

*Dedicated to Professor Ionel Haiduc,  
President of The Romanian Academy at his 70<sup>th</sup> anniversary*

## KINETICS AND OXIDATION MECHANISM OF LACTIC AND MALIC ACIDS BY PERMANGANATE IN ACIDIC MEDIA

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**ABSTRACT.** Kinetic studies on the oxidation of malic and lactic acids by permanganate in acidic solutions have been carried out. In the presence of Mn(II) three ways of consumption of Mn(VII) are involved: a direct oxidation of the hydroxy acid, an oxidation of Mn(II) to Mn(III) and a catalytic route. The experimental rate law is quite complex. It involves a condensed esteric type compound for the direct oxidation by permanganate and two other parallel ways: one leading to a first-order and the other to a second order term with respect to Mn(II) as catalyst.

**Key Words:** Kinetics, reaction mechanism, lactic acid, malic acid, oxidation, permanganate, autocatalysis, catalysis.

Although the kinetic study of oxidation by permanganate has received considerable attention for well over a century, there are still unanswered questions concerning the mechanism of many processes [1]. The oxidation reactions in alkaline solutions [2] are better understood, but in acidic media they are usually multi-stage processes due to the ability of manganese to exist in a multitude of oxidation states.

Numerous permanganate oxidation reactions exhibit autocatalysis [3, 4]. Among these, the  $\text{MnO}_4^- - \text{C}_2\text{O}_4^{2-}$  reaction has attracted much attention [5-7]. It is the base of a titration method, which involves autocatalysis. The overall reaction  $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$  can be split into two composite stoichiometric processes [8, 9]: the oxidation of Mn(II) to Mn(III) by  $\text{MnO}_4^-$  followed by the rapid formation of a Mn(III)-oxalate complex, that further undergoes a redox decomposition. The first process obeys a first-order law in  $\text{MnO}_4^-$  and a second-order in Mn(II) [10] in aqueous acidic solutions and exhibits various dependencies on hydrogen ion concentration [11-13]. Similar autocatalytic effect has been observed for the oxidation of malic acid [14]. The oxidation of  $\alpha$ -hydroxy acids by various oxidizing agents will yield keto acids [15] or carbonyl compounds and  $\text{CO}_2$  [16]. Transition metal ions exhibit

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catalytic effect in the oxidation by Cr(VI) or Mn(VII) [17]. Therefore some kinetic methods for analysis could be set off for traces of these metal ions [18].

This work has undertaken the study of the oxidation of the two title  $\alpha$ -hydroxy acids as an attempt to determine the dependence of the rate on Mn(II) concentration as well as to establish a satisfactory mechanism.

### Experimental

All chemicals employed in the study were of certified analytical reagent grade from commercial sources and therefore used without further purification. The solutions were prepared in twice distilled water. Stock solutions of  $\text{HClO}_4$  and  $\text{LiClO}_4$  were prepared and standardised by titration with a NaOH solution. Aliquots of the  $\text{LiClO}_4$  solution were passed over a cationic resin Amberlite IR 122 in the H-form. The resulted acid was titrated. The solutions of reagents were freshly prepared and standardised before each set of runs.

The course of the reaction was followed spectrophotometrically at 525 nm by using a Jasco V-530 spectrophotometer interfaced to a computer and equipped with a cell holder connected to a Lauda M-12 recirculation bath. A 5-cm path length glass cell has been used. Three to seven replicate runs were performed for each set of experimental conditions, and calculated rate constants did not differ to more than  $\pm 3\%$ . The process was initiated by injecting permanganate solution, kept in the temperature bath, directly into the cell over the mixture of other reactants. Mixing time did not exceed 0.5 sec.

The stoichiometry of the process was determined by means of photometric titration. Various mixtures having known initial molar ratio were allowed to react to completion for at least ten half-lives at room temperature, constant acidity (0.32 mole/L) and ionic strength (0.75 mole/L). The final absorbance values were measured and compared to the one obtained with a solution containing the same mixture except for the hydroxy acid. In order to allow for potassium permanganate self decomposition or water oxidation, this solution was kept for the same period as the slowest reaction mixture [19].

