

Decomposition of the permanganate/oxalic acid overall reaction to elementary steps based on integer programming theory

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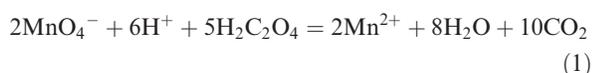
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A systematic method to obtain chemically acceptable decompositions of the overall autocatalytic reaction permanganate/oxalic acid into elementary steps is presented. The decomposition process was based on integer programming theory and chemical evidence, and it can be applied to elucidate other mechanisms as well. As a result, we obtained mathematical justification of the well-known autocatalytic nature and of the less-known crucial role of radical CO_2^- . By inspecting the obtained decompositions, one can find reaction steps inaccessible to chemical intuition, and these point out the direction of further experimental investigations.

1 Introduction

The principles for the automatic generation of chemical reaction mechanisms seem to be well elaborated.¹ However, while simulation programs are generally available, mechanism generation programs are not available either on a commercial basis or in the public domain.

In the present paper we provide a systematic and chemically acceptable decomposition of the overall autocatalytic reaction



into elementary steps. It is a well-known reaction which has been studied since 1866,² and was recently investigated by several groups.^{3–8}

The basis of our decomposition method has been outlined in ref. 9; an alternative method can be found in ref. 10; a review of earlier methods is given in ref. 1. A reaction is considered elementary in this paper if no more than two species (molecules, ions, atoms, radicals) meet to react.

The authors of ref. 6 have defined a mechanism consisting of eight reversible and six irreversible steps, of which three are not elementary in the sense defined above. The reaction mechanism includes the following 18 species:

$\text{H}_2\text{C}_2\text{O}_4$	HC_2O_4^-	H^+
$\text{C}_2\text{O}_4^{2-}$	Mn^{2+}	MnC_2O_4
MnO_4^-	MnO_2	Mn^{3+}
CO_2	H_2O	$[\text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4]$
CO_2^-	$[\text{Mn}(\text{C}_2\text{O}_4)]^+$	$[\text{Mn}(\text{C}_2\text{O}_4)_2]^-$
H_2SO_4 ,	HSO_4^- ,	SO_4^{2-} ,

Here the square bracket $[\]$ refers to encounter pairs or triplets,¹¹ if they contains more than one species. Based upon chemical evidence (see Subsection 2.1), neither the entire set of species, nor the set of elementary steps are acceptable

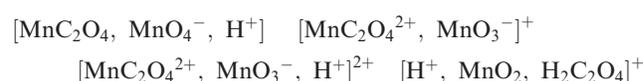
without alterations. We redefined species, reaction steps, and requirements.

2 Materials and methods: Computational and chemical

2.1 Species

The above set of species is accepted with a few minor modifications. We omit SO_4^{2-} , HSO_4^- , and H_2SO_4 , because sulfuric acid is not an essential component of the medium.

On the other hand, there is a need to bridge the gap between Mn(VII) and Mn(IV). For this purpose we assume the presence of the hypothetical transient species



(of which three are binuclear manganese complexes). Thus, our set of 19 species is as follows:

$\text{H}_2\text{C}_2\text{O}_4$	HC_2O_4^-	H^+
$\text{C}_2\text{O}_4^{2-}$	Mn^{2+}	MnC_2O_4
MnO_4^-	MnO_2	Mn^{3+}
CO_2	H_2O	$[\text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4]$
CO_2^-	$[\text{Mn}(\text{C}_2\text{O}_4)]^+$	$[\text{Mn}(\text{C}_2\text{O}_4)_2]^-$
$[\text{MnC}_2\text{O}_4,$	$[\text{MnC}_2\text{O}_4^{2+},$	$[\text{MnC}_2\text{O}_4^{2+},$
$\text{MnO}_4^-, \text{H}^+]$	$\text{MnO}_3^-]^+$	$\text{MnO}_3^-, \text{H}^+]^{2+}$
$[\text{H}^+, \text{MnO}_2,$		
$\text{H}_2\text{C}_2\text{O}_4]^+$		

These species are made of five different atoms, if electrons are also considered as an atomic constituent: C, H, Mn, O, e. The *transpose* of the atomic matrix D of the species is as follows.

	C	H	Mn	O	e
H ₂ C ₂ O ₄	2	2	0	4	0
HC ₂ O ₄ ⁻	2	1	0	4	1
H ⁺	0	1	0	0	-1
C ₂ O ₄ ²⁻	2	0	0	4	2
Mn ²⁺	0	0	1	0	-2
MnC ₂ O ₄	2	0	1	4	0
MnO ₄ ⁻	0	0	1	4	1
MnO ₂	0	0	1	2	0
Mn ³⁺	0	0	1	0	-3
CO ₂	1	0	0	2	0
H ₂ O	0	2	0	1	0
[MnO ₂ , H ₂ C ₂ O ₄]	2	2	1	6	0
CO ₂ ⁻	1	0	0	2	1
[Mn(C ₂ O ₄) ⁺	2	0	1	4	-1
[Mn(C ₂ O ₄) ₂] ⁻	4	0	1	8	1
[MnC ₂ O ₄ , MnO ₄ ⁻ , H ⁺]	2	1	2	8	0
[MnC ₂ O ₄ ²⁺ , MnO ₃ ⁻] ⁺	2	0	2	7	-1
[MnC ₂ O ₄ ²⁺ , MnO ₃ ⁻ , H ⁺] ²⁺	2	1	2	7	-2
[H ⁺ , MnO ₂ , H ₂ C ₂ O ₄] ⁺	2	3	1	6	-1

