

Carbon Dioxide Production in the Oxidation of Organic Acids by Cerium(IV) under Aerobic and Anaerobic Conditions

KARA BUTLER, OLIVER STEINBOCK,* BETTINA STEINBOCK,* NAR S. DALAL

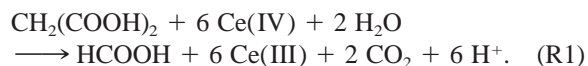
Florida State University, Department of Chemistry, Tallahassee, Florida 32306-3006

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ABSTRACT: The stoichiometry of CO₂ production during the ceric oxidation of various organic acids is measured under conditions with organic acid excess. Measurements utilize a photometric methodology. For anaerobic conditions stoichiometries $[\text{CO}_2]_{\text{produced}} : [\text{Ce(IV)}]_{\text{reduced}}$ of about 0 (malonic acid), 0.5 (e.g., glyoxylic acid), and 1.0 (oxalic acid) are found. Oxalic acid showed an oxygen-induced decrease of CO₂ production, while other compounds such as malonic acid increased the amount of produced CO₂ or showed no changes (e.g., tartronic acid). In the case of mesoxalic acid the stoichiometry is increased from about 0.5 to 2.0 due to the presence of molecular oxygen. The results are discussed on the basis of simple reaction mechanisms demonstrating that useful information on reaction pathways and intermediates can be extracted from these simple measurements. © 1998 John Wiley & Sons, Inc. *Int J Chem Kinet* 30: 899–902, 1998

The study of oxidation of relatively low molecular weight carbonic acids by metal ions has been an active area of kinetics [1]. In particular the oxidation of malonic acid (CH₂(COOH)₂) and similar compounds by Ce(IV) in acidic solution have caught remarkable attention [2–5], since these reactions coincide with the organic subset of the self-organizing Belousov–Zhabotinsky (BZ) reaction [6]. Despite these efforts, the corresponding reaction mechanisms are not fully understood, because some of them are highly complex

and involve numerous organic acids and radicals as intermediates [4,7]. A common characteristic, however, is that most organic acids are oxidized to carbon dioxide. Hence, the determination of the stoichiometry between produced CO₂ and reduced metal ions for the overall reaction mechanism reveals valuable information. A text book example is the ceric oxidation of malonic acid, where the overall reaction is written as [8]:



While measurements of the overall CO₂ stoichiometry are fairly frequent in the literature [9], we are not aware of systematic data on the CO₂ production from oxidation experiments with large excess organic acid

*Present address: Otto-von-Guericke-Universität, Institut für Experimentelle Physik, Universitätsplatz 2, D-39106 Magdeburg, Germany

Correspondence to: O. Steinbock

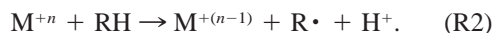
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in which dissolved oxygen is explicitly considered. Under reaction conditions in which the organic acid is in excess, it can be assumed that only a small number of intermediates are formed. In other words, the relevant reaction mechanism is minimized to a few “starting” reactions of the complex overall mechanism. Most oxidation reactions between an organic acid RH and a metal ion M^{+n} (e.g., Ce(IV) start with the formation of an organic radical $R\cdot$ (e.g., the malonyl radical)[1,2,7]:



The following reactions of the radical $R\cdot$ leading to the first stable intermediate determine the stoichiometry $f = [\text{CO}_2]_{\text{produced}} : [M^{+n}]_{\text{reduced}}$ between the amounts of produced CO_2 and reduced metal ions in excess of organic acid. In this report the stoichiometry f is measured for ten organic compounds ($57 < M_r < 183$) under anaerobic as well as aerobic reaction conditions. Cerium(IV) is used as the oxidizing agent. Measurements are performed on the basis of a photometric methodology [10]. The data obtained reveal interesting insights into the chemistry of the involved radicals and allow to some extent predictions on the identity of relevant intermediates. It is therefore felt that the presented approach is a useful aid for complementing other analytical techniques (e.g., NMR or EPR) that are sometimes difficult to apply.

All chemicals were obtained commercially (analytical grade) and used as received. Cerium(IV) sulfate, oxalic acid dihydrate, glyoxylic acid monohydrate, mesoxalic acid disodium salt, tartronic acid, L (-) malic acid, malonic acid, and glyoxal solution were obtained from Fluka. Chemicals purchased from Fluka include: tartaric acid, sodium hydroxide (N/10) solution, and sulfuric acid (10 N). Miscellaneous chemicals include: dihydroxy tartaric acid (Sigma), phenol red sodium salt (Aldrich), ferrous ammonium sulfate solution (0.1 N; LabChem), and citric acid (Mallinckrodt). All stock solutions were prepared from double-distilled water.

