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Superoxide Ions Entrapped in Water Cages of Ionic Clathrate Hydrates

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Unlike nonionic clathrate hydrates stably formed by van der Waals interaction between a guest molecule and a surrounding host framework, ionic clathrate hydrates are stabilized by ionic interaction between an ionic guest molecule and the host water framework.[1] Notable physicochemical characteristics of ionic clathrate hydrates such as ionic conductivity enhancement, melting point increase much above room temperature, abnormal magnetic transition behavior, and vacant cage generation by forming specific structures might lead to clathrate hydrates to be converted to quite promising hydrate-based functional materials that are hardly ever synthesized in cases in which nonionic clathrate hydrates are involved.[2−8] The potential applications of ionic clathrate hydrates are promising, but their inherent nature still remains adequately unanswered through both microscopic and macroscopic approaches.

Recent research results confirmed ionic conductivity enhancement, stable enclathration of metal ions, and fresh cage-structure formation by cohost inclusion in ionic clathrate hydrates and further demonstrated the significant role of these findings on inclusion chemistry.[2,4,7] In addition, we realized that the introduction of nonionic guest molecules (NIGM) into the hydrogen-bonded anionic host cages of ionic clathrate hydrates results in an unexpected charge transfer phenomenon and thus in an unnatural electron distribution.[6] We particularly note that through X-irradiation into ionic clathrate hydrates the trapped electrons are generated in polycrystalline clathrate hydrates together with intermediate free radicals.[9,10] It was also identified that atomic, diatomic, and polyatomic radicals that are so reactive with other molecules can be stably entrapped in cages. Yeon et al.[11] demonstrated that a hydrogen molecule can split into two hydrogen atomic radicals by irradiation and their cage occupancy. The unique inclusion phenomena occurring in the clathrate hydrate materials rather stimulate us to explore the physicochemical behavior of water reactive superoxide radicals that has been of considerable interest in a variety of surface chemistry fields.[12−14]

From this study, we would like to answer the following two key issues: (1) Is it possible to stably store superoxide ion radicals in a hydrogen-bonded water framework of clathrate hydrates? (2) Can we tune structural and cage dimensions by generating the superoxide ion so that icy clathrate hydrates change into target-specific functional materials? To draw reliable evidence concerning these two issues we especially attempted to adopt both magnetic and spectroscopic approaches using the Magnetic Property Measurement System (MPMS; MPMS XL7, Quantum Design), Electron Spin Resonance (ESR; JES PX2300, JEOL) spectroscopy, and High Resolution Powder Diffraction (HRPD) equipped at the Pohang Accelerator Laboratory (PAL) Synchrotron.

Me_4NOH was chosen as the ionic guest for forming the clathrate hydrate. The ionic Me_4NOH clathrate hydrate, which is readily stabilized by ionic interaction between Me_4N^+ and OH^-, exhibits three different crystalline structures: β-$Me_4NOH \cdot 5H_2O$ with a space group of cubic *Im*3*m*, β-$Me_4NOH \cdot 7.5H_2O$ with a space group of tetragonal *I*4/*mcm*, and $Me_4NOH \cdot 10H_2O$ with a space group of orthorhombic *Pnma*.[15] However, for the present experiments the liquid solution of $Me_4NOH \cdot 16H_2O$ is made by adding ultrahigh purity water to solid $Me_4NOH \cdot 5H_2O$ powder, freezing the mixture at 213 K for at least 1 day, and finally grinding it to a fine powder (∼200 μm). This fine powder sample is placed into a precooled high pressure cell with a volume of 20 mL and is exposed to O_2 gas up to 120 bar at 213 K for at least 1 week. In our previous work we confirmed that the exposure of Me_4NOH ionic clathrate hydrate to nonionic guest molecules such as N_2 and H_2 leads to structure transformation into cubic *Fd*3*m*, called a structure II hydrate (sII).[6] Here, we note that with one unpaired electron the superoxide ion is a free radical and, like dioxygen, is paramagnetic.[16] Accordingly, the magnetic pattern of ($Me_4NOH + O_2$) clathrate hydrate is first examined using the isothermal M−H curve. The weighed powder sample was packed into a quartz tube and then mounted on MPMS. The temperature was fixed at 1.9 K with changing magnetic fields. Due to unpaired spins of the outermost two electrons of the oxygen molecule, the magnetization value of the oxygen molecule is expected to be 2.0 μ_B, which is also verified by our previous result (1.95 μ_B/O_2 for THF + O_2 clathrate hydrate as shown in Figure 1).[17,18] In contrast, the magnetic moment of O_2 entrapped in small 5^{12} cages (sII-S) of ($Me_4NOH + O_2$) clathrate hydrate significantly decreases to 1.53 μ_B per one O_2 at 7 T, which is ∼75% of the theoretical value. This discrepancy implies that the strong paramagnetic oxygen molecules lose some of their unpaired spins, inducing the relevant charge transfer.[6] The magnetic analogy (paramagnetic) between superoxide ion and dioxygen makes it possible for

