Ozone-Containing Hydrates

DOI: 10.1002/anie.201104660

Molecular Storage of Ozone in a Clathrate Hydrate Formed from an $O_3 + O_2 + CO_2$ Gas Mixture**

*Takahiro Nakajima, Satoru Akatsu, Ryo Ohmura, Satoshi Takeya, and Yasuhiko H. Mori**

Owing to its strong oxidizing power, ozone (O_3) is utilized in various industrial processes and commercial activities, such as the decontamination of air and water, disinfection of medical instruments and hospital equipment, sterilization of perishables, and bleaching of organic compounds. However, ozone in the gaseous state reacts with itself and rapidly decomposes to oxygen (O_2). Owing to this reaction, it is generally considered that ozone cannot be stored and transported like other industrial gases.

In 1964, McTurk and Waller[1] presented the idea of storing ozone in the form of a clathrate hydrate, a crystalline solid compound framed by interlinked cages made up of hydrogen-bonded water molecules, in which the ozone molecules could be separated from each other by the cage walls and thus prevented from mutually interacting to cause the ozone-to-oxygen reaction. In this pioneering study, the authors experimentally demonstrated the formation of an sII $O_3 + CCl_4$ double hydrate from pure ozone and carbon tetrachloride (CCl_4) and showed ten sets of four-phase (hydrate + O_3-rich gas + CCl_4-rich liquid + H_2O-rich liquid) equilibrium pressure–temperature data, in which the CCl_4 served as the "help-guest substance" for decreasing the hydrate-forming pressure. However, they reported no actual test of preserving the enclathrated ozone. No subsequent study on ozone-containing hydrates has been reported in the literature for more than 40 years. In the patent application document released in 2007, Masaoka et al.[2] stated that they formed an $O_3 + O_2$ hydrate by spraying water into a reactor charged with an $O_3 + O_2$ gas mixture (containing O_3 at a mole fraction of about 5%) and maintained at 13 MPa and −25 °C. Based on an analysis of the gas released from this hydrate while being decomposed, they estimated the ozone content in the hydrate to be 2.3 g L^{-1} (ca. 0.2% in mass fraction). They also described that the hydrate could be preserved for 10 days in a closed container conditioned at 13 MPa and −25 °C without causing a substantial loss of its ozone content.

More recently, we showed that hydrates formed from an $O_3 + O_2$ gas mixture and CCl_4 or xenon (Xe) and cooled to around −20 °C can preserve ozone at a mass fraction on the order of 0.1% for over 20 days under atmospheric pressure.[3] It should be noted that such in-hydrate ozone concentrations are higher than the typical ozone concentration in "ozonated water" for disinfection use by three orders of magnitude. Besides the ozone preservation tests, we measured the four-phase equilibrium for the $O_3 + O_2 + CCl_4$ hydrate-forming system (O_3 mole fraction in the gas phase = 6.9 ± 0.8%) in the temperature range from 2.4 to 4.1 °C.[4] These studies revealed that the use of CCl_4 or Xe as the "help-guest substance" is effective for decreasing the hydrate-forming pressure and for facilitating the ozone storage at atmospheric pressure. However, neither CCl_4 nor Xe is favorable for practical use because of toxicity or high price. An alternative help-guest substance is therefore required that is neither toxic nor expensive. Furthermore, this substance must be unaffected by ozone. Note that some compounds best recognized as the help guests for hydrate formation from a small-molecule guest gas, such as hydrogen, do not meet the latter requirement. For example, tetrahydrofuran (THF) and tetra-*n*-butylammonium bromide (TBAB), the compounds confirmed as effective help guests for forming H_2-containing hydrates,[5,6] will be readily oxidized by ozone. In our recent study,[4] we found that even a highly halogenated hydrocarbon, 1,1-dichloro-1-fluoroethane (CH_3CCl_2F, known as R141b), was oxidized by ozone.[4] Thus, we have fewer choices of the help-guest substance for the purpose of this study compared to the cases of hydrate formation from chemically stable gases. Herein we describe our attempt at using carbon dioxide (CO_2) as the help-guest substance and investigating the preservability of ozone encaged in an $O_3 + O_2 + CO_2$ hydrate stored under atmospheric aerated conditions.