This means that

$$D = \begin{pmatrix} 2 & 2 & 0 & 2 & 0 & 2 & 0 & 0 & 0 & 1 & 0 & 2 & 1 & 2 & 4 & 2 & 2 & 2 & 2 \\ 2 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 2 & 0 & 0 & 0 & 1 & 0 & 1 & 3 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 0 & 0 & 1 & 0 & 1 & 1 & 2 & 2 & 2 & 1 \\ 4 & 4 & 0 & 4 & 0 & 4 & 4 & 2 & 0 & 2 & 1 & 6 & 2 & 4 & 8 & 8 & 7 & 7 & 6 \\ 0 & 1 & -1 & 2 & -2 & 0 & 1 & 0 & -3 & 0 & 0 & 0 & 1 & -1 & 1 & 0 & -1 & -2 & -1 \end{pmatrix} \quad (2)$$

2.2 Computation of reaction steps

Our first requirement is that all the steps should fulfil the law of atomic and charge balance. An elementary reaction step is either uni- or bimolecular. Reversible steps are considered as pairs of a forward and a reverse reaction, *i.e.* they are two steps. All the possible uni- and bimolecular steps that fulfil the first requirement are to be constructed first.

Unimolecular steps are constructed in the following way. We select one of the species. Let d be the corresponding column of the atomic matrix, and let x be the 19×1 product (column) vector of the elementary step to be constructed. Then, it should obey the conditions (the first of which is the law of atomic balance)

$$Dx = d, \quad x \text{ is a vector of nonnegative integers} \\ x \text{ has a zero component corresponding to the reactant.} \quad (3)$$

Let us take an example. If the species to be decomposed is H₂C₂O₄, then $d^T = (2 \ 2 \ 0 \ 4 \ 0)$, and as H₂C₂O₄ → 2H⁺ + C₂O₄²⁻, in this case

$$x^T = (0 \ 0 \ 2 \ 1 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0),$$

thus, really, $Dx = d$. As we have 19 species in our concrete problem, 19 equations of this type will be obtained.

If two species react, they can be either identical, or different, consequently there are two types of *bimolecular* elementary steps. In the first case, we select one of the species. Let d be the corresponding column of the atomic matrix, and let x be the product vector of the elementary step to be constructed. Then, it should obey the equation

$$Dx = 2d, \\ x \text{ is a vector of nonnegative integers} \\ x \text{ has a zero component corresponding to the reactant.} \quad (4)$$

An example to illustrate this case is the equation 2[Mn(C₂O₄)₂]⁻ → 3C₂O₄²⁻ + 2CO₂ + 2Mn²⁺ (*cf.* eqn. (20) below.)

On the left hand side we have $2d = 2(4 \ 0 \ 1 \ 8 \ 1)^T$, whereas the right hand side is obtained from $x = (0 \ 0 \ 0 \ 3 \ 2 \ 0 \ 0 \ 0 \ 0 \ 2 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0)^T$, and again $Dx = 2d$ holds. As we have 19 species, again 19 equations of this type will be obtained.

In the second case, we select two of the species. Let d_1 and d_2 be the corresponding rows of the atomic matrix, and let x be the product vector of the elementary step to be constructed. Then, it should obey

$$Dx = d_1 + d_2, \\ x \text{ is a vector of nonnegative integers} \\ x \text{ has two zero components corresponding to the reactants.} \quad (5)$$

The equation Mn²⁺ + HC₂O₄⁻ → MnC₂O₄ + H⁺ illustrates this case (*cf.* eqn. (38) below). On its left hand side we have $d_1 + d_2 = (0 \ 0 \ 1 \ 0 \ -2)^T + (2 \ 1 \ 0 \ 4 \ 1)^T$, while the right hand side is obtained from $x = (0 \ 0 \ 1 \ 0 \ 0 \ 1 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0)^T$, and again $Dx = d_1 + d_2$ holds. As we have 19 species, the number of pairs of different species formed from these is $\binom{19}{2}$, which means that 171 equations of this type will be obtained.

Thus, in the present particular case we have altogether 19 + 19 + 171 = 209 systems of linear diophantine equations to solve. We have solved all the systems of equations using an enumerative type method of integer programming.¹²

We eliminated on the basis of energetic evidence the reactions (elementary steps suggested by the mathematical model) in which more radicals are generated than electrons transferred. Further eliminations of reaction steps are analyzed in the Section 6. The result consists of 673 elementary reactions. The corresponding reaction vectors can be found in the electronic supplement *Reduced*, see also.¹³ These elementary reaction steps are used to generate decompositions of the overall reaction.