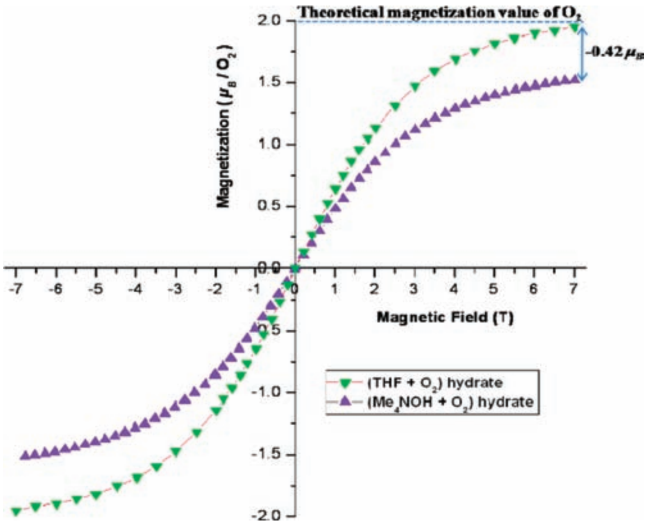

Figure 1. M−H curve of ($THF + O_2$) and ($Me_4NOH + O_2$) clathrate hydrates at 1.9 K. The maximum magnetization difference between the two is observed to be 0.42 μ_B. To determine the net magnetic behavior of ($THF + O_2$) and ($Me_4NOH + O_2$) clathrate hydrates, the magnetization values of pure THF clathrate hydrate and $Me_4NOH \cdot 16H_2O$ were subtracted.[6,18]

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charge transfer and electron migration concepts to be generally exchangeable with each other. In particular, we realize that the magnetic properties for the clathrate hydrate materials, particularly those containing superoxide ions, cannot be directly measured at the present experimental level. However, the present magnetic results are sufficient for the identification of charge transfer occurrence.