### Results and Discussion

*Stoichiometry.* Because Mn(II) has a contribution to the disappearance of Mn(VII) by means of reaction  $\text{MnO}_4^- + 4 \text{Mn}^{2+} + 8 \text{H}^+ \rightarrow 5 \text{Mn}^{3+} + 4 \text{H}_2\text{O}$ , the stoichiometry of the oxidation process was determined in its absence in the starting reaction mixture. In acidic media, the stoichiometry corresponds to the oxidation to the oxo-acids: oxalylacetic and pyruvic acid, respectively.

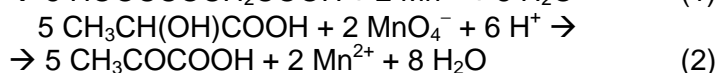
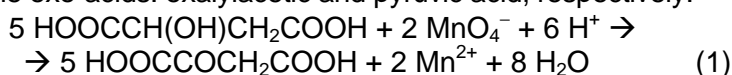
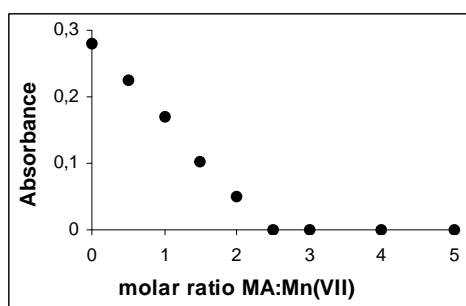


Figure 1 shows the dependence of the final absorbance values on the initial molar ratio in the case of DL-hydroxybutanedioic acid oxidation (symbolised by MA). A similar dependence has been found with lactic acid (LA) – results not shown. It is obvious that a clear intercept of the lines is obtained at the ratio 2.5, indicating consumption molar ratios as presented in equations (1) and (2). If hydroxy acids were oxidized by some Cu(II) permanganate complex, oxo acids were also obtained [20]. The oxidation of C–OH to carbonyl takes place even in some heterogeneous reactions [21]. The involvement of *free radicals* has been proved by the initiation of polymerisation. Polymer has been also isolated.



**Figure 1.** Absorbance measurements at the end of the reaction at various malic acid - permanganate initial molar ratios.

*Reaction kinetics.* The reaction starts for both hydroxy-acids, either in the presence or in the absence of initial Mn(II), with a steep decay of the colour within a short period of 10 to 15 sec. Afterwards the absorbance decreases quite slowly to its final value. This fast process involves only the hydroxy-acid and permanganate. Because of the lack of a stopped-flow device, we report here only the data for the slow stage. However, by analogy with permanganate oxidation of other substrates [22, 23], one can suppose that some rapid equilibrium yielding an ester takes place. This condensed compound has a smaller molar absorptivity as compared to that of permanganate ion at 525 nm. It can explain the initial steep decrease of the absorbance.

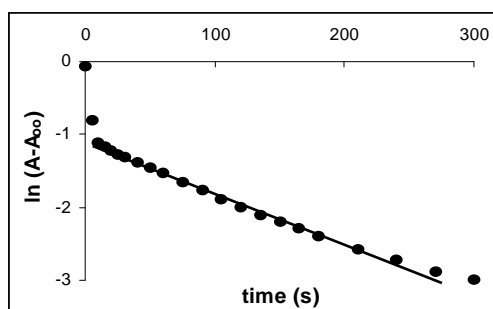


On the other hand, the oxidation of Mn(II) to Mn(III) by permanganate under the same acid concentration is slower than the oxidation of organic substrate itself (see table 1, where MA stands for malic acid and LA for lactic acid, respectively). When Mn(II) has not been added to the mixture, a sigmoid shape of the absorbance versus time plot has been noticed [14]. This is characteristic for reactions with an induction period. Intermediate valence states

of manganese are important oxidising entities [4]. The process went to completion more rapidly when Mn(II) was initially present in the reaction mixture.

**Table 1.**  
Average values of the first-order rate coefficients at various concentrations of hydroxy acids;  $[H^+] = 0.32$ ,  $[Mn^{2+}] = 5.0 \times 10^{-2}$ ,  $[MnO_4^-] = 1.0 \times 10^{-4}$ ,  $\mu = 0.75$  and 297 K.

