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Oxygen Bleach under the Microscope: Microchemical Investigation and Gas-Volumetric Analysis of a Powdered Household Product

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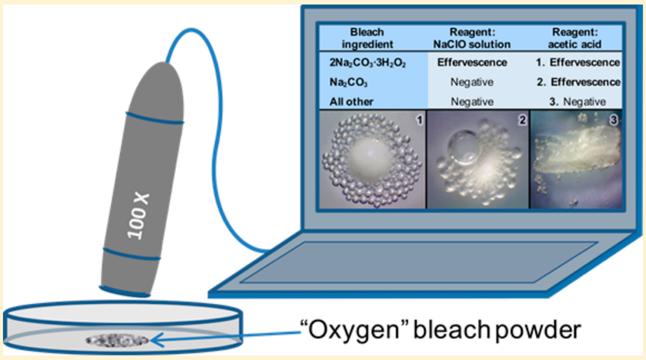
Supporting Information

ABSTRACT: A closer look at particles of a solid oxygen-based bleach household product is proposed, both figuratively and literally, to help develop observation and critical thinking skills and to link everyday life to chemistry concepts like acid–base equilibrium, redox reactivity, gas laws, gas volumetry, stoichiometry, and morphology of a heterogeneous solid mixture. In a microchemical approach, students learn to discriminate particles by their morphology under an optical (or low-cost USB) microscope and to investigate how they react with (a) hypochlorite solution (or household chlorine bleach); and (b) acetic acid (or vinegar). Aware of the ingredients listed on the product's label, and searching for the structure and formula of percarbonate ($2Na_2CO_3{\cdot}3H_2O_2$), a hydrogen peroxide–sodium carbonate adduct, they end up concluding that the particles showing effervescence with both reagents consist of sodium percarbonate, and those bubbling only in contact with acetic acid are sodium carbonate, while other minor ingredients do not react visibly. In products with perborate replacing percarbonate as H_2O_2 source, bubbling occurs only with hypochlorite. Next, students are challenged to determine the content of sodium percarbonate and sodium carbonate in a weighed amount of bleach by performing the same reactions in scaled-up experiments of quantitative gas volumetry of O_2 and CO_2. A graduated cylinder filled with water and turned upside down into a beaker is suitable for the task of collecting the volume of O_2 or CO_2 evolving in a Kitasato flask containing the sample and coupled to a syringe for reactant injection. The volume of released O_2, measured at ambient conditions, allows the students to calculate the concentration of sodium percarbonate in the weighed sample by applying the ideal gas law and the reaction's stoichiometry. The volume of CO_2 measured in excess to that originated only from the decomposition of the percarbonate lets them calculate the sodium carbonate content.



KEYWORDS: *High School/Introductory Chemistry, First-Year Undergraduate/General, Analytical Chemistry, Demonstrations, Hands-On Learning/Manipulatives, Acids/Bases, Gases, Oxidation/Reduction, Qualitative Analysis, Titration/Volumetric Analysis*

INTRODUCTION

Microchemical analysis or chemical microscopy[1] is an important branch of chemistry since the end of the 19th century,[2] so much so that the Nobel Prize in Chemistry was awarded to Fritz Pregl in 1923[3] for the invention of the method of microanalysis of organic substances. Optical chemical microscopy has evolved meanwhile to single-molecule fluorescence microscopy, the subject of the 2014 Nobel Prize in Chemistry awarded to Eric Betzig, Stefan W. Hell, and William E. Moerner.[4] Microchemical analysis is however largely absent from the current high school and undergraduate chemistry curricula.

A practical demonstration of the isolation and chemical testing of particles of a household product under a microscope is featured in this work. The separation of compounds is performed in a fashion that resembles the experiments performed by Pasteur in his work aimed toward the isolation and test of morphologically different particles of tartaric acid crystals from a racemic mixture, announced in 1848, which led to the discovery of optical isomerism.[5]

Experimenting with materials familiar to students like household products is a valuable approach for lab classes and lecture demonstrations. As a rule these materials are reasonably safe and cheap, the experiments catch great interest, and they can be eventually repeated (or tried first) at home. Household products based on sodium percarbonate (an adduct of sodium carbonate and hydrogen peroxide, also known as a perhydrate)[6] or sodium perborate are commercially known as "active oxygen", oxygen-based bleaches or also as stain removers and can be purchased under several different brands. With respect to decomposition during storage, these solid compounds are stable anhydrous sources of hydrogen peroxide, a widely used industrial and domestic oxidizing agent, commonly applied as an alternative to chlorine bleach especially for laundry.