Figure 1 shows a photograph of two different hydrate samples. One was formed from an $O_3 + O_2 + CO_2$ gas mixture (typically in a 0.011:0.114:0.875 molar ratio) controlled at about 0.1 °C and about 1.9 MPa, and the other from an $O_2 + CO_2$ gas mixture (in a 0.125:0.875 molar ratio), similarly controlled (see the Experimental Section). The photographs were taken after a short exposure to room air controlled at −20 °C. As can be observed, the $O_3 + O_2 + CO_2$ hydrate exhibits a pale blue color, which is probably due to the ozone molecules contained in it.

Figure 2 summarizes the results of the preservation tests in the form of a time series of ozone-in-hydrate concentration data obtained with each hydrate sample formed as described above and stored in an aerated test tube. The initial

[*] T. Nakajima, S. Akatsu, Dr. R. Ohmura, Dr. Y. H. Mori
Department of Mechanical Engineering, Keio University
3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522 (Japan)
E-mail: yhmori@mech.keio.ac.jp
Dr. S. Takeya
Research Institute of Instrumentation Frontier, National Institute of Advanced Industrial Science and Technology (AIST)
Central 5, Higashi 1-1-1, Tsukuba 305-8565 (Japan)

[**] This study was supported in part by a Grant-in-Aid for the Global COE Program for the "Center for Education and Research of Symbiotic, Safe and Secure System Design" from the Ministry of Education, Culture, Sport and Technology (Japan). The authors thank Fumihito Takeuchi, a former student in Keio University, for his help in the preliminary stages of this study.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201104660.

Figure 1. Lumps of an $O_3+O_2+CO_2$ hydrate (left) and an O_2+CO_2 hydrate (right). Each lump is about 5 mm in linear dimension. The pale blue color of the $O_3+O_2+CO_2$ hydrate lumps had faded somewhat during their short exposure to the room air before the picture was taken owing to icing on their surfaces, but their color is still distinguishable from the milk-white color of the O_2+CO_2 hydrate lumps.

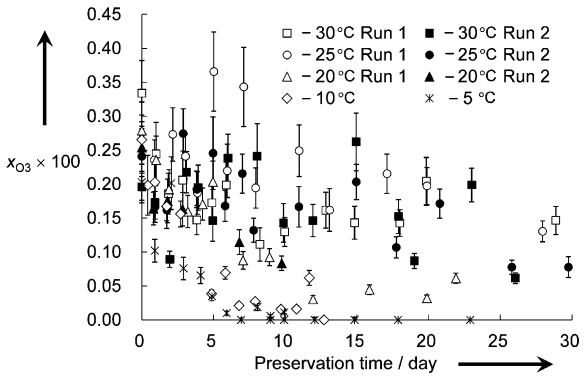

Figure 2. Time evolution of ozone concentration in an $O_3+O_2+CO_2$ hydrate stored under an aerated atmospheric-pressure conditions: comparison of the ozone preservation test data obtained at different storage temperatures. The error bar for each data point represents the uncertainty of the ozone-concentration measurement by iodometry.

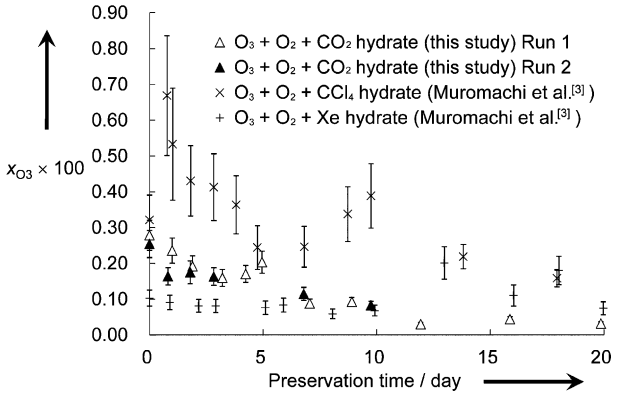

Figure 3. Time evolution of ozone concentrations in hydrates formed with different "help guests": comparison of ozone-preservation test data for an $O_3+O_2+CO_2$ hydrate (this study) and those for $O_3+O_2+CCl_4$ and O_3+O_2+Xe hydrates (Muromachi et al.[3]). All of these data were obtained at −20 °C.

