

# Catalytic Decomposition of Hydrogen Peroxide by Molybdate - Colourful Insights into the Essence of Catalysis

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**Abstract** The use of catalysts in chemistry and biology is ubiquitous. To help students understand the nature of catalysis, several experiments on catalysis are used in schools. These all have one drawback - the cause of the lowered activation energy remains unknown. In this article we present the catalytic decomposition of hydrogen peroxide using molybdate ions. This model catalyst provides a detailed insight into the reaction process through two coloured intermediates, allowing direct phenomenological conclusions to be drawn about the alternative reaction pathway. This is the true reason for the reduced activation energy.

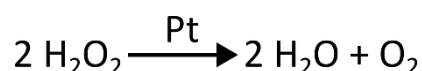
**Keywords:** Catalysis, hydrogen peroxide, molybdate, chromate, alternative reaction pathway

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## 1. Introduction

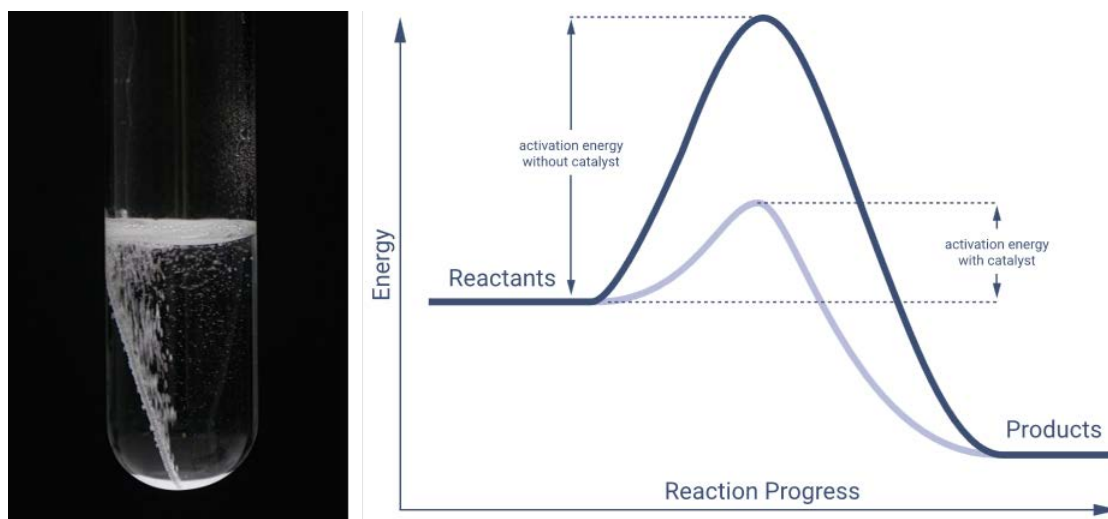
Catalysts play a significant role in our life. They enable the synthesis of many industrial chemicals that form the basis of many consumer products. They are critical components of technologies such as Power-to-X technologies, help reduce nitrogen oxide emissions from cars and, as enzymes, are an indispensable part of our physiology. The importance of catalysts is reflected in the fact that a total of six Nobel Prizes in Chemistry have been awarded in this field, including the Nobel Prize in 2021. Given its importance to industry, biology, technology and science, it is not surprising that catalysis has long been an integral part of the educational curricula.

The catalytic decomposition of hydrogen peroxide is part of the standard canon of school experiments. The experiment is phenomenologically very illustrative, as the oxygen produced rises from the solution and can be easily detected by a glow rod test. Several catalysts are available for this experiment. For example, manganese dioxide, iron salts or metallic platinum (shown in [Figure 1](#)) catalyse the reaction. What these catalysts have in common is that they allow a reaction to occur that would not have occurred at room temperature namely the decomposition of hydrogen peroxide into oxygen and two molecules water simply by the presence of the catalyst.



Even when a hydrogen peroxide solution is heated, the rate of decomposition is so low that the glow rod test is negative. The reason for this is the first and rate-determining decomposition step, in which hydrogen peroxide reacts to form two hydroxyl radicals. This thermolysis requires 211 kJ/mol [1].

