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# SYNTHESIS AND CHARACTERIZATION OF KRYPTON AND XENON CLATHRATE COMPLEXES

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## Abstract

Gradient cooling of aqueous hydroquinone solutions under 25–35 atmospheres of krypton or xenon yields β-hydroquinone/noble gas clathrate complexes having the stoichiometry $[3\ C_6H_4(OH)_2] \cdot M$, where M is the inert gas guest atom. Direct measurement of the entrapped gas was made using a Toepler pump and its identity was verified by mass spectroscopy. The gas retention ability of the clathrate is unaffected by grinding or gentle heating but dissolving or heating the compound to 175 °C will release the entrapped gas. These materials provide an extremely efficient way to deliver gases in a solid matrix.

## Introduction

A clathrate compound, as defined by Powell,[1] is a two component molecular system in which one component forms a discrete closed cavity, or cage, that imprisons the other component.[2] The species forming the cage is called the host and the contained species is referred to as the guest. Clathrates are a subset of the group known as multimolecular inclusion compounds. Other notable members of this group are the channel type compounds such as those formed by urea hosts and the layer or intercalation compounds typified by graphite hosts.

The quintessential clathrate host is 1,4-dihydroxybenzene, also known as hydroquinone (Figure 1). The crystal structure of the molecular compound made by hydroquinone and sulfur dioxide was determined[3] by Powell; a more recent study by Mak[4] has examined hydrogen sulfide guests. In both cases (and, indeed, in all hydroquinone clathrates) the general formula for the molecular compound may be written $[3\ C_6H_4(OH)_2] \cdot x\ M$, where M is the guest species with a site occupancy factor, $x$, between zero and one. Each cage in the clathrate host lattice is formed by six walls, a ceiling, and a floor (Figure 2). Each wall in the cage is defined by the region between two adjacent hydroquinone molecules; there are six hydroquinone molecules situated equatorially around the cavity. Thus, the hydroquinone molecules make up the bars of the clathrate cage. The floor and ceiling of the cage are hexagons formed by six oxygen atoms that are held together by a hydrogen-bonded framework involving hydroxyl groups. The cavities provided by the hydroquinone host lattice are roughly spherical with a free diameter of *ca.* 4.8 Å each. As noted above, the maximum guest:host ratio is 1:3. This may be understood when one realizes that each hydroquinone molecule provides a common bar for two adjacent cages; since each cage is made up of six hydroquinones, there can be at most one guest per three host molecules. This ratio will be lower if all available cages aren't occupied.

The host lattice structure just described is called β-hydroquinone to distinguish it from the α-hydroquinone lattice which forms when the material is crystallized from solvents or solutions which cannot be enclathrated due to size limitations of the potential guest. Thus, for example, helium is too small to be contained while benzene is too large. The formation of substantial quantities of α-hydroquinone also results when the concentration of guest molecules of the proper size is too low.