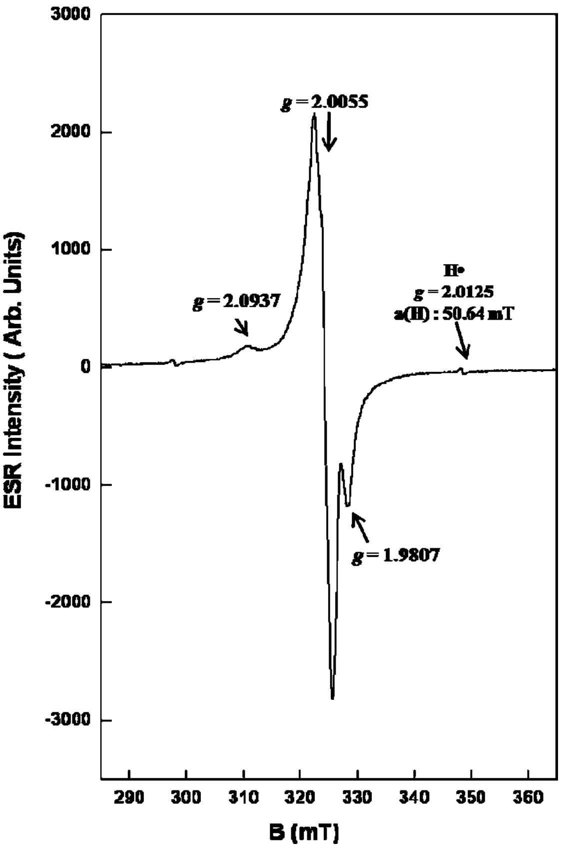

Figure 2. ESR spectrum of 30KGy ($(Me_4NOH + O_2)^*$) clathrate hydrate at 77 K.

On the other hand, through two subsequent spectroscopic approaches the physicochemical nature of superoxide radical ions could be more precisely revealed. For radical generation we irradiated the ($Me_4NOH + O_2$) clathrate hydrate samples using the ^{60}Co γ-ray source. For ($Me_4NOH + O_2$)* clathrate hydrate samples[19] we determined the ESR signals at a 30KGy dose and observed an asymmetric line-shape pattern (Figure 2), which clearly shows the dynamic electron behavior that tends to be strongly influenced by neighboring guest molecules. With experimental conditions of microwave frequency (9102.247 MHz), modulation frequency (100 kHz), and measurement temperature (77 K), we obtained the **g** factors of $\mathbf{g}_{xx} = 1.9807$, $\mathbf{g}_{yy} = 2.0055$, and $\mathbf{g}_{zz} = 2.0937$ and could assign the orthorhombic ESR signal to superoxide ions, O_2^{-}.[12−14] On the contrary, we did not observe ESR signals matching CH_3• and $(CH_3)_3N^+CH_2$•, which confirms no influence of generating electrons on Me_4N^+ ions. Meanwhile, Bednarek et al.[9,10] detected that the X-irradiated $Me_4NOH \cdot 5H_2O$ clathrate hydrate develops a blue coloration, which results from electrons entrapped in the 4^66^8 cage. Interestingly, as shown in Figure 3, we observed a rather yellow coloration for ($Me_4NOH + O_2$)*, caused by significant reaction between generated electrons from host and oxygen molecules in the sII-S. The intensity of the ESR signal and yellow color of the ($Me_4NOH + O_2$)* sample were not reduced even after several months, under the liquid nitrogen temperature and atmospheric pressure. The characteristic color of superoxide ion and KO_2, RbO_2, and CsO_2 (stable solid salts of superoxide ions) was reported to be yellow or orange, and thus this color change of the γ-irradiated sample plainly implies the formation of superoxide ions in the ($Me_4NOH + O_2$)* hydrate.[16,21,22]

A notable observation is that the γ-irradiated nonionic clathrate hydrates of pure O_2 and binary THF + O_2 did not exhibit yellow coloration, indicating that the O_2 molecules cannot draw the electrons to form the superoxide ions from the water host (see Figure S1). The HRPD (PAL) was used to identify the changes of diffraction patterns between ($Me_4NOH + O_2$) and ($Me_4NOH + O_2$)* (60 KGy dose at 77 K) clathrate hydrates and thus possibly to detect the sensitive transformation of structural and lattice dimensions. During the measurements, a $\theta/2\theta$ scan mode with a fixed time of 2 s and a step size of 0.005° for $2\theta = 0° - 120°$ and the beamline with a wavelength of 1.5490 Å were used for each sample. The loading of the ($Me_4NOH + O_2$)* clathrate hydrate was performed at 70 K to minimize possible sample damage. Particularly, liquid helium was used to lower the temperature to 5 K and collect temperature-dependent diffraction patterns at each temperature with increasing sample temperature. Figure S2, showing the full range of HRPD patterns indexed by the Checkcell program,[20] basically confirms the sII cubic *Fd*3*m* structure for both clathrate hydrates. Here, we see the discrete peak patterns with the (404) and (513) planes in the range $28.5° < 2\theta < 32°$ (Figure S3). The genuine ($Me_4NOH + O_2$) clathrate hydrate before irradiation shows highly intensive and sharp peaks with a unit cell dimension of $a = 17.1554(15)$ Å, while the γ-irradiated one exhibits asymmetric peaks, which can be deconvoluted into two peaks (see Figure S4).