concentration in the hydrate used for each preservation test, that is, the concentration in the hydrate just after its formation, was typically in the range of 0.20 to 0.35 % (mass basis). The concentration gradually decreased with time. Such a decrease in the ozone concentration in the hydrate (to be exact, a mixture of an $O_3+O_2+CO_2$ hydrate and water ice) is reasonably ascribable to the progressive hydrate dissociation, which was inevitable because of the partial ozone pressure in the surrounding aerated atmosphere inside the test tube being less than the equilibrium pressure corresponding to the preservation temperature.

It may appear puzzling that in Figure 2 (and also in Figure 3) the ozone concentration at a given temperature occasionally increased in an irregular manner, thus exhibiting fluctuations. This apparently anomalous fact, which was already observed in our previous study,[3] was reasonably ascribed to the spatial non-uniformity of the ozone concentration in the hydrate particles (or, to be more exact, the particles of a hydrate + ice-Ih mixture) stored in the test tube for each preservation test. Depending on the particles arbitrarily removed from those located on the bottom of the test tube for iodometric measurement each time, the ozone concentration could be determined to be higher or lower than that determined by the preceding measurement using different particles.

The experimental data plotted in Figure 2 indicate that the rate of decrease in the ozone concentration was significantly sensitive to the preservation temperature. As expected, the decrease in the concentration was subdued better at lower temperatures. It should be noted that, at preservation temperatures of −25 °C or lower, the ozone concentration was maintained on the order of 0.1 % for 30 days.

Figure 3 compares the results of the ozone preservation tests for three different ozone-containing mixed hydrates (the $O_3+O_2+CO_2$ hydrate tested in this study and $O_3+O_2+CCl_4$ and O_3+O_2+Xe hydrates tested in our previous study[3]) obtained at the same preservation temperature, namely −20 °C. Regarding the ozone concentration, the $O_3+O_2+CO_2$ hydrate was consistently inferior to the $O_3+O_2+CCl_4$ hydrate but slightly superior to the O_3+O_2+Xe hydrate for over the first ten days. However, the $O_3+O_2+CO_2$ hydrate consistently showed a steeper decrease in the ozone concentration than the O_3+O_2+Xe hydrate, resulting in lower ozone concentrations than those in the O_3+O_2+Xe hydrate at the later stages beyond the first ten days. The higher rate of decrease in the ozone concentration observed with the $O_3+O_2+CO_2$ hydrate can be reasonably ascribed to the higher phase-equilibrium pressure for the $O_3+O_2+CO_2+H_2O$ system compared to those for the $O_3+O_2+Xe+H_2O$ and $O_3+O_2+CCl_4+H_2O$ systems. Based on the above observations, it can be stated that the appropriate temperature for storing the $O_3+O_2+CO_2$ hydrate for preserving ozone for over a week or even longer is more or less lower than −20 °C.