The experiment (e. g. platinum) is usually followed by an energy diagram showing the activation energies ( $E_A$ ) with and without a catalyst. The catalyst is responsible for lowering the activation energy and the reaction occurs at a lower temperature. The reaction pathway appears to be the same, but the energy of the transition state is somehow lower. This description doesn't fit the definition of catalysis and omits essential parts of a catalyst. A catalyst is defined as follows: "A catalyst speeds up a chemical reaction. The conversion of reactants and products takes place on a different reaction pathway with the help of the catalyst. This pathway has a lower activation energy than the pathway without the catalyst." [2]. In addition, the catalyst is not consumed in the reaction and may be recovered unaltered. The fact that the reaction takes a different reaction pathway and that this altered reaction process is the reason for the reduced activation energy is not evident from this experiment.



**Figure 1.** Left: Reaction of hydrogen peroxide on a platinum wire. Right: Reaction diagram explaining the processes of catalysis.

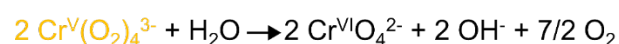
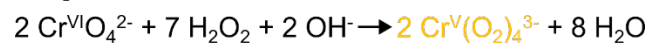
The alternative reaction pathway is rarely discussed in chemistry lessons due to the lack of appropriate experiments. Although there is a similar lack of illustrative experiments in biology classes, the alternative reaction pathway has a firm place in enzyme kinetics. An enzyme catalyses via an enzyme-substrate complex, the intermediate stage of an enzymatic reaction pathway. Not only does the explanation seem more detailed, but these biocatalysts enable reactions that chemists could only dream of until now in terms of their scope and specificity. These include nitrogen fixation with molecular nitrogen directly from the air (nitrogenase) or the use of  $\text{CO}_2$  as a reactant to incorporate it into organic substrates (RuBisCO) [3].

Observable intermediates are rare, especially in heterogeneous catalysis. The common explanation does not go beyond adsorption, bond breakage/formation and surface diffusion. To date, research on heterogeneous catalysis is often based on trial and error research. The mechanism is only understood years later, or not at all [4], because it is extremely difficult to study the processes that take place at the surface. Not for nothing did Wolfgang Pauli, Nobel Prize winner and one of the most important physicists of the 20th century, say: "God created the volume, the devil created the surface" [5].

In order to teach essential aspects of chemical catalysis, it seems useful to make the alternative reaction pathway a topic in the classroom.

The catalytic decomposition of hydrogen peroxide by chromate ions is an experiment that makes this possible. When a colourless hydrogen peroxide solution is added to a yellow chromate solution, the resulting solution turns dark brown. After a short time, gas bubbles rise from the solution and the solution gradually decolours back to the original yellow of the chromate solution. The brown complex must be an intermediate compound which is responsible for the decomposition of hydrogen peroxide at room temperature. The reaction does not take the usual pathway via the colourless hydroxyl radicals, but enters an alternative reaction pathway with a lower activation energy via a coloured intermediate. In solution, chromate ions first react to form a peroxo complex, which decomposes with the release of oxygen. The peroxo

complexes colour the initially yellow solution deep brown. Increasing recoloration indicates an unchanged catalyst [6]. The use of chromate in schools has been banned in Germany due to higher safety standards. Chromate ions can cause genetic defects and are therefore potentially carcinogenic [7]. The German Social Accident Insurance (Deutsche Gesetzliche Unfallversicherung DGUV) has therefore imposed a ban on activities involving chromate for teachers and pupils. A special substitute substance test is required [8].



The substitution test starts with the simple fact that elements in the same group in the periodic table have similar properties. Consequently, the heavier homologue of chromium was studied in the course of the substitution test. Molybdenum occurs completely analogous to chromium in the oxidation state +VI in the form of molybdate. In this form, molybdenum is required by the body as an essential trace element. The uptake and release of molybdenum is regulated by the body. In the cytosol, molybdate is converted into the biologically active molybdenum cofactor, which is found in the active centres of some enzymes. These include, for example, sulphite oxidase, aldehyde oxidase or xanthine dehydrogenase [9]. The oral  $\text{LD}_{50}$  value of sodium molybdate is 4 g per kg in rats [10]. It is in the range of salt, which has an oral  $\text{LD}_{50}$  3 g per kg in rats [11]. The hazard potential of molybdate is significantly lower. The substitution test was successful in the toxicological sense. The question arises as to whether molybdate can be profitably used as a catalyst in teaching.