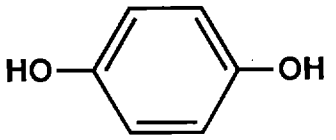


**Figure 1.** Hydroquinone

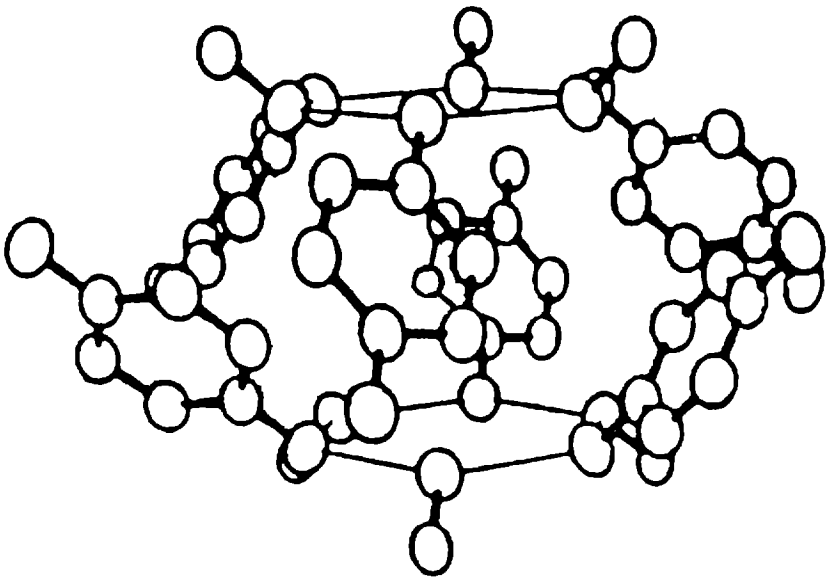

**Figure 2.** β–Hydroquinone crystal lattice
(from *J. Chem. Soc. Perkins Trans. II*, 1169, 1976)

The α–hydroquinone structure does not contain any molecular-sized cavities and, as a result, does not form clathrate complexes. Macroscopic examination is usually sufficient to discern the presence of either lattice type: Crystals of α–hydroquinone are thin hexagonal needles while β-hydroquinone displays hexagonal prisms with rhombohedral faces as its crystal habit.

As part of our research on gas delivery systems we have examined hydroquinone/noble gas clathrates. Powell, in his pioneering work, studied argon,[5] krypton,[6] and xenon[7] clathrate complexes. In these studies, the gas content was determined indirectly by weight loss upon heating and no attempt was made to identify the evolved gas. These experiments also omitted any investigations of gas evolution in response to mechanical or thermal stress. In an effort to broaden the scope of these early investigations, the work reported herein describes the direct measurement and identification of all enclosed gas and examines the effect of mechanical and thermal stress on the gas retention ability of β-hydroquinone clathrates.

## Experimental

**General considerations.** Crystallizations were performed in a glass-lined Parr Mini Reactor (Model 4561). Temperature control was achieved using a Neslab Endocal circulating bath with a MTP-5 temperature programmer. Mass spectra were recorded on a Hewlett-Packard Model 5985 mass spectrometer using electron impact ionization with 70 eV electron energy; the samples were introduced directly into the mass spectrometer by gas syringe. Hydroquinone (Aldrich, Gold Label), krypton, and xenon (Airco, Research Grade) were used as received.

**Preparation of hydroquinone/inert gas clathrates.** In a typical experiment 10 g of hydroquinone in 80 mL distilled water was heated (40-50 °C) to dissolve all solids. The solution was allowed to cool to room temperature during which time excess hydroquinone precipitated from solution. 70 mL of this saturated solution was decanted into a 100 mL glass reaction vessel and an additional 2 g of hydroquinone was added to the solution. The glass vessel was placed in a Parr Mini Reactor which was then sealed, flushed with krypton or xenon gas, and pressurized to 400-500 psi. The reactor was placed in a circulating bath for the crystal growth procedure: The bath was heated from 25 °C to 85 °C in three hours, held at 85 °C for one hour, and cooled to 25 °C over a twelve hour period. The reactor was vented to atmospheric pressure, the glass insert was removed, and the crystals were collected and air dried.

**Quantitative analysis of entrapped gas.** Following any special pre-treatment (e.g. grinding or mild heating), 200 mg of the clathrate complex was placed in a 25 mL round-bottom flask which was then sealed with a Teflon needle valve. The sample was cooled to -80 °C and the flask evacuated to < 1 mtorr on a high vacuum system (Hg diffusion pump). The sample was quickly heated to its melting point (~175 °C) in an oil bath to free the entrapped gas. Upon cooling to room temperature, the evolved gas was quantitatively transferred by means of a Toepler pump into a calibrated volume. The pressure of the contained gas was read on a manometer and the precise quantity of gas was calculated using the ideal gas law. These results are listed in Table I.

**Mass spectroscopic analysis of gas.** For each preparation of the clathrate complex the identity of the enclosed gas was qualitatively determined by mass spectroscopy using the following procedure. A 1.0 g sample of the clathrate complex was placed in a 25 mL Schlenk flask fitted with a Teflon needle valve on the ground glass joint and a rubber septum on the sidearm. The flask was then evacuated and heated as described above for the quantitative studies. The evolved gas was removed from the flask through the septum using a gas-tight syringe and injected directly into the mass spectrometer. The presence of the parent ion for either krypton or xenon and the absence of any ions assignable to nitrogen or oxygen were used to establish the identity and purity of the gas.