2.3 Computation of reaction mechanisms

The overall reaction (1) can be described by the vector:

$$b = (-5, 0, -6, 0, 2, 0, -2, 0, 0, 10, 8, 0, 0, 0, 0, 0, 0, 0, 0, 0).$$

Let us define the stoichiometric matrix Γ : its rows correspond to species, and columns correspond to reaction steps, therefore it is for our special reaction a 19×673 matrix. An element γ_{ij} of the stoichiometric matrix contains the stoichiometric coefficient of species i in reaction step j . Species i is a reactant if $\gamma_{ij} < 0$, and is a product if $\gamma_{ij} > 0$. $|\gamma_{ij}|$ gives the stoichiometric number (*i.e.* number of copies) of species i that are consumed/produced in reaction step j .

A decomposition is a vector of nonnegative integer weights of the elementary reactions such that if the equations of the elementary reactions are multiplied by these weights and are summed up then a positive integer multiple of the overall reaction is obtained.

If the decomposition is described by the vector y , a 673-dimensional vector of nonnegative integer elements, then it obeys

$$\Gamma y = nb \quad y \text{ is a vector of nonnegative integers,} \quad (6)$$

with a positive integer n .

Using stoichiometric notions only, the underlying mathematical background is the following. Any reaction which can take place in the mechanism, can be described by a nonnegative vector w and an appropriate right-hand side c such that the equation

$$\Gamma w = c \quad (7)$$

holds. If this reaction is not an elementary one, *i.e.* it can be decomposed into at least two reactions which might be either elementary or non-elementary, then two nonnegative and

non-zero integer vectors and appropriate right-hand sides, say w_1 , w_2 and c_1 , c_2 , respectively, exist such that

$$\Gamma w_1 = c_1 \quad \Gamma w_2 = c_2 \quad (8)$$

and

$$w = w_1 + w_2. \quad (9)$$

The most important special cases of (7) are the elementary reactions. In the case of the j th elementary reaction w is the j th unit vector e_j , i.e. the vector of which all of the components are zero with the exception of the j th one which equals to 1.

Eqns. (8) and (9) can be interpreted in an opposite way, too. Assume that w_1 and w_2 are nonnegative and non-zero integer vectors satisfying (8) with the appropriate right-hand sides c_1 and c_2 . Then $w = w_1 + w_2$ also satisfies a type (7) equation with the right-hand side $c = c_1 + c_2$.

The usual linear algebraic interpretation of matrix Γ is that it maps the w vectors into the c vectors. This mapping is not necessarily a one-to-one correspondence, i.e. several vectors w can be mapped into the same c . In our case the vectors w are nonnegative integer vectors. In general a set \mathcal{C} is called a cone if the following two conditions hold: (i) for all nonnegative real numbers λ and for elements u of \mathcal{C} the vector λu is an element of \mathcal{C} , too, (ii) for any two elements u_1 and u_2 of \mathcal{C} the vector $u_1 + u_2$ is an element of \mathcal{C} , too. A cone is *polyhedral* if it is the set of vectors satisfying finitely many homogeneous linear inequalities. The set into which Γ maps the nonnegative orthant, is itself a polyhedral cone with rational extremal directions. It is well-known that such a cone has a Hilbert basis. The *Hilbert basis* of a cone is a finite set of its integer vectors such that all integer vectors of the cone can be generated from the elements of the Hilbert basis with nonnegative integer weights. More precisely the following theorem holds.

Theorem. *If \mathcal{C} is a polyhedral cone with rational extremal directions then there is a finite subset $\mathcal{H} = \{u_1, \dots, u_k\}$ of \mathcal{C} consisting of integer vectors such that for all $v \in \mathcal{C}$ if v is an integer vector then there are nonnegative integer weights μ_1, \dots, μ_k such that*

$$v = \mu_1 u_1 + \dots + \mu_k u_k. \quad (10)$$

Assume that \mathcal{C} is the cone obtained from the nonnegative orthant by the mapping Γ . Then the appropriate mechanism is completely described by elementary reactions if \mathcal{C} has a Hilbert basis $\mathcal{H} = \{u_1, \dots, u_k\}$ such that the sum of the negative components of each element of $\{u_1, \dots, u_k\}$ is either -1 or -2 . The reason for that is the following. In an elementary reaction there are either one or two reactant. Therefore the stoichiometric vector of the reaction contains either once or twice -1 or a single -2 . If the required Hilbert basis exists then any overall reaction which satisfies the stoichiometric conditions of the mechanism can be decomposed into a sequence of elementary reaction steps. The weight μ_j defines how many times the reaction belonging to the j th element of the Hilbert basis must take place to produce the required overall reaction.

As a first phase we generated 294 different solutions (decompositions) to eqn. (1) semiautomatically by the iterative use of the `ConstrainedMin` function of *Mathematica* aimed at solving linear programming problems. In each iteration a new decomposition was generated by forcing the program to include elementary reaction steps not used before.