Figure 4 shows a PXRD pattern of the $O_3+O_2+CO_2$ hydrate measured at 93 K. This pattern indicates that the hydrate samples we prepared were a mixture of a hydrate in structure I (sI) with the lattice constant of 11.8280(8) Å and

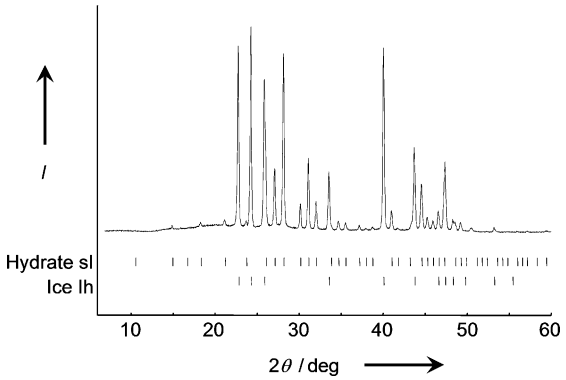

Figure 4. PXRD profile of an $O_3+O_2+CO_2$ hydrate at 93 K. The solid curve shows the observed intensities. The upper row of tick marks represent the calculated peak positions for the structure I hydrate, and the lower row represent those for hexagonal ice Ih.

hexagonal ice Ih. The mass fraction of the hydrate was estimated to be only about 0.3. This fraction may be substantially raised by modifying the hydrate-forming technique, resulting in a substantial increase in the effective mass-based ozone concentration in the hydrate samples.

In summary, we have presented the first successful attempt at forming an ozone-containing hydrate using CO_2 as the "help guest" for lowering the hydrate-forming pressure and showing the utility of the formed hydrate (that is, an $O_3+O_2+CO_2$ hydrate) for preserving ozone for 1–4 weeks in an aerated, moderately refrigerated normal-pressure atmosphere. The mass-based ozone concentration in the hydrate (actually a mixture of the hydrate and water ice) was found to be maintained on the order of 0.1 %. It should be emphasized that this hydrate should release, during its dissociation, only an $O_3+O_2+CO_2$ gas mixture and water, thereby causing neither chemical nor biological pollution of the surroundings. Based on the findings and reasoning outlined above, we can conclude that the $O_3+O_2+CO_2$ hydrate can be an efficient medium for storing and/or transporting ozone for use in various industrial and consumer applications.

Experimental Section

Apart from the use of CO_2 instead of CCl_4 or Xe, the general design of the experimental work in this study follows what we developed in the first study of this series.[3] A description of the experimental work performed in this study is provided below.

The raw materials used for forming the $O_3+O_2+CO_2$ hydrate were oxygen certified to the purity of 99.9 % (volume basis) and carbon dioxide certified to the purity of 99.995 % (volume basis) by their supplier (Japan Fine Products Corp., Kawasaki, Kanagawa Prefecture, Japan), and water deionized and distilled in our laboratory. Oxygen gas was used for generating an O_3+O_2 gas mixture (> 11 % in mole fraction of O_3) with the aid of an dielectric-barrier-discharge-based ozone generator (ED-OGS-HP1, EcoDesign Co., Ltd., Saitama Prefecture, Japan).

The major portion of the experimental setup used to form the ozone-containing hydrates (Supporting Information, Figure S1) was a vertically oriented 96 cm^3 (32 mm ID) reactor made of a borosilicate glass cylinder and flange-type stainless-steel lids. The reactor was immersed in a temperature-controlled bath containing an aqueous ethylene glycol solution. A stainless-steel chamber with a 1000 cm^3 capacity was then added for premixing the O_3+O_2 gas mixture supplied from the ozone generator with CO_2 gas supplied from a high-pressure cylinder. To specify the O_3+O_2 gas mixture produced by the ozone generator, an ozone monitor was employed to measure the ozone concentration in the mixture with an uncertainty of 0.1 % (mole basis) based on ultraviolet absorptiometry.

