Transient isotopic studies on 1-butene oxidation over a $\text{VO}_x\text{-TiO}_2$ catalyst in presence of water vapour

W. Y. Suprun^{1,*}, D. P. Sabde¹, B. Kubias³, H.-K. Schädlich², H. Papp^{1,*}

¹⁾ Institut für Technische Chemie, Universität Leipzig, Linnèstr 3, D-04103 Leipzig, Germany

²⁾ Institut für Chemische Verfahrenstechnik, Technische Universität Clausthal, Leibnizstr 17, D-38678, Clausthal-Zellerfeld, Germany

³⁾ Fritz-Haber-Institut der Max-Planck-Gesellschaft, Abteilung Anorganische Chemie, Faradayweg 4-6, D-14195 Berlin, Germany

* Corresponding authors

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Abstract

The catalytic oxidation of 1-butene was studied in the temperature range of 390 to 550 K in presence and absence of O_2 and water vapour. An increase in acetic acid yield was observed with increasing temperature up to a maximum at 510 K. The addition of water promoted the formation of acetic acid and suppressed total oxidation reactions. Transient isotopic experiments with $^{18}\text{O}_2/^{16}\text{O}_2$ and $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ were carried out to investigate the role of gas oxygen and water in the formation of acetic acid. In absence of water the isotopic exchange was slow and complete at high temperatures. On the contrary, a fast but incomplete isotopic exchange in acetic acid was observed in presence of water. Isotopic transient experiments with $^{18}\text{O}_2$ and H_2^{18}O revealed that ^{18}O from H_2^{18}O was more readily incorporated into acetic acid than ^{18}O from $^{18}\text{O}_2$ pointing to a role of water as a reactant.

Keywords: VO_x -catalyst, oxidation, 1-butene, transient isotopic studies, role of water

1. Introduction

Acetic acid (AcOH) is an important intermediate product for the production of many value added chemicals like vinyl acetate. Currently it is mainly produced by carbonylation of methanol and oxidation of ethylene according to the Wacker process [1]. Some attempts were made in the last decades to develop a process for the production of AcOH by catalytic gas phase oxidation of light hydrocarbons on MeO_x supported catalysts [2-7]. Various redox catalysts were proposed for the selective oxidation of C_4 -hydrocarbons mostly on the basis of vanadium oxide [3,4]. Especially $\text{VO}_x\text{-SbO}_y$ containing catalysts supported on TiO_2 (anatase) have shown promising results in the C_4 oxidation [7]. Only a few older papers [2-4] were devoted to the mechanism of the catalytic oxidation of C_4 hydrocarbons to AcOH . However, none of these publications explained un-

ambiguously the oxidative cleavage of 1-butene to AcOH and, hence, the mechanism is still a matter of discussion [8,9]. Seiyama et al. [4] proposed an oxidative cleavage mechanism, which involves water as one of the reactants and 2-butanol as the primary intermediate product. In contrast, Kaneko et al. [3] suggested a reaction mechanism without the participation of water. Other authors [10, 11] studied the influence of water vapour on the oxidative dehydrogenation of hydrocarbons (HC) on VO_x catalysts and observed different effects of water on the formation of the reaction products. So, in the oxidation of HCs at low temperatures, the formation of carboxylic acid was promoted by addition of water [8]. On the contrary, water was found to suppress the rate of oxidative dehydrogenation reactions at high temperatures [10, 12].

Transient isotopic experiments are a suitable tool to elucidate the role of water in the catalytic oxidation of HCs . It was pointed out that the O-exchange in the lattice of vari-

ous metal oxides depends on the type of the metal oxide and on temperature [13-18]. Doornkamp et al. [17] and Weckhuysen et al. [18] determined the rate constants of oxygen exchanges for period IV metal oxides at different temperatures in absence of water and revealed that on vanadium based oxides both oxygen atoms from a gas phase O_2 molecule are exchanged by lattice surface oxygen according to the so called R^2 -mechanism. Iglesia et al. [19, 20] studied the oxidative dehydrogenation of $\text{C}_2\text{-C}_3$ HCs and concluded that the reaction proceeds according to a Mars-van Krevelen mechanism. Studies of the content of oxygen isotopes in H_2O formed in-situ during oxidative dehydrogenation of ethane on a VO_x catalyst revealed that lattice oxygen was exchanged by isotopic gas phase oxygen and reversible formation of water.