$10^3 [ROH]$ (mole/L)	$10^3 k_{obsd} (s^{-1})$ - MA	$10^3 k_{obsd} (s^{-1})$ - LA
0.00	1.48	1.48
1.66	3.91	2.53
2.50	4.62	2.93
3.33	5.44	3.53
4.16	6.27	3.73
5.00	7.13	4.23
5.83	7.67	4.60
6.66	8.13	4.98



**Figure 2.** First-order plot for the oxidation of malic acid:  $[MA] = 5.0 \times 10^{-3}$ ,  $[MnO_4^-] = 1.0 \times 10^{-4}$ ,  $[Mn^{2+}] = 5.0 \times 10^{-2}$ ,  $[HClO_4] = 0.32$ ,  $\mu = 0.75$  and 290 K.

The oxidation process follows a first-order dependence on the coloured species. Figure 2 presents the linear semi-logarithmic plot. Linearity has been obeyed up to 90 % of reaction extent. Calculation of line parameters was carried out statistically. The first points (corresponding to the steep decay of the absorbance) and the last ones (close to the final value) were excluded. The rate coefficients depend upon the organic substrate concentration,  $[Mn(II)]$ ,  $[HClO_4]$ , ionic strength and temperature.

The dependence of first-order rate constants on the hydroxy -acid concentration is presented in Table 1. It proves the existence of at least two parallel reaction paths consuming  $MnO_4^-$  during the slow stage. One that is independent of the substrate concentration may be assigned to the direct reduction of permanganate by Mn(II), while the other to the consumption of

Mn(VII) by DL-hydroxybutanedioic or 2-hydroxypropionic acid. Mn(II) catalyses the process.

By subtracting the contribution  $k_0$  of the Mn(II)-Mn(VII) reaction, a non-linear dependence of  $\Delta k_{\text{obsd}}$  as a function of the organic substrate has been obtained. It is possible to make such difference because both processes follow a first-order dependence with respect to Mn(VII). A tendency of levelling off has been observed. It is more pronounced for malic acid.

Strictly speaking, the difference  $\Delta k_{\text{obsd}}$  should also contain the autocatalytic effect of generated Mn(II). Because Mn(II) has been used in large excess, the autocatalytic effect of produced Mn(II) is insignificant as compared to the catalytic one. At constant acidity the increment of observed rate coefficient on substrate concentration could be described by equation (4) where [ROH] stands for the concentration of the substrate. It is of the "one-plus" form of the rate law [24] and can be transposed into a linear form by making reciprocals (see equation 5). Such a rate law indicates the involvement of a pre-equilibrium [24].

$$\Delta k_{\text{obsd}} = \frac{a[\text{ROH}]}{1 + b[\text{ROH}]} \quad (4)$$

$$\frac{1}{\Delta k_{\text{obsd}}} = \frac{b}{a} + \frac{1}{a} \frac{1}{[\text{ROH}]} \quad (5)$$

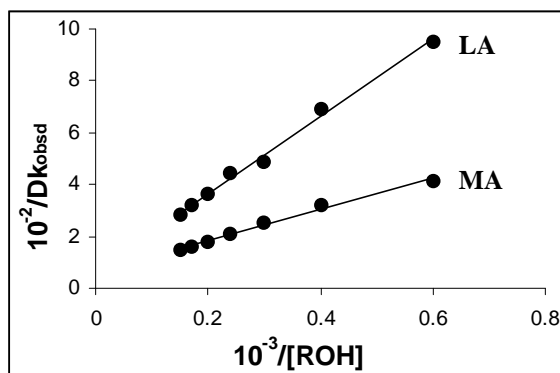
As presented in figure 3, the plot of equation (5) has given straight lines with good correlation coefficients. In the case of malic acid oxidation  $r = 0.9951$  and the parameters  $b/a = 64.6 \pm 1.6$  (s) and  $1/a = 0.60 \pm 0.06$  ( $\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}$ ). In the case of lactic acid the corresponding values were:  $r = 0.9971$ ,  $b/a = 69.0 \pm 5.0$  (s) and  $1/a = 1.48 \pm 0.14$  ( $\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}$ ). The similar behaviour proves that both hydroxy acids react likewise.

**Table 2.**

The effect of  $\text{HClO}_4$  concentration on the slow step;  
 $[\text{Mn}^{2+}] = 5.0 \times 10^{-2}$ ,  $[\text{MnO}_4^-] = 1.0 \times 10^{-4}$ ,  $[\text{ROH}] = 5.0 \times 10^{-3}$ ,  $\mu = 0.75$  and 297 K.