In addition to an active oxygen compound, most oxygen-based bleaches also contain sodium carbonate and may contain, as minor ingredients, compounds like surfactants, optical brighteners, silicates, enzymes, and/or an activator.[7,8]

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A thermal decomposition experiment has been previously reported in this *Journal* to quantify percarbonate and carbonate in solid bleach samples.[9] In spite of the simplicity of the procedure, the presence of humidity and ingredients of low thermal stability, like enzymes, may result in an overestimation of the percarbonate in most commercial formulations. The standard test method ASTM 2180 for active oxygen in bleaching compounds[10] is also susceptible to interference by organic material, frequently present in commercial bleaches. Having informed the students that the method consists of a volumetric titration with permanganate, they may be asked to explain the reason for the overestimation of the active oxygen content in such cases.

The sequence of experiments presented here overcomes these limitations and enlightens the application of chemical microscopy to the identification of percarbonate, perborate, and carbonate in domestic oxygen bleaches and quantifies percarbonate and carbonate afterward by gas volumetry. The assayed bleach consists of a powdered multicomponent heterogeneous mixture of solids (e.g., Vanish in the U.K. and South America or OxiClean Versatile Stain Remover in the United States). Furthermore the qualitative tests and the quantitative determinations are based on the reactions of the sample with two more household products: vinegar (acetic acid) and chlorine based bleach (sodium hypochlorite). These experiments need no expensive equipment and are simple, cheap, and well suited for high school or first-year chemistry students as hands-on experiments in the laboratory or even at home, as well as for lecture room demonstrations. The pedagogical value of this activity includes introducing microchemical analysis; applying the ideal gas equation; practicing with redox reactions, acid–base equilibrium, and reaction stoichiometry; and experiencing qualitative and quantitative analytical chemistry.

HAZARDS

Sodium percarbonate, dry ice, acetic acid, sodium hypochlorite, and the oxygen bleach sample should be handled with care. In addition to the lecturer's assistance, gloves, safety goggles, and an appropriate apron should be worn when performing these experiments.

SETUP AND PROCEDURE FOR IDENTIFYING PARTICLES

An optical microscope coupled with a digital camera (Coleman model NSZ-405) was used to observe the bleach particles and to take the pictures shown in this article. Inexpensive USB digital microscopes of lower resolution and sharpness are appropriate for students' hands-on experimentation; probably the microchemical observations can also be made with inexpensive clip-on microscopes for smartphones (not tested here). In lecture room demonstrations, the images (live or prerecorded) can be also projected on a screen.

A small portion of the heterogeneous solid sample was randomly taken from the bleach package and spread on a Petri dish placed under the microscope and particles of similar morphology were grouped using fine-tipped tweezers. Each group of particles was reacted with a few drops of reagents (acetic acid or sodium hypochlorite), added with a dropper or micropipette.

COMPOUND IDENTIFICATION

At least four morphologically different particle types were distinguishable in the bleach. The white particles with nearly spherical form and a typical diameter range of 0.5 to 1 mm reacted rapidly with both of the reagents (acid and hypochlorite) as revealed by the immediate formation of gas bubbles (Figure 1), exactly the behavior expected for percarbonate (eqs 1−5 in the Supporting Information).

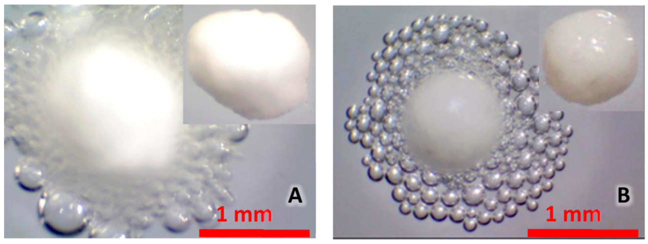

Figure 1. White spherical particles with a size range from 0.5 to 1.0 mm reacting with acetic acid solution (A) and sodium hypochlorite solution (B). Insets: dry particles.