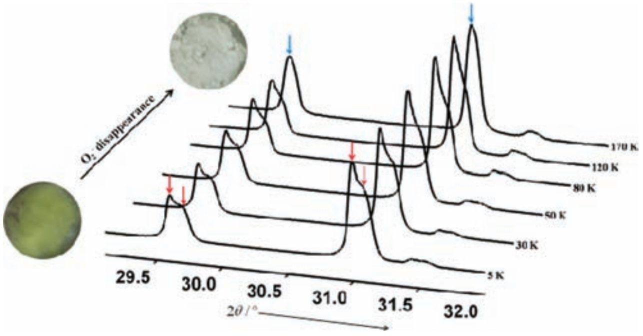

Figure 3. HRPD patterns of 60KGy ($Me_4NOH + O_2$)* clathrate hydrate with various temperatures. Red arrows indicate two independent structural (cage) dimensions of ($Me_4NOH + O_2$) and ($Me_4NOH + O_2$)* clathrate hydrate. The temperature increase to 170 K makes the ($Me_4NOH + O_2$)* clathrate hydrate samples gradually lose their yellow coloration, indicating that only one structural dimension of ($Me_4NOH + O_2$) clathrate hydrate remains (blue arrow).

The diffraction peak difference of 0.01° confirms the existence of two independent structural (cage) dimensions of the ($Me_4NOH + O_2$) clathrate hydrate with a unit cell dimension of $a = 17.1561(25)$ Å and the ($Me_4NOH + O_2$)* clathrate hydrate with $a = 17.0984(12)$ Å. Thus, due to the appearance of superoxide ions as guest molecules, the lattice dimensions contract by a value of 0.0577 Å at 5 K, which is equivalent to a 1.01% volume contraction. In the (THF + O_2) clathrate hydrate, nonionic system having identical cage structure, the 1% volume reduction is accompanied by a decrease of temperature of ~90 K.[23] The guest size of superoxide ion (the bond distance of O_2^{-}; 1.33 Å) is larger than that of an oxygen molecule (the bond distance of O_2; 1.21 Å);[24] thus, the volume reduction of the ($Me_4NOH + O_2$)* clathrate hydrate is a quite abnormal behavior due to the general trend of lattice size with guest size suggested by Udachin et al.[25] through single crystal X-ray diffraction.

We further explored the dimensional change of the ($Me_4NOH + O_2$)* cage lattice by examining temperature-dependent HRPD patterns, as shown in Figure 3. The lattice parameters of the asymmetric peaks of $(Me_4NOH + O_2)^*$ were calculated from the higher peaks of the (224) and (333) planes in Figure S5a; (404) and (513) planes in Figure 3; (822) and (555) planes in Figure S5b (for deconvolution, see Figure S4). We particularly note that the asymmetric peaks maintain a consistent temperature range of 5−80 K, confirming the quite stable entrapment of superoxide ions. At 120 K the asymmetric shoulder pattern becomes much weaker; however, the yellow coloration is still observed. At the highest temperature of 170 K $(Me_4NOH + O_2)^*$ is completely converted to one cubic *Fd*3*m* structure with impurities of hexagonal ice and $Me_4NOH \cdot nH_2O$, having white coloration.