$[\text{H}^+]$ (mole/L)	0.08	0.16	0.32	0.48
$10^3 \times k_{\text{obsd}} (\text{s}^{-1})$ - MA	9.39	8.35	7.13	6.26
$10^3 \times k_{\text{obsd}} (\text{s}^{-1})$ - LA	4.35	4.27	4.23	4.20

The effect of hydrogen ion concentration on the rates is presented in table 2. It proves the slowing down of rate with increasing acid concentration. The inverse dependence on  $[\text{H}^+]$  suggests some complex formation between Mn(II) and the  $\alpha$ -hydroxy acids. Similar dependence on  $[\text{H}^+]$  has already been established for oxalic acid oxidation [7, 8, 13].



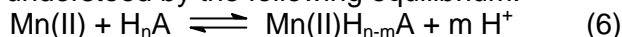
**Figure 4.** The plot of equation (5) for both malic and lactic acid under experimental conditions given in Table 1.

**Table 2.**

The effect of  $\text{HClO}_4$  concentration on the slow step;  
 $[\text{Mn}^{2+}] = 5.0 \times 10^{-2}$ ,  $[\text{MnO}_4^-] = 1.0 \times 10^{-4}$ ,  $[\text{ROH}] = 5.0 \times 10^{-3}$ ,  $\mu = 0.75$  and 297 K.

$[\text{H}^+]$ (mole/L)	0.08	0.16	0.32	0.48
$10^3 \times k_{\text{obsd}} (\text{s}^{-1})$ - MA	9.39	8.35	7.13	6.26
$10^3 \times k_{\text{obsd}} (\text{s}^{-1})$ - LA	4.35	4.27	4.23	4.20

The fact that malic acid is more influenced as compared to lactic acid could be understood by the following equilibrium:



In equation (6)  $m$  is greater for malic acid than for lactic acid. Autocatalysis by  $\text{Mn(II)}$  is caused by the involvement of the  $\text{Mn(II)}$ -hydroxy acid complex in the reduction of  $\text{Mn(VII)}$ . Since  $\text{Mn(II)}$  is either an auto-catalyst if absent from the initial mixture or a catalyst if present at the beginning of run, it is essential to determine the order of the reaction with respect to it. Measurements have been made using various concentration of  $\text{Mn(II)}$ . The observed first-order rate constants are given in table 3.

By plotting  $k_{\text{obsd}}$  versus the catalyst concentration, a parabolic dependence was obtained. Fitting of data leads to the relationships (7) and (8) for malic and lactic acid, respectively.

$$k_{\text{obsd}} = 0.0020 + 0.016 [\text{Mn(II)}] + 0.54 [\text{Mn(II)}]^2 \quad (\text{s}^{-1}) \quad (7)$$

$$k_{\text{obsd}} = 0.0022 + 0.014 [\text{Mn(II)}] + 0.49 [\text{Mn(II)}]^2 \quad (\text{s}^{-1}) \quad (8)$$

Correlation coefficients are 0.9948 and 0.9932, respectively. Equations (7) and (8) suggest the involvement of two reaction paths, one of first-order and the other of second-order with respect to  $\text{Mn(II)}$ . These have comparable contributions to the overall rate.

**Table 3.**

The effect of Mn(II) concentration upon apparent first-order rate constants;  
 $[H^+] = 0.32$ ,  $[ROH] = 5.0 \times 10^{-3}$ ,  $[MnO_4^-] = 1.0 \times 10^{-4}$  and  $\mu = 0.75$ .

[Mn(II)] (mole/L)	$10^3 k_{obsd} (s^{-1})$ - MA (at 290.5K)	$10^3 k_{obsd} (s^{-1})$ - LA (at 297 K)
0.00	2.01 *	2.21 *
$1 \times 10^{-4}$	2.13	---
$1 \times 10^{-3}$	2.25	2.66
$1 \times 10^{-2}$	2.31	3.00
$2 \times 10^{-2}$	2.52	---
$3 \times 10^{-2}$	3.16	3.10
$4 \times 10^{-2}$	3.38	---
$5 \times 10^{-2}$	4.00	4.13
$6 \times 10^{-2}$	4.53	---
$7 \times 10^{-2}$	---	5.66
$9 \times 10^{-2}$	---	7.20

\*) measured after the induction period

The results can be explained in mechanistic terms by the involvement, beside  $MnO_4^-$ , of a monomeric and a dimeric Mn(II) – substrate complex, respectively. As presented in table 4, modification of ionic strength has some effect on the rates.  $LiClO_4$  has been used to obtain the desired ionic strength. The effect is quite different for the two oxidised substrates: a decreasing effect on malic acid and a slight increasing effect on the lactic acid oxidation.