The white capsule-shaped (spherocylinder or "rice grain") particles, with dimensions of about 0.5 × 1 mm (Figure 2), presented intense bubble formation only by reaction with acetic acid. With hypochlorite, some very little bubbles slowly appeared, probably indicating superficial contamination of these particles with finely powdered percarbonate. The observations are compatible with the presence of carbonate in the formulation.

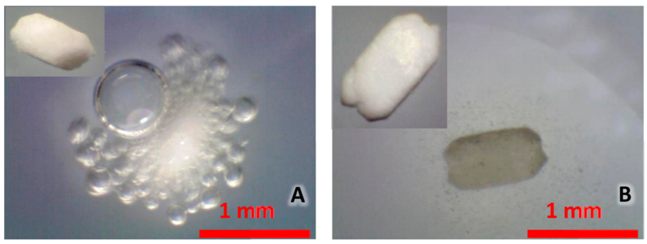

Figure 2. White particles with spherocylinder shape and width of 0.5 mm or less. Acetic acid exhibited fast and intense reaction with these particles (A), while the hypochlorite reacted minimally, with barely detectable gas formation on the particles' surface (B). Insets: dry particles.

Small amounts of two more kinds of particles were found in the bleach formulation (Figure 3). None did lead to gas evolution after exposure to hypochlorite and acetic acid solutions, disregarding the few tiny bubbles attributable to superficial contamination with powdered percarbonate and carbonate.

The described microchemical tests with acetic acid and sodium hypoclorite can also be performed with sodium perborate ($NaBO_3{\cdot}H_2O$) in formulations where it replaces percarbonate as the H_2O_2 source (e.g., in dishwasher solid detergents, such as Surf Laundry Detergent Powder[11] or Kwit Triple Action Dishwasher Tablets[12]). The hydrogen peroxide released by the compound reacts when exposed to hypochlorite (O_2 formation), but no reaction is observable with acetic acid.

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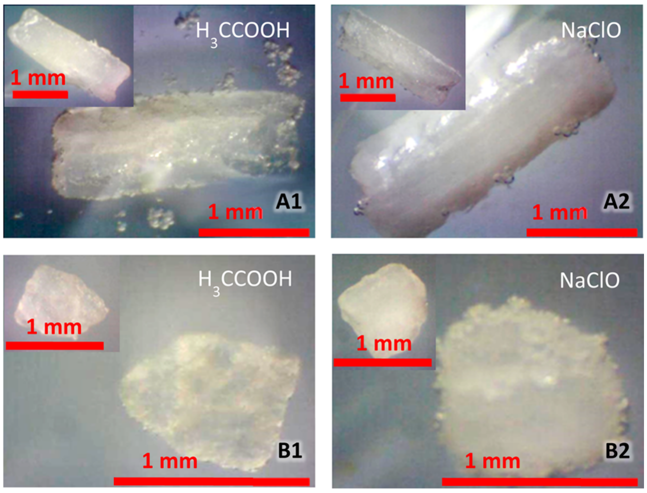

Figure 3. (A) Colorless particles with cylindrical shape and length of about 2.0 mm. No gas evolution observed with both indicated reagents. (B) Colorless particles with amorphous aspect and approximate diameter in the range of 0.5 and 1.0 mm. No reaction evidenced with both reagents. Insets: dry particles.

SETUP AND PROCEDURE FOR QUANTITATIVE ANALYSIS OF THE MAJOR INGREDIENTS

To carry out the quantitative experiments, aimed toward homogeneity and better representativeness of the sampled material, a mass of about 10 g of the sample was ground in a mortar and a portion of about 2 g was weighed to the milligram and transferred to a 500 mL Kitasato flask capped with a rubber stopper, perforated to press-fit the tip of a disposable hypodermic syringe. The outlet of the Kitasato flask was connected by a polymeric tube to a 500 mL graduated cylinder, filled with water and inverted in a 2 L beaker containing 1.4 L of water (Figure 4). An aliquot of 50 mL of reagent (25% v/v acetic acid or 2.5% m/m sodium hypochlorite solution from chlorine-based bleach) was aspirated into a 60 mL syringe. The syringe was firmly attached to the perforation in the rubber stopper, and the reactant was injected into the Kitasato flask. Afterward, the solution was stirred until the gas evolution stopped (about 3 min). All the produced gas was collected and measured in the graduated cylinder at room temperature and pressure, after leveling-out the water inside and outside the cylinder. The volume of injected reagent, measured with the syringe, was subtracted from the collected gas volume.