With minor modifications the experimental setup is based on the earlier reported by Maxon and Johnson [10]. The key idea of this approach is to transfer the produced carbon dioxide from the sample into a basic phenol red solution (typically 200 ml: [phenol red] = 10^{-5} M, [NaOH] = 10^{-4} M). According to the equilibrium between gaseous carbon dioxide and aqueous bicarbonate ion, the influx of CO_2 gives rise to a pH change which is detected spectrophotometrically via the absorbance of phenol red. The detection limit for the system was about 2.2 mg CO_2 . Prior to each ex-

periment the setup was calibrated by measuring the CO_2 production of a 25 mM NaHCO_3 solution which was acidified by injecting 1 ml concentrated H_2SO_4 . All oxidation reactions were carried out in 1.0 M H_2SO_4 at 25.0 ± 0.5 °C. Typical reactant concentrations were: $[\text{organic acid}]_0 = 0.1$ M and $[\text{Ce(IV)}]_0 = 1.9 \times 10^{-3}$ M. The Ce(IV)(SO_4)₂ stock solutions were titrated with $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2$ using ferroin as an indicator. The reaction solution (typical volume: 25–30 ml) was equilibrated with either nitrogen or oxygen for 40 min prior to any measurement. Depending on the reaction conditions nitrogen or oxygen were also used as carrier gases for transferring the produced CO_2 from the reaction vessel into the phenol red solution. For simplicity, we will denote reactions carried out with oxygen-saturated solutions as aerobic reactions.

Results for the stoichiometric value $f = [\text{CO}_2]_{\text{produced}} : [\text{Ce(IV)}]_{\text{reduced}}$ obtained under anaerobic and aerobic reaction conditions are summarized in Table I. For anaerobic reaction conditions six of the organic acids had a stoichiometry f of approximately 1 : 2. Exceptions found are (i) oxalic acid which produces one mole of CO_2 in the reaction with one mole of Ce(IV) and (ii) malonic acid which showed no significant CO_2 production. In addition, citric acid gave rise to a surprising stoichiometry of approximately 0.35. For comparison, we also studied the oxidation of the diketone glyoxal, which is obviously not likely to produce any carbon dioxide. Notice, that for anaerobic reaction conditions the results for malonic acid and glyoxal are identical.

The comparison between results obtained under anaerobic and aerobic reaction conditions reveals interesting differences for four of the organic acids (oxalic, mesoxalic, malonic, and citric acid). Oxalic acid decreases its CO_2 production by a factor of two, while mesoxalic acid shows a large increase by a factor of about four. Malonic acid, the classic organic substrate of the Belousov–Zhabotinsky reaction, and citric acid produce under the given aerobic reaction conditions carbon dioxide with a stoichiometry of approximately $f = 1 : 2$. The organic compounds glyoxylic acid, tartaric acid, malic acid, and glyoxal showed no significant dependence of the stoichiometry on the oxygen content of the reaction solution.

The presented results reveal three major stoichiometry values for the production of carbon dioxide: $f = 0.0, 0.5,$ and 1.0 . The value $f = 2$, found for mesoxalic acid, is only realized under aerobic reaction conditions. What are the underlying reaction mechanisms, which can give rise to these stoichiometries? As discussed in the Introduction, all of the studied reactions are likely to start with the formation of a radical $R\cdot$ (compare, R1). In the absence of molecular

Table I Stoichiometric Ratios $f = [\text{CO}_2]_{\text{produced}}/[\text{Ce(IV)}]_{\text{reduced}}$ under Anaerobic and Aerobic Reaction Conditions

Organic Compound	Molecular Formula	f (anaerobic)	f (aerobic)
Oxalic acid	HOCCOOH	1.03 ± 0.05	0.55 ± 0.05
Glyoxylic acid	HCOCOOH	0.51 ± 0.05	0.45 ± 0.05
Mesoxalic acid	HOCCOCOOH	0.55 ± 0.05	1.97 ± 0.1
Tartaric acid	HOOCCH(OH)CH(OH)COOH	0.45 ± 0.05	0.43 ± 0.05
Dihydroxy tartaric acid	HOCC(OH) ₂ C(OH) ₂ COOH	0.48 ± 0.05	0.51 ± 0.05
Tartronic acid	HOCHC(OH)COOH	0.49 ± 0.05	0.46 ± 0.05
Malic acid	HOCHC(OH)CH ₂ COOH	0.43 ± 0.05	0.43 ± 0.05
Citric acid	HOCCCH ₂ C(OH)(COOH)CH ₂ COOH	0.35 ± 0.05	0.50 ± 0.05
Malonic acid	HOCCCH ₂ COOH	<0.1	0.48 ± 0.05
Glyoxal	HCOCHO	<0.1	<0.1

The stoichiometry f of carbon dioxide production in the ceric oxidation of small organic compounds with respect to the amount of reduced Ce(IV). Notice, that the initial amount of Ce(IV) is reduced completely, since the organic compound is in excess. Aerobic conditions correspond to an initial oxygen concentration of approximately 1.2 mM (near saturation) and oxygen is also delivered during the entire course of the reaction.

oxygen, the following reaction scenarios are capable of generating the observed major stoichiometries.