The aim of this phase was that all elementary reaction steps which can occur in a decomposition must be included at least in one generated decomposition. Some of these decompositions satisfied (6) with a positive integer n greater than 1, although the greatest common divisor of the components of the appropriate vector y was in all cases 1. The total number of possible decompositions is unknown and is with several magnitude higher than 294. A decomposition may not contain

all the 19 species. Of the 673 elementary steps we have found 314, not taking part in any of the decompositions, and they cannot even take part in any decomposition. If we prescribe the presence of any of them in a decomposition then (6) will have no solution.

By repeated applications of the simplex method our mathematical analysis has proved that the two steps



must take part in all decompositions. The presence of the species in the above steps may be detected with spectroscopic measurements. We could, however, also state that the fact of taking part of these species just in the given reaction steps is not easy to be demonstrated even by kinetic analysis, or pulse radiolysis experiments. We also underline that these results can be obtained *a priori*, without any measurements. Our aim was twofold: to present the effectiveness of the mathematical method on a relatively known example, and also to shed light on less known features of the same reaction.

2.4 Selection by chemical evidence

In such a complex system as in eqn. (1) one has to introduce chemical evidence to control the search procedure. From the mathematical point of view the set of feasible solutions is decreased if one prescribes the presence or absence of species or reaction steps.

Species MnO_4^- , $\text{H}_2\text{C}_2\text{O}_4$ are the reactants present initially in the reaction vessel. Experiments show that MnO_2 and $[\text{Mn}(\text{C}_2\text{O}_4)_2]^-$ are always present. In the light absorption spectra the peaks corresponding to these species can always be identified.⁴⁻⁸ Therefore, decompositions not containing all the above four components have been eliminated to leave 249 decompositions altogether of the total 294 decompositions. An autocatalytic reaction cannot start unless a substance is present which takes the role of the catalytic end product (in this particular case Mn^{2+}) at the beginning. Some of the species (mainly hypothetical, chemically unobservable complexes) can never be initial species; they may have a certain explanatory significance.

3. Levels of species and reaction steps

There is another necessary condition to be fulfilled by the decompositions. At the very beginning only reaction steps among the initial species can take place. Then, reaction steps using the products of these reactions can also enter the scene, and so on. This chemical hierarchy can be formalized as follows.

Let a nonempty subset M_0 of the species M be called as *initial species*, and assign the zero index to these *species*. Let us also assign zero as an index to all the *elementary steps* which can take place using only initial species.

In the next step let us assign index 1 to all the so far unindexed *species* which can be obtained as products of reaction steps of zero index. (A species having zero index but also produced by some reaction of zero index, is *not* getting index 1.) Let the same index 1 be given to all the so far unindexed *reaction steps* that can take place using species of index not greater than one. The indexing procedure goes on by induction, and as we have a finite number of species and reaction steps, sooner or later it ends.

To advance even higher with abstraction, let R be the set of elementary steps. Let us denote by $S(r)$ the set of reactant species of the reaction step $r \in R$. Let M be the set of species, and $P(R)$ be the product species produced by the reaction steps in the set of an arbitrary subset \bar{R} of the reaction steps R . Suppose the set M_0 of initial species is given. Then the set of

reaction steps with index 0 is defined as follows:

$$R_0 := \{r \in R | S(r) \subset M_0\}.$$

Similarly,

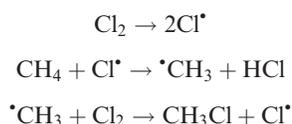
$$\begin{aligned} M_1 &:= P(R_0) \setminus M_0, \quad \dots, \\ R_i &:= \{r \in R | S(r) \subset \cup_{j=1}^i M_j\}, \\ M_{i+1} &:= P(R_i) \setminus \cup_{j=0}^i M_j \end{aligned} \quad (13)$$

This procedure will be called the *levelling process*.

Some of the species and/or reaction steps may not have indices at this stage. This means chemically that the given initial species were not enough to produce all the species present in all the reaction steps of the given decomposition. This situation may possibly be changed if the set of initial species is enlarged. However, if finite indices can only be obtained when at least one intermediate species is added to the set of initial species, then the decomposition is chemically meaningless. In our case the complexes denoted by square brackets are certainly such intermediate substances.

Let us assign the index $+\infty$ to all the remaining species and reaction steps. Note that the intuitively obvious fact that the concentration of species with an infinite index is zero for all subsequent times, is a mathematical theorem (ref. 14, p. 356).