The procedure of forming an $O_3+O_2+CO_2$ hydrate was commenced by charging the reactor with 23 g of water. The reactor was then immersed in a temperature-controlled bath at 0.1 °C. Simultaneously, the mixing chamber was first charged with the O_3+O_2 gas supplied from the ozone generator until the pressure increased to 0.30 MPa. The CO_2 gas was then supplied to the chamber until the pressure increased to 2.4 MPa. The ozone mole fraction in the $O_3+O_2+CO_2$ mixture thus prepared in the mixing chamber was estimated to be 1.1 %. Following the above preparatory operations, the reactor was flushed three times with the $O_3+O_2+CO_2$ mixture supplied from the mixing chamber at a pressure of 0.3 MPa, then charged with the same mixture until the pressure increased to 1.9 MPa. At this stage, a batch operation for forming a hydrate was started by stirring using a magnetic stirring bar inside the reactor. When the pressure decreased to 1.6–1.7 MPa as the result of the CO_2 dissolution into liquid water and also hydrate formation, the reactor was again charged with the gas mixture supplied from the mixing chamber to increase the pressure to its initial level of 1.9 MPa. Such a gas-replenishing operation and the subsequent batch hydrate-forming operation were repeated about 7 times over a period of several hours until the pressure no longer decreased during each batch operation. After a sufficient amount of the hydrate was formed, the reactor was pulled out of the temperature-controlled bath and cooled by liquid nitrogen. The formed hydrate was then removed from the reactor.

The hydrate was immediately crushed in a chilled vessel into particles of 5–7 mm in linear dimension. These particles were then placed in a Pyrex test tube 35 mm in diameter and 210 mm in height, which was immersed in a constant temperature bath containing an aqueous ethylene glycol solution, leaving its top 40–50 mm exposed to air (Supporting Information, Figure S2). To prevent water condensation from the air onto the hydrate, we inserted a Teflon-film separator into the top portion of the test tube that allowed aeration between the inside and the outside of the test tube. The bath was controlled at the prescribed temperature in the range between −30 and −0.5 °C with a fluctuation of less than ±0.5 °C throughout each preservation test, which typically lasted 20 days. During the test, small samples (1–2 g each) were removed from the preserved hydrate at intervals of one day or longer. Each sample was subjected to an iodometric measurement to determine the ozone content.

An $O_3+O_2+CO_2$ hydrate sample was subjected to powder X-ray diffraction (PXRD) measurements to confirm its crystallographic structure and, at the same time, to examine the fraction of the condensed water phase inevitably involved in the sample. The sample was finely ground in a nitrogen atmosphere at a temperature below 100 K, then top-loaded on a copper-made specimen holder. The loaded sample was exposed to $Cu_{K\alpha}$ radiation generated by an Ultima III diffraction system (Rigaku Corp., Tokyo, Japan) in a parallel-beam alignment. Each measurement was performed in the $\theta/2\theta$ scan mode with a step width of 0.02° at 93 K. The analyses of the lattice constant of the hydrate sample was performed by the whole pattern fitting method using the RIETAN-2000 program.[7]

Received: July 6, 2011
Published online: September 14, 2011

Keywords: clathrate hydrates · crystal growth · gas hydrates · inclusion compounds · ozone

[1] G. McTurk, J. G. Waller, *Nature* **1964**, *202*, 1107.

[2] T. Masaoka, A. Yamamoto, K. Motoi, Jpn. Patent Publication 2007-210881, **2007**. Released online in the Patent and Utility Model Gazette DB of the Japan Patent Office, 23 August 2007. (http://www.ipdl.inpit.go.jp/homepg.ipdl).
[3] S. Muromachi, R. Ohmura, S. Takeya, Y. H. Mori, *J. Phys. Chem. B* **2010**, *114*, 11430 – 11435.
[4] S. Muromachi, T. Nakajima, R. Ohmura, Y. H. Mori, *Fluid Phase Equilib.* **2011**, *305*, 145 – 151.
[5] L. J. Florusse, C. J. Peters, J. Schoonman, K. C. Hester, C. A. Koh, S. F. Dec, K. N. Marsh, E. D. Sloan, *Science* **2004**, *306*, 469 – 471.
[6] A. Chapoy, R. Anderson, B. Tohidi, *J. Am. Chem. Soc.* **2007**, *129*, 746 – 747.
[7] F. Izumi, T. Ikeda, *Mater. Sci. Forum* **2000**, *321 – 323*, 198 – 203.