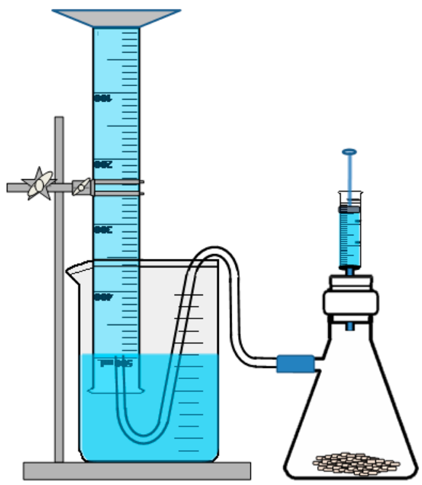

Figure 4. Experimental setup used for the reactions and the gas collection for quantitative determination.

QUANTIFICATION OF HYDROGEN PEROXIDE AND SODIUM PERCARBONATE

After dissolution of percarbonate salt in water with release of H_2O_2 and carbonate ions (eq 1 of the Supporting Information), these two species can be decomposed in reactions that lead to quantitative formation of the gaseous products. An example is the reaction of H_2O_2 with sodium hypochlorite (eq 6 of the Supporting Information).

The liberated carbonate is involved in the well-known pH dependent equilibrium with bicarbonate, carbonic acid, and CO_2 (eqs 2−5 of the Supporting Information).

By using the gas laws and taking into account the vapor pressure of water (24 mmHg at 25 °C), the volume of O_2 measured with the described apparatus can be used for the calculation of the amount of H_2O_2 in the weighed sample (detailed calculation in the Supporting Information). From the H_2O_2 content, the concentration of sodium percarbonate can be directly determined, since its minimum formula is known, $2Na_2CO_3{\cdot}3H_2O_2$. As calculated in the Supporting Information, a concentration of 53.9% (m/m) was found for sodium percarbonate, which is within the range of 30 to 60% specified by the product safety data sheet.[13]

QUANTIFICATION OF TOTAL SODIUM CARBONATE

The measured volume of evolved CO_2 embraces the reaction of the acid in excess with all the carbonate coming from the dissolution of sodium percarbonate and sodium carbonate. Once the percarbonate concentration is known beforehand (from the previous experiment) and 1 mol of $2Na_2CO_3{\cdot}3H_2O_2$ originates 2 mol of CO_2 (eqs 1−4 in the Supporting Information), the excess CO_2 is attributable to the extra Na_2CO_3 in the sample (calculation in the Supporting Information).

Aiming the minimization of error caused by the non-negligible solubility of CO_2 in water (with partial conversion into H_2CO_3 and HCO_3^-, reactions presented in eqs 3−5 in the Supporting Information), the water in the beaker and graduated cylinder was presaturated with CO_2 by addition of dry ice. If dry ice is not available, underestimation of the CO_2 volume can be reduced by acidification of the water or by inserting the flexible gas conducting tube until it reaches the bottom of the inverted cylinder, in order to avoid the bubbling. In this configuration, a correction of the difference in hydrostatic pressure should be made (details in the Supporting Information).

For this experiment, the calculations (see the Supporting Information) resulted in a concentration of 14.3% of free sodium carbonate and 50.7% (m/m) of total sodium carbonate (free plus dissociated from sodium percarbonate), which is within the manufacturer's wide range of 30 and 60%.[13]

CONCLUSION

Oxygen-based bleaches for daily use, commercially available worldwide (e.g., OxiClean or Vanish), offer a great deal of experiments to illustrate classical concepts of chemistry. The reactants used in the experiments, acetic acid and hypochlorite, are common in the laboratory as well as in many households in

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the form of vinegar and in the chlorine-based bleaches, respectively. The experiments are safe (once the appropriate safety rules are observed) and well suited for high school or college first-year lab classes.[14] The presented gas volumetric analysis relies on the gas laws, and the sodium carbonate determination involves a classical example of acid−base equilibrium. The gas volumetric determination of hydrogen peroxide, in turn, highlights a redox reaction. For the qualitative initial study of both, the identification of the gases with a flame, for example, a burning match, might be interesting because O_2 works as an oxidizing reactant and CO_2 as an extinguisher. The microscale experiments under the microscope enlighten the heterogeneity of the solid sample and allow the identification of the major constituents of the bleach formulation, attractively introducing the students to chemical microscopy, a field recently extended to the observation of single fluorescent molecules in living cells.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00148.