## 2. Experimental Part

### 2.1. Chemicals

A 10% hydrogen peroxide solution, a 10% potassium chromate solution and a 10% sodium molybdate solution

were used. To prepare 100 mL of a 10% hydrogen peroxide solution (w/w), 33.33 g of a 30% hydrogen peroxide solution is mixed with 66.67 g of distilled water. To prepare a 100 mL 10% sodium molybdate solution or potassium chromate solution (w/w), 10 g sodium molybdate or potassium chromate, respectively, are dissolved in 90 mL of distilled water. For the water detection, a urea-hydrogen peroxide adduct (UHP) in tablet form containing at least 16.5% hydrogen peroxide was used. All chemicals were purchased from Carl Roth GmbH.

## 2.2. Experiments

### 2.2.1. Catalytic Decomposition of Hydrogen Peroxide by Platinum

A test tube is filled to the 2 cm level with hydrogen peroxide solution. The platinum wire is placed in the tube. Gas develops along the platinum wire. The gas produced can be identified as oxygen by means of the glow rod test.

### 2.2.2. Catalytic Decomposition of Hydrogen Peroxide by Potassium Chromate

5 mL potassium chromate solution was added to 10 mL hydrogen peroxide solution. The solutions react with red colouration. After a short time, gas is produced. The solution heats up. In the course of the reaction, the solution increasingly discolours to a yellow tone, the original colour of the potassium chromate solution. The gas can be identified as oxygen by means of the glow rod test.

### 2.2.3. Catalytic Decomposition of Hydrogen Peroxide by Sodium Molybdate

Add 5 mL sodium molybdate solution to 10 mL hydrogen peroxide solution. The reaction starts shortly after the addition. The release of oxygen can be accelerated by heating briefly. A dark red solution forms from the two colourless initial solutions. After a short time, bubbles rise from the solution. The subsequent gas results in a positive glow rod test. As the reaction progresses, the colour of the solution changes from dark red to orange, yellow and ultimately becomes colourless. The reaction stops when the solution is completely discoloured. A positive glow rod test confirms oxygen as a reaction product.

### 2.2.4. Crystallisation of the Intermediate

4 mL hydrogen peroxide solution (30%) and 10 mL sodium molybdate solution are placed in separate test tubes. 70 mL of ethanol are added to an Erlenmeyer flask. All solutions are cooled in an ice bath. The sodium molybdate solution is then added to the hydrogen peroxide solution. Immediately afterwards, the reaction mixture is poured into the Erlenmeyer flask with the cooled ethanol. This solution is cooled for 10 minutes in an ice bath. The suspension obtained is vacuum filtered. The residue is washed twice with ice-cold ethanol. A small portion of the crystals obtained is dissolved in distilled water. After the

addition of the sodium molybdate solution, a dark red solution is obtained. No gas bubbles form. After the transfer into ethanol, the solution clears slightly and a dark red precipitate forms during the waiting time. After filtering, a red solid is obtained. If the solid is dissolved in water, the solution turns dark red, gas bubbles form after a short time and the reaction proceeds as described above.

### 2.2.5. Preparation of Sodium Diperoxomolybdate

A water bath is preheated to 30 °C. A small amount of the sodium tetraperoxomolybdate is placed in a test tube and kept in the water bath for 2-4 minutes until the solid turns yellow. After the yellow solid is obtained, the test tube is kept on ice. The red sodium tetraperoxomolybdate decomposes to a yellow solid. Water is released in the process, which can be seen as a result of the streaks formed. The yellow solid obtained is sodium diperoxomolybdate.