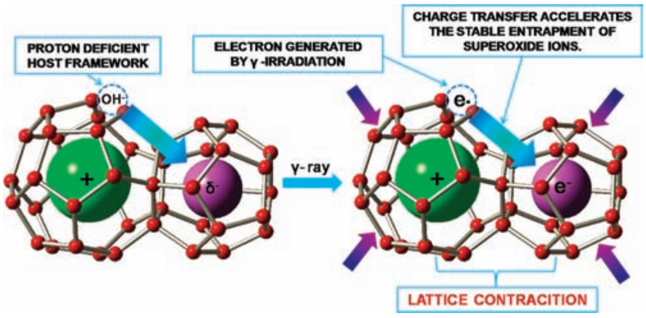

Figure 4. Stable entrapment of superoxide ions in sII-S cages of $(Me_4NOH + O_2)^*$ clathrate hydrate. Proton deficient anionic host-framework induces a charge transfer phenomenon, accelerating the stable entrapment of superoxide ions. Due to the direct guest−guest interaction between Me_4N^+ and O_2^-, the $(Me_4NOH + O_2)^*$ clathrate hydrate undergoes the lattice contraction. Red ball, oxygen atom in framework; green ball, Me_4N^+; purple ball, oxygen molecule, but hydrogen atoms in framework are omitted.

We have identified the effects and the temperature dependence of the superoxide ion in the lattice contraction behavior of the $(Me_4NOH + O_2)^*$ clathrate hydrate through ESR and HRPD studies. These results have become the key solutions for solving our questions suggested in the early stage: (1) the mechanism of formation and stable existence of superoxide ion in hydrate cages and (2) the effect of superoxide ion on the lattice characteristics and the reason for this effect, as shown in Figure 4. The γ-irradiation into the Me_4NOH + NIGM clathrate hydrate, such as H_2, N_2 and O_2, can lead to the generation of free electrons due to the decomposition of H_2O or OH^-. In the $(Me_4NOH + O_2)^*$ clathrate hydrate, balanced by Me_4N^+ in sII-L and O_2^- in sII-S, the generated free electrons cannot affect the electron trapping in the Me_4N^+ ion of the sII-L cages due to a charge transfer phenomenon occurring in the $(Me_4NOH + O_2)$ clathrate hydrate. In the early stages, we suggest that the oxygen molecule in sII-S of the $(Me_4NOH + O_2)$ clathrate hydrate is influenced by the anionic host framework and that this influence can cause the decrease of the magnetization value of O_2 in sII-S of the $(Me_4NOH + O_2)$ clathrate hydrate.[6] Therefore, through γ-irradiation generated free electrons cannot be consumed by Me_4N^+ in sII-L of the $(Me_4NOH + O_2)^*$ clathrate hydrate, and a charge transfer phenomenon accelerates the formation of the superoxide ion. The superoxide ion with a minus charge carrier can be stabilized by the charge transfer phenomenon as well as by the direct guest−guest interaction between the Me_4N^+ ion with a plus charge carrier and the superoxide ion, and this is the reason that the superoxide ions readily exist in the hydrate cage framework composed by water molecules. Particularly, evidence of the direct guest−guest ionic interaction of Me_4N^+ and the superoxide ion is supported by significant lattice contraction occurring in the $(Me_4NOH + O_2)^*$ clathrate hydrate.

The stable inclusion of specific radicals in clathrate hydrate materials tends to strongly alter the electron dynamics of cage surroundings, thus inducing totally different cage dynamics. The results of this study also imply that the structural and dimensional changes by cage (lattice) expansion/contraction can be achieved through the suitable choice of ionic guests. Particularly, we note that ionic-induced dimensional change is much greater than thermal-induced change. These unique electron behaviors and ionic interactions might provide new insights for understanding the complex inclusion phenomenon of ions and radical stabilization in hydrogen-bonded host water frameworks. More significantly, the entrapped radicals can develop strong reactivity with neighboring guest molecules, conceptually creating nanoreactors. One of the next challenges might be to synthesize target-specific functional materials based on icy clathrate hydrates.