Against this background, the aim of the present investigation was to investigate the reaction mechanism of the selective oxidation of 1-butene in the presence of a $\text{VO}_x\text{-TiO}_2$ catalyst by steady state transient isotopic experiments taking into account especially the role of H_2O .

2. Experimental

2.1. Catalyst

The $\text{VO}_x\text{-TiO}_2$ catalyst (6 wt-% V_2O_5) was prepared by spray-drying of TiO_2 (Millenium GmbH) and vanadiumV-oxide. The sample was first dried at 370K and then calcined at 620K for 5h. It was characterized by N_2 adsorption (ASAP 2000, Fa. Micromeritics), temperature programmed desorption of NH_3 and oxygen (Oxylyt-Oxytherm, Sensotech GmbH), temperature programmed reduction with H_2 and n-butane, and XPS. The BET-surface area of the catalyst was $79 \text{ m}^2/\text{g}$ and the average pore diameter amounted to 13 nm. A detailed description of the results of catalyst characterization was reported elsewhere [21].

2.2. SSITKA-apparatus

The catalytic measurements were carried out in a self-constructed SSITKA-micro-apparatus (Fig.1). Temperature, pressure, and gas flow were controlled by PC.

The reaction was performed in a quartz reactor (i.D: 0.5 cm; L: 10 cm) at atmospheric pressure in the temperature range of 390 -550 K using 0.05-0.2g of catalyst and a constant 1-butene to oxygen ratio of 1:4 (GHSV: 3600 h^{-1} , const.). The oxidation of 1-butene over the $\text{VO}_x\text{-TiO}_2$ catalyst was carried out in presence and absence of both, H_2^{16}O and H_2^{18}O and the oxygen isotopes $^{16}\text{O}_2$ and $^{18}\text{O}_2$. A typical reaction mixture contained 1.2% 1-butene, 5% O_2 , balance He, whereas in case of the reaction in presence of water the mixture contained additionally 17 % water vapour.

Fig. 1: SSITKA apparatus. R: quartz tube micro reactor; GSS: gas stream selector; MS: mass spectrometer, MK: mixer, F: microfilter; K: condenser, MFC: mass flow controller; LFC: liquid flow controller, TIRC: temperature controller.

2.3. Isotopic-transient-experiments

For isotopic transient experiments cylinders containing 10% $^{16}\text{O}_2$ in He and 10% $^{18}\text{O}_2$ in He, respectively, were used (purities: $^{18}\text{O}_2$: 95.5%, balance $^{16}\text{O}_2$; H_2^{18}O : 98.5%, balance H_2^{16}O). Before the isotopic experiments the catalyst was activated with a mixture of 5% $^{16}\text{O}_2$ and He for 60 min and cooled to the desired temperature before admitting the reactant gases. After steady state conditions were achieved, $^{16}\text{O}_2$ was replaced by $^{18}\text{O}_2$. In case of experiments with water H_2^{18}O the catalytic reaction was carried out first in absence of water and then in presence of H_2^{18}O , which was dosed by a Liquid-Flow-Evaporator (Bronkhorst Hi-Tec) to the feed. Following isotopic transient experiments were performed: i) in presence of H_2^{16}O and H_2^{18}O , respectively, by replacement of $^{16}\text{O}_2$ by $^{18}\text{O}_2$, ii) in absence of water by replacement of $^{16}\text{O}_2$ by $^{18}\text{O}_2$, iii) in absence and presence of water and $^{16}\text{O}_2$.

2.4 On line-MS analysis

The reaction products were analyzed by an on-line mass spectrometer (GSD 300 C2; QMS 200; 1-200 amu, Omnistar, Pfeiffer Vacuum) in time intervals of 15 seconds. The effluent gases passed to the mass spectrometer via a gas stream selector (GSS 300) which was kept at 393 K. A vari-

ety of products were obtained during oxidation such as $\text{C}_1\text{-C}_4$ -carboxylic acids: formic acid (FA), propionic acid (PA), crotonic acid (CA), maleic anhydride (MA), 2-butanol (2-BuOH), furan (F), methyl vinyl ketone (MVK), methyl ethyl ketone (MEK) and CO_x . Although MS fragments of all the products were recorded, in this work only MS fragments of the main products such as acetic acid (m/e 60, 62, 64) and water (m/e: 18 and 20) are discussed. For a quantitative determination the respective MS intensities were converted into concentrations using individual calibration coefficients.

