^{-1}$.

termination in process M14. The solid lines in Figure 8 are the results from the computations and show that the extended NFT model is able to describe the rather long inflection times observed in the presence of malonic acid.

Discussion

Further Evidence for $\text{BrO}_2/\text{HBrO}_2$ Production in Illuminated Systems without Organic Substrate. As seen in Figures 3 and 4, computations with both a simple autocatalytic model as well as with an extended NFT mechanism provide

further evidence that light produces HBrO_2 in Ru(II)-bromate systems in absence of organic substrate. This provides further support for the earlier suggestions by Kádár et al.,²⁴ Kaminaga and Hanazaki,³⁰ as well as Sørensen et al.³⁷

The increased inflection time (IT) in the presence of chloride ions is well described by the Jacobs–Epstein mechanism,³³ which removes both HBrO_2 and BrO_2 by processes M29 and M32 and thus increases IT.

Influence of Organic Substrates. As seen in Figures 1 and 5, the presence of malonic acid and its derivatives increases the inflection time both in darkness and light conditions, which is apparently related with the removal of BrO_2 by organic radicals (M10) or by peroxy-radicals (M12).

In darkness, the inflection time corresponds with the Taft sigma constant (Figure 1) and appears to be related to the “easiness” how $\text{RMA}\bullet$ radicals are produced: MeMA, EtMA, and BuMA show decreasing inflection times, which correlate with the expected heats of formation³⁸ for the $\text{RMA}\bullet$ radicals.

On the other hand, the influence of light (producing HBrO_2) in the presence of different organic substrates is not as easily explained because EtMA now shows larger inflection times compared with MeMA, while MeMA has larger inflection times compared with BuMA (Figure 5). Apparently in the presence of light, both the easiness to create the $\text{RMA}\bullet$ radicals and their reactivities toward BrO_2 are important. Neglecting MA for the moment, the stability of $\text{RMA}\bullet$ radicals should increase (because of the inductive effect by R) when R is changed from the methyl- to the ethyl- group, but little additional stabilization is expected to occur when going to larger R-substituents (such as *n*-butyl). Looking at the Ru(II)-bromate system in the presence of BuMA, the additional effect of BuMA• (or BuMAOO•) radicals is small compared with a system that has no organic substrate (Figure 5b) indicating that the reactivity of BuMA• (or BuMAOO•) radicals is less than for the corresponding methyl- or ethyl- radicals. The reactivity of the EtMA• radical appears to be optimal (probably because of a combined optimum in stability and reactivity of EtMA•) and shows the largest inflection times for this group (Figure 5a).

Influence of Malonic Acid. Because of its high reactivity, malonic acid has an extraordinary influence on the autocatalytic oxidation of Ru(II) by bromate compared with the other organic substrates, which is clearly seen when Figure 5 and Figure 8 are compared. While with the other organics increasing light pulses are able to reduce/abolish the inflection time because of an increased HBrO_2 production by light, MA inflection times stay high even at continuous illumination. The reason for this is the relative high production rate/concentration of MA• and MAOO• radicals, which can keep BrO_2 at a low level for a much longer time and thus considerably delay the onset of the autocatalysis.

For a small malonic acid concentration window, we observed (prior to the inflection point) “rhythmogenesis”, that is, the occurrence of oscillations at constant illumination, while for the same initial conditions in darkness no oscillations were observed (Figure 7). Similar oscillations can be observed in the extended NFT model when an increased reactivity between Ru(III) and MA is assumed (i.e., increasing k_{17} in process M9) and by treating the recombination process M14 between MA radicals as a second-order reaction (Figure 10). The occurrence of small-amplitude oscillations is discussed in more detail in the next section.

Small-Amplitude Oscillations. Of considerable interest we find the small-amplitude oscillations observed in the BzMA and MA systems (Figures 2 and 7). Earlier predictions²⁵ and the