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Supporting Information Available: γ-irradiated hydrate sample images, HRPD patterns, cage occupancy information of hydrate, and the calculating lattice parameters details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Jeffrey, G. A. *Inclusion Compounds*; Academic Press: London, 1984; Vol. 1.
(2) Cha, J.-H.; Shin, K.; Choi, S; Lee, H. *J. Phys. Chem. C* **2008**, *112*, 10573–10578.
(3) Choi, S.; Shin, K.; Lee, H. *J. Phys. Chem. B* **2007**, *111*, 10224–10230.
(4) Shin, K.; Choi, S.; Cha, J. -H.; Lee, H. *J. Am. Chem. Soc.* **2008**, *130*, 7180–7181.
(5) Cha, J. -H.; Shin, K.; Choi, S.; Lee, H. *J. Phys. Chem C* **2008**, *112*, 10573–10578.
(6) Shin, K.; Cha, M.; Choi, S.; Dho, J.; Lee, H. *J. Am. Chem. Soc.* **2008**, *130*, 17234–17235.
(7) Cha, J.-H; Lee, W.; Lee, H. *J. Mater. Chem.* **2009**, *19*, 6542–6547.
(8) Shin, K.; Cha, J,-H.; Seo, Y.; Lee, H. *Chem.—Asian. J.* **2010**, *5*, 22–34.
(9) Bednarek, J.; Ericson, R.; Lund, A.; Schlick, S. *J. Am. Chem. Soc.* **1991**, *113*, 8990–8991.
(10) Bednarek, J.; Erikson, R.; Schlick, S. *J. Phys. Chem. C* **1996**, *100*, 3910–3916.
(11) Yeon, S.-H.; Seol, J.; Park, Y.; Koh, D.-Y.; Kang, Y. S.; Lee, H. *J. Am. Chem. Soc.* **2008**, *130*, 9208–9209.
(12) Matsuishi, S.; Hayashi, K.; Hirano, M.; Tanaka, I.; Hosono, H. *J. Phys. Chem. B* **2004**, *108*, 18557–18568.
(13) Carter, E.; Carley, A. F.; Murphy, D. M. *J. Phys. Chem. C* **2007**, *111*, 10630–10638.
(14) Yu, J.; Chen, J.; Li, C.; Wang, X.; Zhang, B.; Ding, H. *J. Phys. Chem. B* **2004**, *108*, 2781–2783.
(15) Moots, D.; Seidel, R. *J. Inclusion Phenom.* **1990**, *8*, 139–157.
(16) Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry*, 3rd ed.: Pearson Education Inc.: NJ, 2004.
(17) Park, Y.; Dho, J.; Seol, J.; Yeon, S.-H.; Cha, M.; Jeong, Y. H.; Seo, Y.; Lee, H. *J. Am. Chem. Soc.* **2009**, *131*, 5736–5737.
(18) M−H curve of $(THF + O_2)$ and $(Me_4NOH + O_2)$ clathrate hydrate was subtracted by the magnetization value of pure THF clathrate hydrate and $Me_4NOH \cdot 16H_2O$. For the cage occupancy of $Me_4NOH + O_2$ hydrate, we measured the volume of releasing gas from $Me_4NOH + O_2$ hydrate. See the Supporting Information for the details.
(19) We expressed as $(Me_4NOH + O_2)$ for unirradiated $(Me_4NOH + O_2)$ sample and $(Me_4NOH + O_2)^*$ for γ-irradiatied $(Me_4NOH + O_2)^*$ sample.
(20) The PXRD patterns were indexed using the Check Cell program. LMGP-Suite Suite of Programs for the interpretation of X-ray Experiments, by Jean laugier and Bernard Bochu, ENSP/Laboratoire des Mate'riaux et du Ge'nie Physique, BP 46. 38042 Saint Martin d'He'res, France (http://www.inpg.fr/LMGP and http://www.ccp14.ac.uk/tutorial/lmgp/).
(21) Seyb, E., Jr.; Kleinberg, J. *Anal. Chem.* **1951**, *23*, 115–117.
(22) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393–400.
(23) Park, Y.; Choi, Y. N.; Yeon, S.-H.; Lee, H. *J. Phys. Chem. B* **2008**, *112*, 6897–6899.
(24) Sawyer, D. T.; Gibian, M. J. *Tetrahedron* **1979**, *35*, 1471–1481.
(25) Udachin, K. A.; Ratcliffe, C. I.; Ripmeester, J. A. *Proceedings of the Fourth International Conference on Gas Hydrates*, 2002; Yokohama, Japan; p 604.

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