### 2.2.6. Detection of Water as a Reaction Product

3-4 UHP tablets are placed in a headspace crimp vial and a spatula tip of sodium molybdate is added. A red solid forms on the contact surface after a short time. The vial is closed with a stopper fitted with a glass tube bent at an angle. Another vial is placed at the end of the tube. The red solid is briefly heated with a burner. The decomposition of hydrogen peroxide then starts and the glass heats up. Gas bubbles form and the tablet begins to liquefy until a yellow solution is obtained, which slowly cools and solidifies. The water formed evaporates, condenses on the glass tube and drips into the adjacent vial.

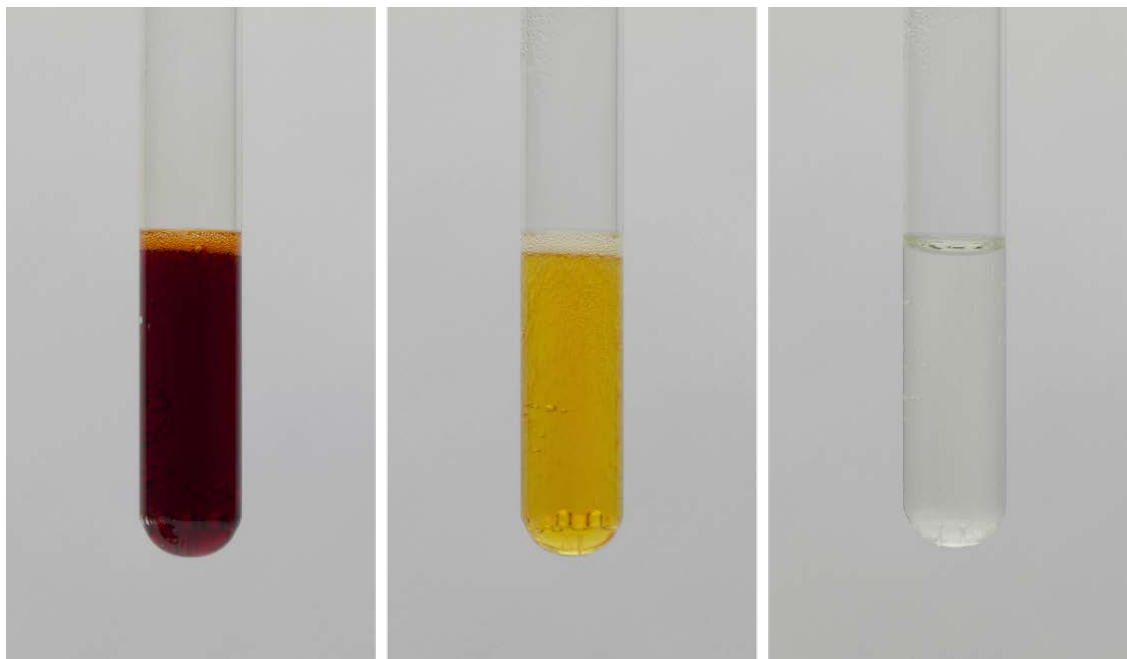
### 2.2.7. Comparison Activation energies

A hotplate is preheated to 200 °C. Equal amounts of sodium tetraperoxomolybdate and sodium diperoxomolybdate are put into two test tubes and placed on the hotplate. After a short time, sodium tetraperoxomolybdate decomposes via a yellow intermediate stage to a colourless solid. The upper edge of the test tube becomes cloudy. After some time sodium diperoxomolybdate also reacts to a colourless solid.

## 3. Results and Discussion

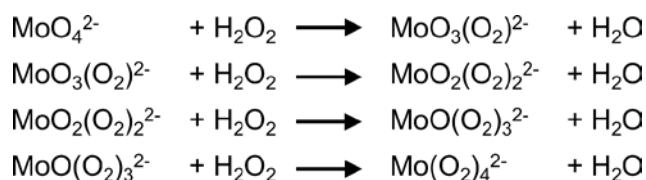
### 3.1. Molybdate as a Model Catalyst

When a colourless molybdate solution is added to a colourless hydrogen peroxide solution, the solution immediately turns dark red. As can be seen in [Figure 2](#), after a short time gas, bubbles rise and the solution changes from dark red to yellow and back to colourless. Similar to chromate, molybdate forms coloured intermediates. These decompose and the catalyst returns to its original state. The reaction also takes an alternative reaction pathway via two coloured intermediates. The reaction diagram can be extended along the reaction coordinate with the observations from the experiment without having to go into reaction mechanisms.