3. Results and discussion

3.1 Influence of reactions conditions

3.1.1 Effect of temperature

Usually, the oxidation of 1-butene was carried out in the temperature range of 390 to 550 K in presence of 17% water vapour at a GHSV of 18.000 h^{-1} . In Fig. 2 the influence of

Fig. 2: Influence of temperature on the formation of oxidation products during the catalytic oxidation of 1-butene on a VO_x/TiO_2 catalyst in presence of 17% water.

temperature on the formation of the oxidation products is illustrated. The major products obtained at various temperatures were AcOH, formic acid, 2-butanol and CO_2 . Other products such as methyl ethyl ketone, methyl vinyl ketone, propion aldehyde (PAD), formic acid, propionic acid, crotonic acid, maleic anhydride, maleic acid and furan were obtained in small concentrations. The yields of the main product AcOH increased with increasing temperature. The maximum yield of AcOH was observed in the temperature range of 520-540 K. In case of the other oxidations products the maximum yields differed with temperature. As expected,

the products of total oxidation also increased with increasing temperature.

3.1.2 Influence of water vapour

The influence of water on the formation of oxygenates was investigated in absence and presence of water vapour (17%) at 433, 493, and 553 K. The oxidation of 1-butene was first carried out in absence of water and after steady state was attained, water was added to the reactants. The selectivities of all oxidation products altered with the addition of water. In Fig. 3, only the change in AcOH concentration before and after addition of water is depicted.

Fig. 3: Formation of acetic acid during the oxidation of 1-butene in absence and presence of water at various temperatures. The arrows indicate the addition of water to feed.

Water promoted the formation of AcOH, 2-BuOH, MVK, and F [21], whereas allylic and total oxidation were suppressed. The influence of water on the formation of the oxidation products strongly depended on reaction temperature, i.e., at lower temperatures of 393 to about 513 K, the formation of AcOH, 2-BuOH, MVK, F, and MAA were promoted, whereas at higher temperatures, i.e., above 530 K no significant influence of the addition of water was observed on the formation of AcOH. The influence of water on the formation of the oxidation products may be attributed to different equilibrium conditions between adsorption /desorption of water, AcOH, and intermediate products at various temperatures on catalyst surface.

3.1.3 Influence of water concentration

The influence of water concentration on the formation of oxygenates was studied at 493 K. As depicted in Fig. 4, the selectivity to AcOH and formic acid increased with in-

creasing water concentration, whereas the selectivity to the total oxidation products decreased. The increase in AcOH concentration after addition of water indicated that water suppressed the total oxidation of 1-butene and promoted the formation of acids.

Fig. 4: Influence of water vapour concentration on the selectivity to AcOH, formic acid, and CO_x in the oxidation of 1-butene at 493 K.

3.2. Oxygen functionalisation of 1-butene with lattice oxygen

The formation of AcOH and CO_x was studied in absence and presence of water on freshly activated catalyst samples under unaerobic conditions. As shown in Fig. 5, in presence of water substantially more AcOH and less carbon dioxide are formed compared to the reaction in absence of water (dry flow). In case of reaction in absence of water, the formation of AcOH was observed after 800 sec. and its concentration decreased drastically after 6000 sec. In presence of water, however, the AcOH formation was observed immediately after addition of 1-butene and for a longer time. This experiment also indicates that the rate of AcOH formation decreased gradually in presence of water. The formation of more AcOH in presence of water may be due to the different activity of VO_x species for oxidation steps involving water as reactant. This experiment supports our hypotheses regarding the mechanism of the butene oxidation [8, 21] that water is directly involved in the formation of AcOH and other oxygenates. In the case of dry gas flow, active lattice oxygen was fast consumed for the formation of oxidation products such as AcOH and CO₂ as long as it was available resulting in rapid decrease of AcOH concentration after 6000 sec. In presence of water the active lattice oxygen was permanently available due to an oxygen transfer either from water or from gas phase oxygen to the catalyst and could subsequently be introduced into oxygenates. In order to investigate the role of water in the formation of acetic acid and other oxidation products, isotopic transient experiments were carried out.