**Table 4.**

The effect of ionic strength on the first-order rate constant;  
 $[ROH] = 5.0 \times 10^{-3}$ ,  $[H^+] = 0.32$ ,  $[Mn(II)] = 5.0 \times 10^{-2}$ ,  $[MnO_4^-] = 1.0 \times 10^{-4}$  and 297 K.

$\mu$ (mole/L)	0.47	0.75	1.07	1.47
$10^3 k_{obsd} (s^{-1})$ - MA	8.33	7.13	6.95	6.51
$10^3 k_{obsd} (s^{-1})$ - LA	4.03	4.23	4.53	5.07

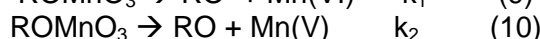
A plot of  $\log k_{obsd}$  as a function of  $\sqrt{\mu} / (1 + \sqrt{\mu})$  gave lines with opposite slopes:  $-(0.89 \pm 0.10)$  for malic acid and  $+(0.83 \pm 0.10)$  for lactic acid, respectively. The correlation coefficients were not very good: 0.9667 and 0.9631, respectively. This unusual behaviour cannot be interpreted only on the basis of the primary salt effect, but should take into consideration the effects of ionic strength on the equilibria involved.

*Reaction mechanism.* Presented data suggest that more complicate rate terms have to be considered to account for the disappearance of permanganate. At least three parallel paths are involved in bringing about the consumption of the oxidising species. These are:

- 1) The direct interaction between hydroxy acid and permanganate ion;
- 2) The reduction of permanganate by Mn(II) ion in acidic media and the formation of Mn(III) species that further oxidise the organic substrate to the products in fast steps;
- 3) The involvement of some Mn(II)-hydroxy acid complexes in reaction with Mn(VII).

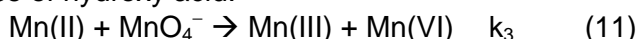
Such detailed reaction paths are consistent with experimental observations and literature data [13].

The formation of an ester by the condensation process (3) is a rapid pre-equilibrium followed by slower steps, yielding either a free radical and Mn(VI) in a mono-equivalent electron transfer process (step 9), or a keto-acid and Mn(V) in a di-equivalent electron transfer process (step 10).

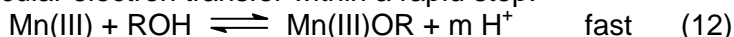


Similar to the case of chromate esters [25-27], the permanganic ester has a smaller molar absorptivity at 525 nm as compared to that of  $\text{MnO}_4^-$ . This fact would explain the steep decrease of the absorbance immediately after mixing. Intermediate oxidation states of manganese are obviously involved in the reaction and will eventually generate Mn(II) in quite rapid steps in acidic media.

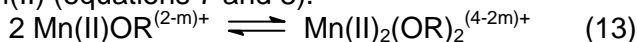
The direct reduction of permanganate by Mn(II) has been observed in the absence of hydroxy acid.



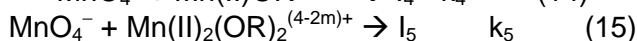
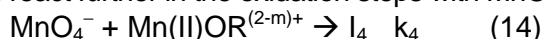
It yields Mn(III) that further interacts with the hydroxy acid to form a complex by binding the substrate as ligand. This complex undergoes an intramolecular electron transfer within a rapid step:



On the other hand, Mn(II) can also interact with the hydrox acid to form some complexes that further suffer the oxidation to Mn(III). The involvement of a dimeric species [28-30] explains the second order with respect to Mn(II) (equations 7 and 8).