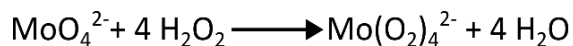


**Figure 2.** Colour gradient of the solution during the catalytic decomposition of hydrogen peroxide using molybdate.

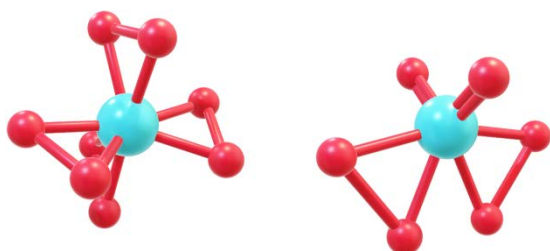
But which species exactly is responsible for the colour of the solution? Molybdate reacts with hydrogen peroxide by exchanging an oxo ligand for a peroxo ligand ( $\eta^2$  ligand) [12]. This produces water, which is the first product of the reaction. There are three other oxo ligands on the molybdenum, which can be exchanged for peroxo ligands in the same way. This reaction sequence is shown in the following diagram. For clarity the peroxo groups are written in brackets.



According to the scheme, four peroxomolybdate species are formed: the mono-, di-, tri- and tetraperoxomolybdate [13]. If there is a large excess of hydrogen peroxide, it can be assumed that the dominant molybdate species is the tetraperoxomolybdate. The reaction equation may be simplified accordingly.



In the literature, the tetraperoxomolybdate is described as red and the diperoxomolybdate as yellow. This allows each intermediate to be associated with a compound of defined geometry [12]. For the oxo and peroxo ligands, a tetrahedral coordination of molybdenum is present throughout. The molecular geometry is shown in Figure 3.



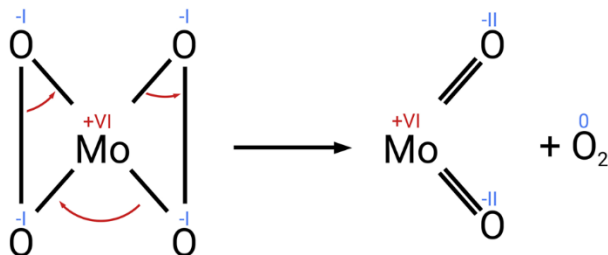
**Figure 3.** Structure of the anions: Tetraperoxomolybdate  $\text{Mo}(\text{O}_2)_4^{2-}$  (left) and diperoxomolybdate  $\text{MoO}_2(\text{O}_2)_2^{2-}$  (right).

The first reaction product, water, is released in the peroxidation step. The disproportionation of hydrogen peroxide also produces oxygen. Where does it come from? A property of peroxomolybdates helps to answer this question. The intermediates can be precipitated out of the solution. If one adds ice-cooled hydrogen peroxide and molybdate solution together, one gets a red solution. However, no gas bubbles form, because the intermediate is stabilised at low temperature and does not decompose. Adding ethanol to the solution reduces the solubility of the intermediate and sodium tetraperoxomolybdate ( $\text{Na}_2\text{Mo}(\text{O}_2)_4^{2-} \cdot 4 \text{H}_2\text{O}$ ) precipitates as a red solid [14]. Since the intermediate can be isolated, it is easy to demonstrate that the decomposition of the peroxo species produces the oxygen. To do this, the solid obtained is vacuum-filtered and dried for a short time to remove excess ethanol. Sodium tetraperoxomolybdate is heated briefly and decomposes from a yellow to a colourless solid. The glow rod test is positive; the oxygen does indeed come from the isolated intermediate compound. Figure 4 shows the observations from the experiment. In addition to the coloured intermediates, one can see how escaping water of crystallisation condenses in the gas space and on the walls of the test tube. The colours of the reaction in solution are mirrored in the solid as it decomposes. The anion is the same species that is present in solution. In the literature, the sodium salt of tetraperoxomolybdate is described as red and the sodium salt of diperoxomolybdate as yellow [12]. The colourless salt is sodium molybdate. To prove that the initial state has been restored, add a small amount of hydrogen peroxide solution to the colourless solid. A red solution immediately forms and the catalysis cycle starts again.