Before applying the levelling process to our models, let us consider the related but oversimplified partial mechanism for the chlorination of methane as an example:



and let $M_0 := \{\text{Cl}_2, \text{CH}_4\} \subset M := \{\text{Cl}_2, \text{Cl}^*, \text{CH}_4, \cdot\text{CH}_3, \text{HCl}, \text{CH}_3\text{Cl}\}$. Then, in the first step species belonging to the initial set M_0 will be assigned the zero index, and also reaction steps which can take place only using reactants from the set of the initial species, thus $R_0 = \{\text{Cl}_2 \rightarrow 2\text{Cl}^*\}$ receives also zero index. Next, species being produced from reaction steps with index zero, *i.e.* species $\{\text{Cl}^*\} = M_1 = P(R_0) \setminus M_0$, will receive index 1, and also reaction steps which can take place only using reactants with indices 0 or 1. This means that step $R_1 = \{\text{CH}_4 + \text{Cl}^* \rightarrow \cdot\text{CH}_3 + \text{HCl}\}$ receives index 1 as well. Next, species $M_2 = P(R_1) \setminus (M_0 \cup M_1) = \{\cdot\text{CH}_3, \text{HCl}\}$ receive index 2. Finally, reaction step $R_2 = \{\cdot\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}^*\}$ receives index 2 as well, and species $M_3 = P(R_2) \setminus (M_0 \cup M_1 \cup M_2) = \{\text{CH}_3\text{Cl}\}$ receives index 3.

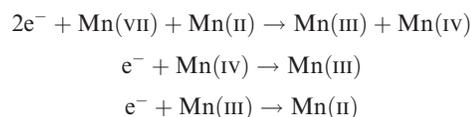
4 Chemical evidence

Besides our effort to elaborate a systematic method for generating reaction mechanisms, we also made an attempt to show how chemical evidence can be used to reduce the number of the obtained mechanisms. Therefore at this point we give a quick overview of the literature of the reaction pointing out those features that we use later on to analyze our decompositions.

The autocatalytic permanganate/oxalic acid reaction was described by Harcourt and Esson nearly 150 years ago.² Soon after experimental results showed that the mechanism is very complex, cannot be described by the initial model proposed by Skrabal.¹⁷ From the plethora of proposed mechanisms one common point is clear: there are two distinct stages of the reaction. The first one is the reduction of Mn(vii) to Mn(iii), being fast, as soon as the induction period has passed, the second one is the reduction of Mn(iii) to Mn(ii), the mechanism of which is fully elucidated by the exhaustive studies of Taube.¹⁵

At normal pH values (in the absence of exogenous base) the second stage involves the decomposition of the bisoxalatomanganese(iii) ion. The transfer of the electron takes place within the complex from one coordinated oxalate ion to the central manganese atom.¹⁵ The process is considerably slow and can be measured either by monitoring Mn(ii) or Mn(iii) concentration or even by following CO₂ evolution. The bisoxalatomanganese is a spectrophotometrically detectable intermediate having an absorption peak at 457 nm.

The last detailed study⁶ of the reaction establishes the following skeleton mechanism:



The third bulk reaction step corresponds to the above mentioned reduction of the bisoxalatomanganese(iii) complex to Mn(ii), however, depending on the pH, it can involve the reduction of other manganese(iii) complexes. In the latter case the process still follows first order kinetics. The authors found that the second bulk reaction step, *i.e.* the reduction of Mn(iv) to Mn(iii) is also of first order. In contrast to the reduction of Mn(iv) and Mn(iii), there's no evident elementary reaction or set of elementary reactions underlying the first bulk step.

5 Chemically interpreted computational results

By the above detailed algorithm we generated further decompositions in a second phase searching for chemically realistic decompositions. Altogether several hundreds of decompositions of the overall reaction (1) were generated. All the chemically unrealistic properties were prohibited in the iterative process by linear constraints which were added to problem (6). We have chosen three mechanisms (*i.e.* decompositions without weights) to demonstrate the performance of the method.

Every reaction that generates one or two species has its anti-reaction among the initial set of elementary reactions. However, such a reaction-antireaction pair doesn't necessarily describe a chemical equilibrium. Thus the algorithm cannot predict the reversibility of the reaction steps. Nevertheless, we also indicated the antireaction (that has not been selected by the algorithm and therefore has 0 weight in the vector of the decomposition) by an \leftarrow arrow if a chemical equilibrium is obvious.

The first mechanism that we chose is as follows:

		Weight
(14)	$\text{H}_2\text{C}_2\text{O}_4 + \text{MnO}_2 \rightarrow [\text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4]$	4
(15)	$\text{H}_2\text{C}_2\text{O}_4 + [\text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4] \rightarrow \text{CO}_2^- + \text{CO}_2 + 2\text{H}_2\text{O} + [\text{Mn}(\text{C}_2\text{O}_4)]^+$	1
(16)	$\text{C}_2\text{O}_4^{2-} + \text{Mn}^{3+} \rightleftharpoons [\text{Mn}(\text{C}_2\text{O}_4)]^+$	3
(17)	$\text{C}_2\text{O}_4^{2-} + [\text{Mn}(\text{C}_2\text{O}_4)]^+ \rightleftharpoons [\text{Mn}(\text{C}_2\text{O}_4)_2]^-$	2
(18)	$[\text{Mn}(\text{C}_2\text{O}_4)]^+ + \text{MnO}_4^- \rightarrow 2\text{CO}_2 + 2, \text{MnO}_2$	2
(19)	$2\text{CO}_2^- \rightarrow \text{C}_2\text{O}_4^{2-}$	2
(20)	$2[\text{Mn}(\text{C}_2\text{O}_4)_2]^- \rightarrow 3\text{C}_2\text{O}_4^{2-} + 2\text{CO}_2 + 2\text{Mn}^{2+}$	1
(21)	$\text{H}^+ + [\text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4] \rightarrow [\text{H}^+, \text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4]^+$	3
(22)	$\text{H}^+ + [\text{H}^+, \text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4]^+ \rightarrow \text{CO}_2^- + \text{CO}_2 + 2\text{H}_2\text{O} + \text{Mn}^{3+}$	3