These complexes react further in the oxidation steps with  $\text{MnO}_4^-$  [13], as follows:



The intermediates  $\text{I}_4$  and  $\text{I}_5$ , which might be some ion-pairs, will produce Mn(III) and eventually the oxidation products.

The above-suggested mechanism should lead to a rate law consistent with the experimental observations. By taking into account both



the rate-determining step for each of the paths and the equilibria involved, the disappearance of the coloured Mn(VII) species that contribute to the absorbance could be written as follows:

$$-\frac{d[Mn(VII)]}{dt} = \left\{ \frac{k_1 K_1 [ROH][H^+]}{1 + K_1 [ROH][H^+]} + k_3 [Mn(II)] + \frac{k_4 K_2 [Mn(II)][ROH]}{[H^+]^m} + \frac{k_5 K_2 K_3 [Mn(II)]^2 [ROH]^2}{[H^+]^{2m}} \right\} [MnO_4^-] \quad (16)$$

The pseudo-first-order rate constant is the expression in parenthesis in equation (16). Because there are no experimental means to discriminate between steps (9) and (10), only process (9) standing for the decomposition by electron-transfer of the permanganate ester has been considered. Anyhow, the formalism is the same. On the other hand, polymerisation experiments proved the presence of free radicals during the oxidation. The rate expression explains the negative dependence on the concentration of hydrogen ion as well as the different behaviour of the two substrates (because  $m$  has different values for malic and lactic acids).

When Mn(II) is not added to the reaction mixture, the last two terms in equation (16) explain the autocatalysis. When it is present from the beginning of the run and also has a relatively high concentration, the terms on Mn(II) dominate in the sum and the contribution of Mn(II) as reaction product is insignificant as compared to the added Mn(II). It explains the influence of hydrogen ion on the rate. If we subtract from the pseudo-first-order rate constant its value in the absence of the substrate, the second and the third term in the first order apparent rate coefficient (equation 17) will disappear:

$$\Delta k_{obsd} = \left\{ \frac{k_1 K_1 [ROH][H^+]}{1 + K_1 [ROH][H^+]} + \frac{k_4 K_2 [Mn(II)][ROH]}{[H^+]^m} + \frac{k_5 K_2 K_3 [Mn(II)]^2 [ROH]^2}{[H^+]^{2m}} \right\} \quad (17)$$

In the absence of Mn(II) and at the beginning of the process the first term prevails, hence:

$$\Delta k_{obsd} = \frac{k_1 K_1 [ROH][H^+]}{1 + K_1 [ROH][H^+]} \quad (18)$$

This expression accounts for the direct interaction between HMnO<sub>4</sub> [31] and the hydroxy acid. It is of the form of equation (6). Hence, one can calculate  $k_1$  (or the sum  $k_1 + k_2$ ) as well as  $K_1$  from the values  $1/a$  and  $b/a$  obtained from the experimental rate constants. The results at 297 K are  $k_1 = (1.55 \pm 0.04) \times 10^{-2}$  (s<sup>-1</sup>) and  $K_1 = 335 \pm 41$  (M<sup>-1</sup>) in the case of malic acid and  $k_1 = (1.45 \pm 0.10) \times 10^{-2}$  (s<sup>-1</sup>) and  $K_1 = 146 \pm 25$  (M<sup>-1</sup>) in the case of lactic acid, respectively.

The decomposition of the ester condensed compound to form free radicals and some intermediate oxidation states of manganese proceeds at

about the same rate for both substrates. The esters formation constants are different but quite large for both hydroxy acids to provide an important fraction of permanganate condensed to these. The value of the ratio

$$\frac{[ROMnO_4^-]}{[Mn(VII)]_t} = \frac{K_1[ROH][H^+]}{1 + K_1[ROH][H^+]}$$

suggests that the reaction takes place

with an important fraction of the product *via* direct interaction between substrate and permanganate.

In conclusion, the oxidation of both malic and lactic acid by permanganate occurs in acidic media by means of a rather complicated mechanism. This involves at least three parallel reaction paths that compete to the consumption of the coloured species. The proposed detailed reaction paths are consistent with the experimental observations, the autocatalytic behaviour as well as with the literature data.

### Acknowledgements

The authors gratefully acknowledge the financial support of Romanian Government, Ministry of Education and Research, Council for Scientific Research in Universities (CNCSIS), grant No. A/337/2006.

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