Figure 4. Reaction in the solid after brief heating on the left.

The literature describes the decomposition reaction in more detail. Nardello et al. propose an intramolecular disproportionation reaction of two peroxy ligands, whereby the oxidation state of the molybdenum does not change [13]. Two peroxy ligands react to form one molecule of oxygen and two oxo ligands, which remain on the molybdenum. This is illustrated again in the following reaction diagram. On the left side, the bonds fold towards the molybdenum to form the oxo ligands with oxidation state -II. On the opposite side, a bond folds onto the oxygen atom of the peroxy ligand, forming molecular oxygen with oxidation state 0.



According to this decomposition mechanism, the tetraperoxomolybdate decomposes to diperoxomolybdate and the diperoxomolybdate to molybdate. Both intermediates can be identified by their characteristic colours.

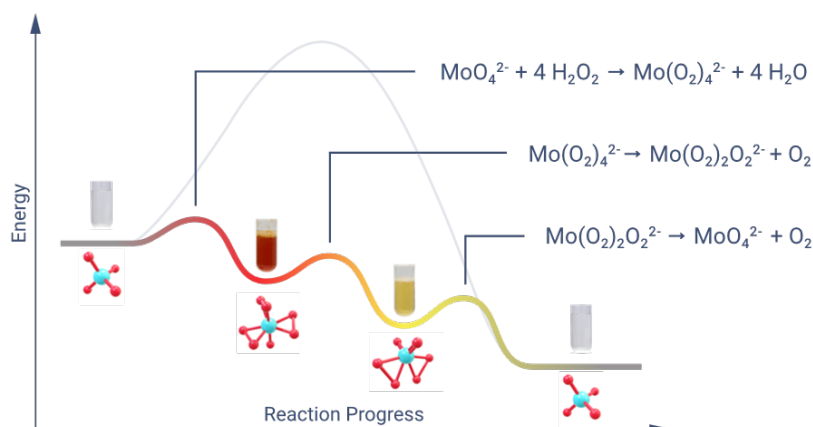


Figure 6. Extended reaction diagram with phenomenological impressions, reaction equations and the present molybdate species on particle level.

The yellow sodium diperoxomolybdate is not directly accessible by crystallisation with ethanol. However, the diperoxomolybdate can be obtained under school conditions. The tetraperoxomolybdate is heated in a water bath at 30°C (see Figure 5). The thermal energy is adequate to induce the decomposition of the red intermediate but insufficient for the yellow intermediate to undergo decomposition. The desired product, sodium diperoxomolybdate, is obtained in this manner. This step provides access to the second intermediate in the pathway. If too much heat is applied, the yellow intermediate will decompose, releasing oxygen and resulting in a positive glow rod test.

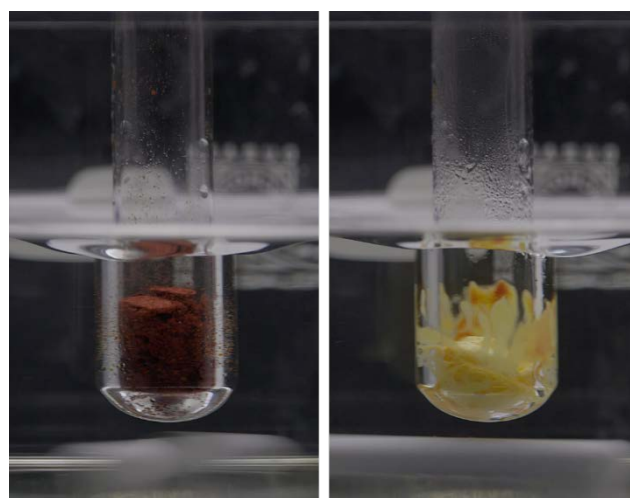
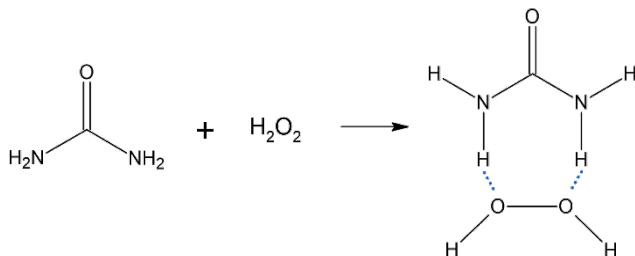


Figure 5. Preparation of sodium diperoxomolybdate in a water bath.