This is stoichiometrically correct but chemically doubtful since the reduction of Mn(iii) to Mn(ii) takes place *via* bimolecular step (20). This reaction is known to be a first order elementary step (see Section 6).

By eliminating all the bimolecular elementary steps in which Mn(iii) was reduced to Mn(ii) we obtained a second decomposition.

		Weight
(23)	$\text{H}_2\text{C}_2\text{O}_4 + \text{MnO}_2 \rightarrow [\text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4]$	4
(24)	$\text{H}_2\text{C}_2\text{O}_4 + [\text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4] \rightarrow \text{CO}_2^- + \text{CO}_2 + 2\text{H}_2\text{O} + [\text{Mn}(\text{C}_2\text{O}_4)]^+$	1
(25)	$\text{C}_2\text{O}_4^{2-} + \text{Mn}^{3+} \rightleftharpoons [\text{Mn}(\text{C}_2\text{O}_4)]^+$	1
(26)	$\text{C}_2\text{O}_4^{2-} + [\text{Mn}(\text{C}_2\text{O}_4)]^+ \rightleftharpoons [\text{Mn}(\text{C}_2\text{O}_4)_2]^-$	1
(27)	$\text{MnC}_2\text{O}_4 + \text{MnO}_4^- \rightarrow \text{CO}_2^- + \text{CO}_2 + 2\text{MnO}_2$	1
(28)	$[\text{Mn}(\text{C}_2\text{O}_4)]^+ + \text{MnO}_4^- \rightarrow 2\text{CO}_2 + 2\text{MnO}_2$	1
(29)	$[\text{Mn}(\text{C}_2\text{O}_4)_2]^- \rightarrow \text{CO}_2^- + \text{CO}_2 + \text{MnC}_2\text{O}_4$	1
(30)	$2\text{CO}_2^- \rightarrow \text{C}_2\text{O}_4^{2-}$	2
(31)	$\text{H}^+ + [\text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4] \rightarrow [\text{H}^+, \text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4]^+$	3
(32)	$\text{H}^+ + [\text{H}^+, \text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4]^+ \rightarrow \text{CO}_2^- + \text{CO}_2 + 2\text{H}_2\text{O} + \text{Mn}^{3+}$	1
(33)	$\text{H}^+ + [\text{H}^+, \text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4]^+ \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} + \text{Mn}^{2+}$	2

This decomposition seems to be consistent with the so far published experiments but has several unusual features (see Section 6).

That's why we went on to find the decomposition that were the closest to the currently accepted skeleton mechanism.⁶ This decomposition does not contain any steps that are in direct contradiction with the so far obtained experimental results (see Section 6):

		Weight
(34)	$\text{H}_2\text{C}_2\text{O}_4 + \text{MnO}_2 \rightarrow [\text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4]$	4
(35)	$\text{H}_2\text{C}_2\text{O}_4 + [\text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4] \rightarrow \text{CO}_2^- + \text{CO}_2 + 2\text{H}_2\text{O} + [\text{Mn}(\text{C}_2\text{O}_4)]^+$	4
(36)	$\text{H}^+ + \text{HC}_2\text{O}_4^- \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4$	3
(37)	$\text{C}_2\text{O}_4^{2-} + \text{H}^+ \rightleftharpoons \text{HC}_2\text{O}_4^-$	1
(38)	$\text{H}^+ + \text{MnC}_2\text{O}_4 \rightleftharpoons \text{HC}_2\text{O}_4^- + \text{Mn}^{2+}$	2
(39)	$\text{C}_2\text{O}_4^{2-} + [\text{Mn}(\text{C}_2\text{O}_4)]^+ \rightleftharpoons [\text{Mn}(\text{C}_2\text{O}_4)_2]^-$	4
(40)	$\text{MnC}_2\text{O}_4 + \text{MnO}_4^- \rightarrow \text{CO}_2^- + \text{CO}_2 + 2\text{MnO}_2$	2
(41)	$[\text{Mn}(\text{C}_2\text{O}_4)_2]^- \rightarrow \text{CO}_2^- + \text{CO}_2 + \text{MnC}_2\text{O}_4$	4
(42)	$2\text{CO}_2^- \rightarrow \text{C}_2\text{O}_4^{2-}$	5

This decomposition can be submitted to the levelling process. The calculated indices of the species are as follows:

Species	Index
MnO_4^-	0
H_2O	0
$\text{H}_2\text{C}_2\text{O}_4$	0
H^+	0
$[\text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4]$	$+\infty$
MnO_2	$+\infty$
$[\text{Mn}(\text{C}_2\text{O}_4)_2]^-$	$+\infty$
$[\text{Mn}(\text{C}_2\text{O}_4)]^+$	$+\infty$
MnC_2O_4	$+\infty$
Mn^{2+}	$+\infty$
HC_2O_4^-	$+\infty$
CO_2	$+\infty$
CO_2^-	$+\infty$
$\text{C}_2\text{O}_4^{2-}$	$+\infty$

All the corresponding reaction steps (34–42) have an infinite index as there is no reaction having reactants with only zero levels. Therefore the elementary reaction steps cannot be arranged into a correct mechanism. Knowing the autocatalytic nature of the reaction it's almost obvious that we have to adjoin MnC_2O_4 to the set of initial species. It is well known that Mn^{2+} catalyzes the overall reaction, and it is widely accepted that during the "spontaneous" starting of the reaction it is also a Mn^{2+} species of unknown origin that reduces

permanganate.^{3,6} The new and final computational result shows that the sequence of the reaction steps is acceptable as follows:

		Index
(40)	$\text{MnC}_2\text{O}_4 + \text{MnO}_4^- \rightarrow \text{CO}_2^- + \text{CO}_2 + 2\text{MnO}_2$	0
(38)	$\text{H}^+ + \text{MnC}_2\text{O}_4 \rightleftharpoons \text{HC}_2\text{O}_4^- + \text{Mn}^{2+}$	0
(34)	$\text{H}_2\text{C}_2\text{O}_4 + \text{MnO}_2 \rightarrow [\text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4]$	1
(36)	$\text{H}^+ + \text{HC}_2\text{O}_4^- \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4$	1
(42)	$2\text{CO}_2^- \rightarrow \text{C}_2\text{O}_4^{2-}$	1
(35)	$\text{H}_2\text{C}_2\text{O}_4 + [\text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4] \rightarrow \text{CO}_2^- + \text{CO}_2 + 2\text{H}_2\text{O} + [\text{Mn}(\text{C}_2\text{O}_4)]^+$	2
(37)	$\text{C}_2\text{O}_4^{2-} + \text{H}^+ \rightleftharpoons \text{HC}_2\text{O}_4^-$	2
(39)	$\text{C}_2\text{O}_4^{2-} + [\text{Mn}(\text{C}_2\text{O}_4)]^+ \rightleftharpoons [\text{Mn}(\text{C}_2\text{O}_4)_2]^-$	3
(41)	$[\text{Mn}(\text{C}_2\text{O}_4)_2]^- \rightarrow \text{CO}_2^- + \text{CO}_2 + \text{MnC}_2\text{O}_4$	4

Step (41) closes the autocatalytic loop since the zero level species MnC_2O_4 is produced (indicated by thick line in Fig. 1).

The appropriate indices of the species are:

Species	Index
MnO_4^-	0
MnC_2O_4	0
H_2O	0
$\text{H}_2\text{C}_2\text{O}_4$	0
H^+	0
MnO_2	1
Mn^{2+}	1
HC_2O_4^-	1
CO_2	1
CO_2^-	1
$[\text{MnO}_2, \text{H}_2\text{C}_2\text{O}_4]$	2
$\text{C}_2\text{O}_4^{2-}$	2
$[\text{Mn}(\text{C}_2\text{O}_4)]^+$	3
$[\text{Mn}(\text{C}_2\text{O}_4)_2]^-$	4

The result shows that the levelling process has successfully ended, since all the species and reaction steps have received a finite index.

6 Discussion

In the *first* presented mechanism the reduction of Mn(III) to Mn(II) takes place *via* the second order elementary step (20). We found that this reaction is inconsistent with the experimental observations. Thus we excluded all the bimolecular elementary steps in which Mn(III) was reduced to Mn(II). This example illustrates that taking simple chemical observations into account permits to reduce significantly the number of the decompositions.

The *second* presented decomposition is not inconsistent with the experimental results but contains several unusual steps which were barely mentioned in the literature before. The reduction of permanganate can be triggered by a collision either with a Mn(II) or with a Mn(III) complex. The first one is the classical pathway that is commonly used to explain autocatalysis (27). The second one is not frequently proposed though there is no obvious evidence leading us to reject this step (28).

The reduction of Mn(IV) takes place also *via* two parallel elementary reactions. The first possibility is the formation of Mn(III) *via* (24) and (32) that is widely accepted in the literature (see Section 4). The two-electron transfer (33) which yields directly Mn(II) is more unlikely, but we have no experimental evidence in hand to exclude this elementary reaction.