In the simplest case, a radical recombination process takes place that produces a stable intermediate R_2 :

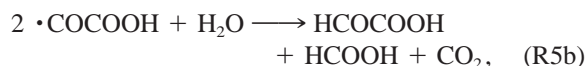
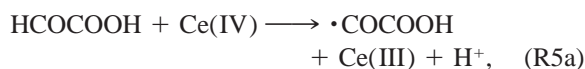


Notice, that the stable product R_2 could in principle react further with the oxidized metal ion, but would do this to no significant extent, since the organic acid RH is in large excess under the given experimental conditions. The resulting stoichiometry is therefore $f = 0$, as found for malonic acid. Indeed, Gao et al. [3] recently identified R_2 in the case of malonic acid as 1,1,1,2-ethanetetracarboxylic acid.

The stoichiometry of 0.5 is one realization of the following reaction scheme:

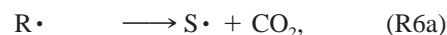


where m is a positive integer. In this scenario an unstable intermediate P_1 is formed by radical recombination which then splits off m carbon dioxide molecules. The corresponding stoichiometry is therefore $f = m / 2$. Notice, that the process (R4b) might as well form more than one stable fragment, with one fragment being possibly the initial organic acid RH. In this case, the system performs a classic disproportionation. The oxidation of glyoxylic acid under anaerobic reaction conditions [11] is a simple example for this behavior



and is obviously in good agreement with the measured stoichiometry of $f = 0.51$.

A different reaction mechanism could be realized in the case of the ceric oxidation of oxalic acid, where the stoichiometry is measured with $f \approx 1.0$. One possible explanation could be based on the reaction scheme R4a/R4b with $m = 2$. An alternative way to describe this reaction, however, is to assume that the primary radical $R\cdot$ splits off CO_2 directly and forms a second radical species $S\cdot$:

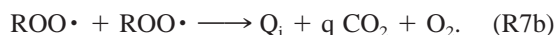


In the case of oxalic acid, $S\cdot$ would be the radical $\cdot\text{COOH}$ and S_2 oxalic acid itself—a mechanism which is also in good agreement with the stoichiometric ratio of 2 between oxalic acid and Ce(IV). An additional reaction which could be of importance for the Ce(IV)/oxalic acid system involves the direct oxidation of the radical [12].



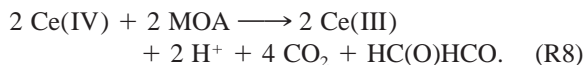
The rate constant of this reaction has been reported as $k_{6c} = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.¹³ The reactions R6b and R6c might coexist and changes in their relative rates would not lead to differences in the stoichiometry of CO_2 production. For a reliable classification of oxalic acid to either the mechanism R5a/R5b or R6a/R6b/R6c additional information on the involved radical(s) is necessary.

Although it is well-known that molecular oxygen can influence the kinetics of the oxidation of organic acids, only little data is available on details of the underlying complex reaction mechanisms. The presented changes of stoichiometry (Table I) from anaerobic to aerobic reaction conditions should apply additional data to elucidate this problem. In the case of the aerobic oxidation of malonic acid an increase of the stoichiometry from about zero to approximately 0.5 is observed. This change can be explained in terms of the following two reactions, which are a subset of standard autooxidation mechanisms [1,2]:



The peroxy radical $ROO\cdot$, which was recently identified for the ceric oxidation of malonic acid [4], undergoes radical recombination (R7b) and splits off q molecules of carbon dioxide. For malonic acid q is found to be approximately one (cf.; Table I). Consequently, this result suggest that the stable fragments Q_i cannot be tartronic acid ($HC(OH)(COOH)_2$) and mesoxalic acid ($CO(COOH)_2$), since in this case one would find $f = q = 0$. In the framework of R7b, however, it seems reasonable to conclude that either tartronic acid and glyoxylic acid ($HCOCOOH$) or mesoxalic acid and hydroxyacetic acid ($H_2C(OH)COOH$) are produced, because both product pairs correspond to a q value of 1 (i.e.; $f = 0.5$).

The interesting oxygen-dependent increase of stoichiometry found for citric acid and especially mesoxalic acid (anaerobic: 0.55; aerobic: 1.97) illustrates the complexity of the studied oxidation reactions. One possibility to summarize the reaction of mesoxalic acid (MOA) in the presence of oxygen is as follows:



However, the presented results require further studies, preferably utilizing EPR spectroscopy and analytical methods, such as HPLC. Also, the oxygen-induced decrease of CO_2 production observed in the ceric oxidation of oxalic acid is an intriguing finding that deserves further experimentation. Although these reactions are difficult to explain at this point of our investigations, they stress the usefulness of the presented approach: The analysis of CO_2 stoichiometry

under excess organic acid conditions allows to distinguish between different reaction schemes and to find unusual behavior that deserves thorough investigations. The presented results also reemphasize that molecular oxygen acts not necessarily as a simple catalyst but introduces oxygen-specific reaction pathways and intermediates.

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