Fig. 5: Formation of CO₂ (a) and AcOH (b) during the oxidation of 1-butene on a freshly activated catalyst sample at 494 K in absence and presence of 17 vol % water. Catalyst weight: 500 mg, 1-butene: 1.0 vol- %. The arrow indicates the addition of 1-butene to the feed

3.3. Isotopic transient experiments

3.3.1. Replacement of ¹⁶O₂ by ¹⁸O₂ in presence of water

The isotopic transient experiments were performed in the temperature range of 390 to 550 K in presence of 17% H₂¹⁶O by switching from ¹⁶O₂ to ¹⁸O₂. Typical reaction profiles after switching ¹⁶O₂ to ¹⁸O₂ at 160 °C are shown in Fig 6. It can be seen (Fig. 6a) that the total oxygen and 1-butene concentrations remained the same after switching from ¹⁶O₂ to ¹⁸O₂. The oxygen isotopic exchange was rapid but limited. Three isotopomers of AcOH were observed (Fig. 6b) at constant total concentration of AcOH.

Fig. 7 shows the formation of these AcOH molecules in dependence on time on stream.

The isotopic composition of an AcOH isotopomer with ¹⁶O-¹⁸O is defined as follows:

$$IC^{16O-18O}_i = C^{16O-18O}_i / (C^{16O-16O}_i + C^{18O-16O}_i + C^{18O-18O}_i) * 100\%$$

(C^{16O-18O}_i is the actual concentration of the respective AcOH isotopomer after oxygen switching). The distribution of the isotopomers of acetic acid at different reaction temperatures and water vapour contents of the feed is presented in Table 1.

Table 1. Oxygen isotopic distribution in AcOH isotopomers in the catalytic oxidation of 1-butene on VO_x/TiO_2 in presence and absence of water after switching from $^{16}\text{O}_2$ to $^{18}\text{O}_2$ (reaction conditions see Fig. 6).

Temp. K	Reaction conditions	Conc. of AcOH (vol-%)	$\tau_{(1/2)}$ (s)	Isotopic distribution in AcOH (%)		
				$^{16}\text{O}\text{-}^{16}\text{O}$	$^{16}\text{O}\text{-}^{18}\text{O}$	$^{18}\text{O}\text{-}^{18}\text{O}$
433	17% water	0.066	400	87.2	9.5	1.20
453	17% water	0.11	300	85.8	13.2	1.27
473	17% water	0.22	190	82.9	16.3	1.39
493	17% water	0.42	120	79.4	20.8	1.49
533	17% water	1.15	80	71.4	26.8	1.85
533	no water	0.28	850	0.5*	5.1*	93.8*

*) after 6000 sec: $\tau_{(1/2)}$: half time of isotopic exchange in AcOH. **Fig. 6:** Reaction profile (a) and formation of AcOH isotopomers (b) during catalytic oxidation of 1-butene on $\text{VO}_x\text{-TiO}_2$ at 330 K in presence 17 vol-% of water. Catalyst weight: 200 mg; GHSV: 3600 h^{-1} . The arrows indicate the addition of 1-butene to the feed and switching from $^{16}\text{O}_2$ to $^{18}\text{O}_2$.

Table 1 shows that with increasing temperature the total concentration of the formed AcOH increased. As expected, the share of the $^{16}\text{O}\text{-}^{16}\text{O}$ isotopomer decreased with increasing temperature, whereas the amount of the isotopomers $^{16}\text{O}\text{-}^{18}\text{O}$ and $^{18}\text{O}\text{-}^{18}\text{O}$ increased. The isotope exchange time (τ) decreased with increasing temperature indicating a faster rate of isotope exchange at higher temperatures. Other characteristic features of the reaction were

Fig. 7: O-isotopic composition in acetic acid in dependence on time after switching from $^{16}\text{O}_2$ to $^{18}\text{O}_2$ during oxidation of 1-butene on $\text{V}_2\text{O}_5\text{-TiO}_2$ at 433K (reaction condition see Fig. 6). **Fig. 8:** Formation of $^{16}\text{O}\text{-}^{18}\text{O}$ and $^{18}\text{O}\text{-}^{18}\text{O}$ AcOH-isotopomers during the oxidation of 1-butene on $\text{VO}_x\text{-TiO}_2$ at 533 K after switching from $^{16}\text{O}_2$ to $^{18}\text{O}_2$ in absence of water.