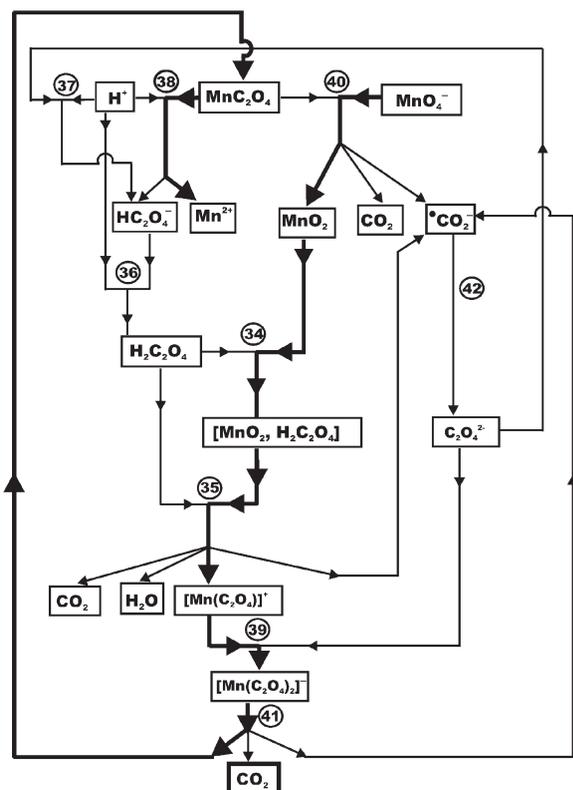


Fig. 1 Reaction pathway of reaction (1) decomposed into elementary steps (34)–(42). The thick line shows the reduction route of manganese. Reaction steps are numbered as above.

The *third* presented decomposition is very close to the recently published⁶ mechanism. Its levelling cannot be carried out if the set of initial species consists only of reactants H^+ , MnO_4^- and $\text{H}_2\text{C}_2\text{O}_4$ of the overall reaction (1). Without MnC_2O_4 all intermediate and product species figuring in the mechanism have infinite index. This is consistent with the experimental fact that the process is autocatalytic, and does not take place unless a small quantity of the product is present at the beginning. Though not necessary to the levelling, we consider H_2O also as an initial species, since the reaction takes place in aqueous solution.

The second levelling of the *third* decomposition has a first reaction step (40) where the IV oxidation state is formed from Mn(VII), and Mn(II). This is reminiscent of the Guyard reaction which takes place even in the absence of oxalic acid. The main difference from Guyard reaction is that here Mn(II) reacts as MnC_2O_4 therefore an oxalate ion is partially oxidized in the process and a radical ion ($\text{CO}_2^{\bullet-}$) is produced. The presence of the Mn(IV) intermediate is evidenced by spectrophotometric studies.^{4–8}

In reaction step (35) the Mn(IV) is reduced to Mn(III) after being complexed by oxalic acid.⁶ Reaction step (39) yields bisoxalatomanganase(III)-ion by addition of one more oxalate ion to the monooxalatomanganase(III)-ion formed in the reaction step (35). The proposed mechanism is consistent with all that we know of the reduction of Mn(III). The reaction step (41) which represents the Mn(III) \rightarrow Mn(II) reduction was confirmed to be the last one by our levelling process since its index turned out to be 4. This is in good accordance with the delayed reduction of the bisoxalatomanganase(III) complex. Furthermore this step (41) is monomolecular which accounts for the first order kinetics of the decomposition.^{3,8}

The reaction step (42) is the recombination of $\text{CO}_2^{\bullet-}$ radical ions. We found that this process is indispensable for decomposing the overall reaction, *i.e.* it appears in all decompositions generated by the algorithm (see Subsection 2.3). This finding

is of particular interest since the elimination pathway of the $\text{CO}_2^{\bullet-}$ radical ion has been subjected to debate in the literature.¹⁶

By the computations presented here on the permanganate/oxalate acid reaction we obtained mathematical support of the well-known autocatalytic nature while the origin of Mn(II) is still an open question.

Fig. 1 shows the reaction pathway of the reaction (1) decomposed into elementary steps by the presented method. It is obvious that the process is more complex than it is given in some recent papers, *e.g.*,⁶ where complex steps are included in the mechanism, *i.e.* only a skeleton mechanism is established. However our method generates decompositions consisting of only elementary reaction steps. The chemically realistic decomposition (34)–(42) is just one such decomposition and at the same time it can be considered as a further decomposed version of the skeleton mechanism of (1).

7 Perspectives

Our algorithm is developed to decompose a complicated chemical reaction into rigorously elementary steps (defined in Section 1) in every possible way. By the computation method the species, consequently also the reaction steps can be arranged in right order, *i.e.* a possible reaction mechanism can be constructed which can then be verified by experimental methods. Using this approach it is possible to

- corroborate the occurrence of previously proposed reaction steps,
- rule out the occurrence of some reaction steps,
- find reaction steps inaccessible to chemical intuition,
- point out the direction of the experiments since further investigations are needed to decide which decomposition corresponds to the real mechanism of the reaction.

The *kinetic* (as opposed to *stoichiometric*) properties of the resulting decomposition can further be investigated based upon the knowledge of reaction rate coefficients and using numerical differential equation solvers. Questions such as inhibition, acceleration and bistability can be addressed in such an approach.

It is obvious that this method can be profitable in case of other complex reactions, too.

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