With these findings, we can revise the energy diagram, which is shown in Figure 6. Along the reaction coordinate, the intermediate steps can now be assigned both a colour impression and a structural formula. Furthermore, a simple reaction equation can be formulated for each transition. First, molybdate reacts with hydrogen peroxide to form water and tetraperoxomolybdate. The peroxy species decomposes via an intramolecular disproportionation with the loss of two peroxy groups to form diperoxomolybdate, which decomposes in the same disproportionation reaction to molybdate. Molecular oxygen is released from the complex during each decomposition step.

Since the catalytic decomposition of hydrogen peroxide is always carried out in aqueous solution, it is impossible to detect water as a reaction product. If another reactant is used, water can be detected. Hydrogen peroxide reacts with urea to form a solid urea-hydrogen adduct (urea hydrogen peroxide  $\triangleq$  UHP) with a mass fraction of up to 35% hydrogen peroxide [15]. The adduct can be dried and is therefore anhydrous. UHP is available in tablet form.



When sodium molybdate is added to a UHP tablet, a red solid is formed. The colour intensifies to dark red within a few minutes. If the red solid is heated briefly, gas bubbles form and the tablet begins to liquefy until a yellow solution is obtained that slowly cools and solidifies.



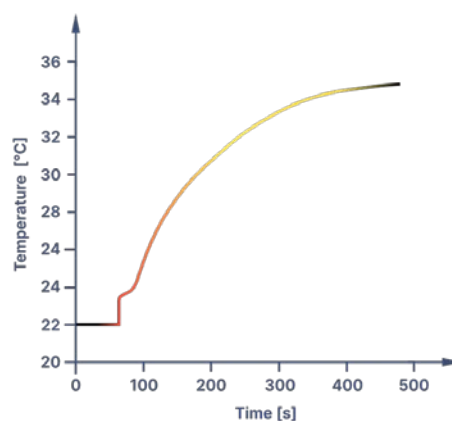
**Figure 7.** Observations during the decomposition of a UHP tablet by molybdate. The resulting water vapour is transferred and detected with anhydrous copper sulphate.

These observations are in line with our previous findings. Upon contact between the adduct and sodium molybdate, the formation of sodium tetraperoxomolybdate occurs. This reaction step produces water, in which the catalyst and UHP dissolve. Sodium tetraperoxomolybdate decomposes to yellow sodium diperoxomolybdate and releases oxygen. The disproportionation thus starts slowly and heats up until the entire tablet with UHP and urea is dissolved in water. After the reaction is complete, the solution cools down, which is why the solution supersaturated with urea solidifies at approx. 50°C. At room temperature, 1000 g of urea will dissolve in one litre of water [16]. In this experimental setup, temperatures up to 90 °C are reached. It is therefore not surprising that all of the residue from the tablet dissolves in the small amount of water. Water can be detected by using Watesmo paper to detect the supernatant water or by passing the evaporating water through a glass tube, as shown in Figure 7. Water can then be detected with anhydrous copper sulphate. Molybdate as a catalyst shows a unique feature because it also reacts with UHP as a solid. Other catalysts, such as manganese dioxide or platinum, do not seem to react directly with the adduct.

Ultimately, as a result of this experiment, we were able to separate the hydrogen peroxide from the water and convert it into a solid, in which form it reacts with sodium molybdate, producing enough water to dissolve the reaction mixture. This heats up and the escaping water can be detected.