i) the main isotopomer formed was the $^{16}\text{O}\text{-}^{18}\text{O}$ isotopomer, and ii) the exchange of ^{16}O by ^{18}O in both AcOH isotopomers increased more than two times in the temperature range studied. In contrast, if the isotopic switching experiment was carried out in absence of water at 533 K obtained as main product. This result indicated that the oxygen exchange proceeds via an isotopic exchange of lattice ^{16}O by ^{18}O from $^{18}\text{O}_2$ followed by the insertion of this oxygen into the AcOH molecules. The typical isotopic exchange profile

for this reaction is shown in Fig. 8. It is clearly seen that initially ^{16}O - ^{18}O AcOH was formed as predominant product as long as ^{16}O from the catalyst lattice was sufficiently available for insertion in AcOH. Later the concentration of ^{16}O - ^{18}O AcOH decreased and only ^{18}O - ^{18}O AcOH was obtained as major product.

3.3.2. Formation of H_2^{18}O

The results of an experiment with $^{18}\text{O}_2$ to investigate a possible formation of H_2^{18}O during reaction are shown in Fig 9. It can be seen that after switching from $^{16}\text{O}_2$ to $^{18}\text{O}_2$ the concentration of H_2^{18}O increased slightly indicating that an isotope exchange took place on the catalyst surface by either an interaction between $^{18}\text{O}_2$ and reaction water formed or a formation of H_2^{18}O via oxidation of 1-butene. After 60 min on stream, H_2^{16}O was added to the reaction feed, causing a drastic increase in the concentration of H_2^{18}O and, thus, pointing to an exchange of ^{18}O between gas phase $^{18}\text{O}_2$ and the catalyst lattice ^{16}O or an interaction with H_2^{16}O on the catalyst surface with ^{18}O .

Fig. 9: Formation of H_2^{18}O (m/e: 20) during oxidation of 1-butene at 533 K in absence and in presence of H_2^{16}O . The vertical arrows indicate the switching of $^{16}\text{O}_2$ to $^{18}\text{O}_2$ and addition of H_2^{16}O to feed.

3.3.3. Formation of AcOH in presence of H_2^{18}O and H_2^{16}O

In Fig. 10 a and b a comparison of the formation of AcOH at 493 K in presence of H_2^{18}O and H_2^{16}O is depicted. The reaction was first studied in absence of water, similar to the the experiment described in chapter 3.1.2. After reaching steady state conditions, H_2^{18}O was added to the feed resulting in a sharp increase in the concentration of AcOH for some time and then attaining a steady state concentration level, which was 2-3 times higher than that of AcOH formed in absence of water. In case of reaction in presence of water as shown in Fig. 10b, the catalyst was pretreated with $^{16}\text{O}_2$ and H_2^{16}O (17%) at 493 K for 1h and then

Fig. 10: Formation of AcOH during the oxidation of 1-butene on a VO_x-TiO₂ catalyst at 533 K, (a) in absence and presence of H_2^{18}O and (b) in presence of H_2^{16}O . The arrows indicate the addition of either 1-butene or water to the feed.

1-butene was added to the feed. It was observed that after the input of 1-butene to the feed AcOH was formed rapidly and reached the steady state concentration level soon. When the reaction was studied in presence of H_2^{18}O , the formation of the three isotopomers of AcOH was observed. The total concentration of all three isotopomers was the same as the concentration of AcOH in case of the reaction carried out in presence of H_2^{16}O . Initially the concentration of AcOH with ^{16}O - ^{16}O went through a sharp maximum and dropped then to the lowest concentration among the three isotopomers. This indicates a strong acceleration of the desorption of AcOH from the catalyst surface by addition of water. With the decrease of the concentration of ^{16}O - ^{16}O AcOH isotopomer the concentration of ^{16}O - ^{18}O AcOH isotopomer increased indicating a partial insertion of ^{18}O from H_2^{18}O into AcOH. It was also observed that the concentration of AcOH with ^{18}O - ^{18}O increased gradually becoming the major one among all isotopomers. This indicates that the insertion of ^{18}O from H_2^{18}O is more dominant than the insertion of ^{18}O from $^{18}\text{O}_2$ and supports the arguments that water is involved as reactant in the oxidation reaction.