present model calculations (Figures 9 and 10) suggest that these oscillations may be due to second-order organic radical termination kinetics and are not related to the bromide-ion control of the oscillations normally observed in BZ system.³⁵ Indeed, this interpretation is in agreement with the earlier proposal by Försterling et al.³⁹ that under certain circumstances, such as for the Racz system,⁴⁰ oscillations in the BZ reaction may become radical-controlled. Radical-controlled and bromide-ion-controlled BZ oscillations have recently been studied by Misra et al.⁴¹ Other small-amplitude oscillations may be interpreted by similar radical-control mechanisms, for example, the unusual oscillatory behavior found in a closed MeMA ferriox-catalyzed BZ system.³⁶ What may cause the possible switch between first-order to second-order termination kinetics in reactions M14 or M18? First-order (or pseudo-first-order) termination kinetics for a certain radical species is expected when it rapidly reacts with another radical-terminating species in a bimolecular manner, but the concentration of the free radical is much lower than the other species.⁴² A switch to second-order termination kinetics ($\text{R}\bullet + \text{R}\bullet \rightarrow \text{P}$) could occur, when radical species $\text{R}\bullet$ is present in relatively high concentrations, because $\text{R}\bullet$ is either easily produced (like MA-radicals) or it is particularly stable such that a radical–radical recombination/termination reaction between the same radical species has a much higher probability to occur. That might be a plausible explanation for the oscillations observed in the BzMA system because of stabilization from the aromatic ring (Figure 2). However, it is not clear why for the light-induced MA oscillations (Figure 7) second-order MA radical termination kinetics should occur only in a low small concentration window of initial MA and only in light. Although we are able to model these kind of oscillations by second-order organic radical termination kinetics of reaction M14 (Figure 10), a more detailed experimental understanding of the organic radical termination reactions is necessary.

Conclusions

The inflection time in the light-perturbed autocatalytic oxidation of Ru(II) ions by bromate ions and in the presence of an organic substrate is influenced by the balance of the HBrO_2 producing reaction by light and BrO_2 removing reactions by organic radicals. Because light produces HBrO_2 , light generally decreases inflection times. In the presence of an organic substrate which is able to produce radicals, these radicals may react with BrO_2 and thus lead to an increase of the inflection time. A highly reactive organic substrate, such as MA, which leads to a (relative) large amount of reactive radicals, is able to counteract the influence of light and lead to high inflection times even at constant illumination. The small-amplitude oscillations that are observed appear to be generated by second-order termination kinetics between the organic radical species.

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Appendix

In case of a single and brief light pulse (we assume that the light-pulse length PL is considerably shorter than the observed inflection time after the pulse; see Figures 4 and 5), autocatalysis can be described by the following simple (autocatalytic) first-order process R1a



where the light pulse leads to the production of the autocatalytically produced species B. We define that $t = 0$ corresponds to the end of the light pulse leading to the initial concentrations $[A]_0$ and $[B]_0$ and the mass balance condition

$$\Delta_0 = [A]_0 + [B]_0 = [A] + [B] \quad (\text{A1})$$

The rate equation corresponding to process R1a is given by

$$\frac{d[B]}{dt} = -\frac{d[A]}{dt} = k[A][B] = k[A]\{\Delta_0 - [A]\} \quad (\text{A2})$$

The condition for the inflection point at $t = t_{\text{infl}}$ is

$$\left(\frac{d^2[A]}{dt^2}\right)_{\text{infl}} = k\left(\frac{d[A]}{dt}\right)_{\text{infl}} \{\Delta_0 - [A]_{\text{infl}}\} - k[A]_{\text{infl}} \left(\frac{d[A]}{dt}\right)_{\text{infl}} = 0 \quad (\text{A3})$$

Because at the inflection point $(d[A]/dt)_{\text{infl}} \neq 0$, we have the condition

$$k\left(\frac{d[A]}{dt}\right)_{\text{infl}} \{\Delta_0 - 2[A]_{\text{infl}}\} = 0 \quad (\text{A4})$$

leading to

$$[A]_{\text{infl}} = \left(\frac{\Delta_0}{2}\right) \quad (\text{A5})$$

In continuous illumination, two pathways R2 may be considered: an uncatalyzed one driven by light with the rate constant k_{hv} , besides the autocatalyzed route:



We now define $\Delta_0 = (k_{\text{hv}}/k) + [A]_0$ and can show analogously to the above derivation that also in this case eq 2 holds and that the inflection time is described by the analogous expression

$$\text{IT} = \left(\frac{1}{k \cdot \Delta_0}\right) \ln\left(\frac{k \cdot [A]_0}{k_{\text{hv}}}\right) \quad (\text{A6})$$

where the time dependence of $[A]$ is given by

$$[A] = \frac{\Delta_0 [A]_0}{[A]_0 + \left(\frac{k_{\text{hv}}}{k}\right) \exp(k \cdot \Delta_0 \cdot t)} \quad (\text{A7})$$

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