Procedures, discussion, and calculations (PDF, DOC)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Chamot, E. M.; Mason, C. W. *Handbook of Chemical Microscopy*, 2 Vols.; Wiley: New York, 1931.

(2) Behrens, H. *A Manual of Microchemical Analysis*; Macmillan: London, 1894. https://archive.org/stream/amanualmicroche00juddgoog#page/n115/mode/2up (accessed Oct 2015).

(3) The Nobel Prize in Chemistry 1923. http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1923/pregl-facts.html (accessed Oct 2015).

(4) The Nobel Prize in Chemistry 2014. http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2014/popular-chemistryprize2014.pdf (accessed Oct 2015).

(5) Flack, H. D. Louis Pasteur's Discovery of Molecular Chirality and Spontaneous Resolution in 1848, Together with a Complete Review of His Crystallographic and Chemical Work. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2009**, *A65*, 371−389.

(6) IPCS—International Program on Chemical Safety. Screening Information Data Set of Sodium Percarbonate. http://www.inchem.org/documents/sids/sids/15630894.pdf (accessed Oct 2015).

(7) Royal Society of Chemistry. Chemistry in Your Cupboard—Vanish. http://www.rsc.org/learn-chemistry/resources/chemistry-in-your-cupboard/vanish/5 and http://www.rsc.org/learn-chemistry/resources/chemistry-in-your-cupboard/vanish/vanish.doc (both accessed Oct 2015).

(8) Clariant. The Clean and Clever Way of Bleaching. http://www.clariant.co.jp/C12575E4001FB2B8/vwLookupDownloads/DetergentsIntermediates_Newsroom_Brochures_Peractive.pdf/$FILE/DetergentsIntermediates_Newsroom_Brochures_Peractive.pdf (accessed Oct 2015).

(9) Bracken, J. D.; Tietz, D. Analysis of OxiClean: An Interesting Comparison of Percarbonate Stain Removers. *J. Chem. Educ.* **2005**, *82* (5), 762−764.

(10) Standard Test Method for Active Oxygen in Bleaching Compounds ASTM D2180. http://www.astm.org/cgi-bin/resolver.cgi?D2180 (accessed Oct 2015).

(11) Unilever. Material Safety Data Sheet of Surf Laundry Detergent Powder. http://artcatering.com/wp-content/uploads/2015/07/SurfLaundryDetergentPowder.pdf (accessed Oct 2015).

(12) Reckitt Benckiser, Inc. Safety Data Sheet of Kwit Dishwasher Tablets. http://www.rb-msds.com.au/uploadedFiles/pdf/Kwit%20Dishwasher%20Tablets-Kwit%20Triple%20Action%20Tabletsv2-D0008474.pdf (accessed Oct 2015).

(13) Reckitt Benckiser, Inc. Safety Data Sheet of Vanish OxiAction. http://www.rb-msds.com.au/uploadedFiles/pdf/Vanish%20Napisan%20OxiAction-v17-31448.pdf (accessed Oct 2015).

(14) Part of these experiments were first presented as a demonstration to 140 high school students during a Chemistry Olympiad, preceding a final examination with questions about the gas laws involved and aspects of redox and acid−base equilibrium. The winner of this São Paulo State Chemistry Olympiad of 2012 earned a silver medal of the 44th International Chemistry Olympiad (Washington, DC, July 2012). See the São Paulo State Chemistry Olympiad, 2012 Web site at: http://allchemy.iq.usp.br/oqsp/oqsp-2012-vencedores.html (accessed Oct 2015). For more information about the 44th International Chemistry Olympiad, see this Web site: https://acswebcontent.acs.org/icho2012 (accessed Oct 2015).

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