3.3.4. Comparison of the contribution of the different oxygen sources to the formation of AcOH

The results concerning the isotopic contribution from H_2^{18}O and $^{18}\text{O}_2$ to the ^{18}O content in AcOH are summarized in Fig. 11. It was observed that the sum of ^{16}O - ^{18}O and ^{18}O - ^{18}O AcOH isotopomers in case of isotopic experiments with H_2^{18}O and $^{18}\text{O}_2$ was 77 % and 32%, respectively. This indicates that ^{18}O in AcOH predominantly stems from H_2^{18}O . This shows further that the oxygen transfer from gas phase oxygen to the molecule occurs probably via the catalyst and/ or via participation of H_2O . This can be seen as an evidence for the participation of water in the reaction as one of the reactants. Iglesia et al. [19, 20] and Lemonidou et al. [10] also observed that water not only enhanced the rate of oxidation and suppressed total oxidation, but also took part as one of the reactants in reaction [22].

Fig. 11: Distribution of oxygen isotopomers in AcOH during oxidation of 1-butene at 493 K on $\text{VO}_x\text{-TiO}_2$ in presence of H_2^{18}O (a) or H_2^{16}O (b) in presence of oxygen $^{16}\text{O}_2$ (a) or $^{18}\text{O}_2$ (b).

3.3.4.1. The mechanism of 1-butene oxidation to acetic acid in presence of water

In the papers on the mechanism of the oxidation of 1-butene to acetic acid of Kaneko et al. [3] and Seiyama et al. [4] different conclusions were drawn on the role of water vapour. Both authors agreed in the assumption of a selectivity promoting effect of water vapour. They further agreed that the reaction proceeds via the formation of a carbocation, which was assumed to be the preliminary step of the reaction chain. According to Kaneko, however, acetic acid is formed by an interaction of an active oxygen species with this carbocation leading to two molecules of acetaldehyde, which are oxidized to AcOH. Water is thought to accelerate the isomerization of 1-butene and to inhibit total oxidation. On the contrary, Seiyama proposed that water reacts with the carbocation to 2-butanol as primary oxidation product. Butanol is then further oxidized to MEK and subsequently cleaved to acetic acid and acetaldehyde.

In our experiments we also observed that water promoted the formation of AcOH. The promotion effect was found to depend on temperature: the AcOH selectivity increased with raising temperature only up to 533 K when water vapour was added. Above that only little effects of H_2O addition on the selectivity of AcOH formation was observed and the reaction mechanism changed to allylic oxidation in the direction of MA formation. Furthermore, our isotopic experiments with $^{18}\text{O}_2$ and H_2^{18}O showed that during 1-butene oxidation ^{18}O from H_2^{18}O is more readily introduced into acetic acid than ^{18}O from oxygen. This finding clearly indicates that water is involved in the reaction as one of the reactants. The observed increase in AcOH selectivity may also be due to an accelerated desorption of AcOH from the catalyst surface caused by water vapour. Li and Shen [22] and Jehng et al. [17] observed

that water altered the catalyst surface by generating hydroxyl species, changing also the oxidation state of vanadium. In absence of water, acetic acid remained attached on the catalyst surface as acetate species, which underwent total oxidation to CO_x [19, 20]. In presence of water, these acetate species were hydrolyzed to acetic acid and may desorb more easily from the catalyst surface [8].

4. Conclusions

The investigation of the mechanism of the catalytic oxidation of 1-butene in the temperature range from 430 to 560 K in presence and absence of water vapour revealed that the yield of acetic acid increased with an increase in temperature. A maximum AcOH yield was obtained at about 513 K. Water was found to suppress the total oxidation of 1-butene and to promote the formation of AcOH. Isotopic transient experiments by switching from $^{16}\text{O}_2$ to $^{18}\text{O}_2$ in presence and absence of H_2^{16}O and H_2^{18}O showed that water not only participated in the reaction but also influenced the adsorption/desorption of various intermediates and final products. Further, the isotopic transient experiments revealed that the reaction rates of isotopic oxygen exchange into acetic acid was dependent on the reaction temperature. In absence of water and at high temperature the isotopic exchange was slow and complete. In contrast, in presence of water a fast but incomplete isotopic exchange in acetic acid was observed. ^{18}O from H_2^{18}O was more readily inserted into the C_4 acid than ^{18}O from gaseous oxygen. These findings indicate that water is involved in the reaction mechanism as one of the reactants. For a further improved understanding of the water participation in the reaction it will be essential to investigate the isotopic exchange of individual intermediate products with labelled water in presence and absence of gas phase oxygen.

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