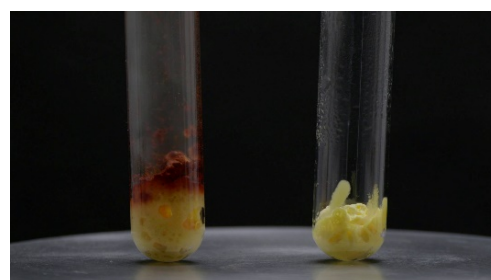
### 3.2. Consideration of Energetic Aspects

This extended energy diagram seems to be sufficient to demonstrate essential aspects of catalysis experimentally in school. A closer look reveals several other properties of the molybdate system. For example, if one measures the temperature of the reaction over time, see Figure 8, one notices a sudden increase in temperature after the addition of hydrogen peroxide. This energy corresponds to the released peroxidation energy. In the literature, a value of -43 kJ/mol is given for this step [13]. The total enthalpy of the reaction is -95 kJ/mol [17]. It is also astonishing that the first reaction step is instantaneous even in ice-cooled solutions. In summary, almost half of the reaction enthalpy is already released in the first reaction step and the activation energy of peroxidation must be very low. We can include both aspects in the energy diagram by lowering the activation energy ( $E_{A1}$ ) of the first reaction and lowering the energy level of the first intermediate step to half of the total reaction enthalpy.

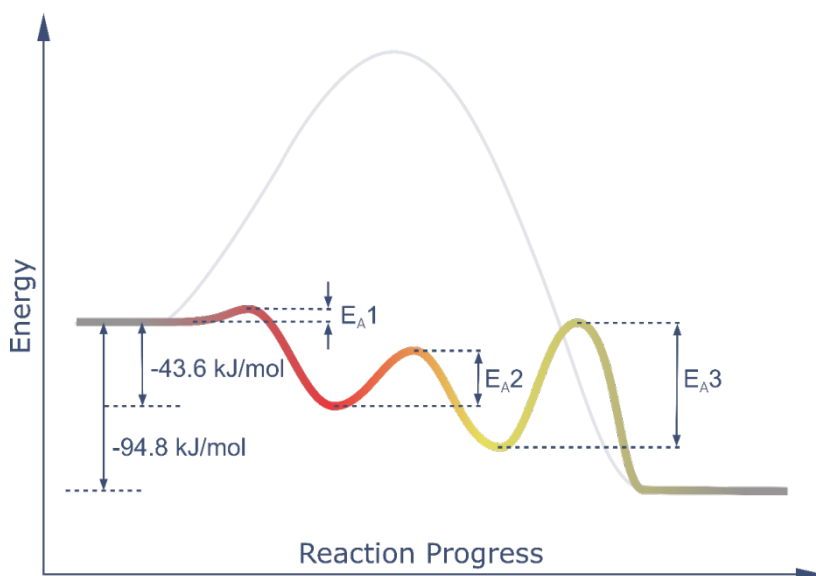


**Figure 8.** Temperature curve of the catalytic decomposition of hydrogen peroxide.

The activation energies of the intermediates differ considerably from each other. If the yellow and red intermediates are heated equally, the red solid reacts rapidly back to molybdate, while the yellow intermediate reacts only gradually and less violently back to the initial catalyst. This experiment is shown in Figure 9. It is precisely this aspect that is exploited in the preparation of the yellow intermediates. Consequently, a qualitative statement can be made about the ratio of the activation energies of the first decomposition reaction ( $E_{A2}$ ) to the second decomposition reaction ( $E_{A3}$ ). The activation energy of the first decomposition step must be lower than that of the second. This aspect can also be included in the energy diagram.



**Figure 9.** Qualitative comparison of the reaction rates in the decomposition of sodium tetra- and sodium diperoxomolybdate.



**Figure 10.** A further extended reaction diagram, which considers the observations from the experiments.

Finally, in the case of **Figure 10**, we obtain an energy diagram that has been differentiated both along the reaction coordinate and along the energy levels.

## 4. Summary

As shown above, the use of molybdate as a model catalyst is more than a simple substitute for chromate. Molybdate offers considerable added value as a result of two coloured intermediates, which show the alternative reaction pathway on a phenomenological level, and as a result of the easy crystallisation of the intermediates, which makes it possible for the experimenter to pause the reaction. The system also impresses with its simple reaction equations, which are well documented in the literature. The molybdate and hydrogen peroxide model system thus allows a detailed insight into the mechanistic events of a catalysed reaction.

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