Table I. Clathrate gas analysis[a]

| Guest[b] | Pressure[c] (psi) | Pre-treatment | Gas content (weight percent) |
|---|---|---|---|
| Kr | 400 | — | 17.6 |
| Kr | 400 | Gentle grinding | 17.6 |
| Kr | 400 | Vigorous grinding | 17.2 |
| Kr | 400 | Room temperature storage for 1 week | 17.7 |
| Kr | 500 | — | 20.4 |
| Kr | 500 | Heat *in vacuo* for 6 hr at 60 °C | 20.6 |
| Xe | 400 | Vigorous grinding | 27.9 |

[a]Determined by Toepler pump analysis of gas evolved upon melting clathrate. Identity and purity of gas confirmed by mass spectroscopy.

[b]Host lattice in all cases is β-hydroquinone.

[c]Gas pressure during clathrate preparation.

## Results and Discussion

We have successfully prepared both krypton and xenon clathrate complexes by slowly cooling aqueous hydroquinone solutions under 400-500 psi of inert gas. The need for relatively high pressure conditions is due to the low solubility of the inert gases in water. Since a dissolved gas atom must be present at the surface of the growing crystal whenever a cage of hydroquinone molecules is formed in order to be enclathrated, increasing the pressure (thereby increasing the concentration of dissolved gas) would be expected to raise the occupancy of gas in the host lattice. The rate of crystallization is also important; rapid crystal formation will result in local depletion of the gas in solution, leaving many cages unfilled. Thus, a high yield of clathrate complex demands the use of slow crystal growth techniques and high pressure to insure the availability of sufficient dissolved gas. The formation of substantial amounts of needle-like α-hydroquinone (the non-clathrate form), usually results when crystal growth conditions aren't optimal.

Our gas evolution measurements are set out in Table I. To place these results in context, we note that the maximum loadings possible are 20.3 and 28.4 weight percent for krypton and xenon, respectively, assuming one gas atom per three hydroquinone molecules in the clathrate. Two points relating to experimental procedure deserve special mention. First, the numbers shown in the table correspond to the direct measurement of released gas; a Toepler pump was used to quantitatively transfer the gas from the reaction flask to a calibrated volume. Second, mass spectra were obtained for all gas samples. This confirmed both the identity and purity of the gas: no evidence was found for any substance other than the inert gas.

Examination of the krypton data suggests that increasing the preparation pressure promotes enhanced gas retention, as discussed above. Thus, a 25% pressure increase results in a 16% greater gas inclusion, assuming other factors are identical for the two preparations. At a pressure of 500 psi, krypton has apparently filled all available cages (100% occupancy) while a 400 psi synthesis using xenon occupies 98% of the available sites. In terms of gas delivery capability, 17 g of the krypton complex or 19 g of the xenon complex can generate 1 atm pressure in a 1 L vessel at 25 °C.

Processing demands often require the generation of homogeneous, finely powdered material. However, the clathrate complexes are usually formed as large crystalline masses which would require grinding in order to obtain small particles. It is possible that powdering of these large crystals might lead

to severe disruptions of the crystal lattice with resultant cage opening and gas loss. It was of interest, then, to study the effect of grinding on the gas retention ability of the clathrates. As shown in the table for the krypton clathrate, gentle powdering with an agate mortar and pestle (yielding an average particle size of 200 microns) did not appear to cause any loss of gas. Even more vigorous pulverizing of the sample to form very fine powder (~80 micron particles) gave only a minimal change in gas content, with 98% of the original gas still in the clathrate. This small loss is not necessarily caused by lattice disruption due to shear forces; we cannot rule out thermal decomposition of the clathrate due to local heating during the grinding process.

Finally, the issue of sample stability during storage is important and two experiments addressed this point. The krypton clathrate was unchanged after one week at room temperature and atmospheric pressure. No special measures were taken to exclude air or provide a krypton-enriched atmosphere. The sample vial was capped during storage but the atmosphere in the vial was normal air. In a related experiment, the krypton clathrate was heated under vacuum for six hours at 60 °C. Here, again, the gas retention ability of the compound was undiminished. Although studies for much longer time periods are necessary to give a better indication of sample stability, these two experiments hold promise for convenient long term storage of these inert gas clathrates, even at elevated temperatures.

## Conclusions

Clathrate complexes based on the β-hydroquinone host lattice have been prepared incorporating krypton and xenon guest atoms. The gas inclusion for these compounds is near the theoretical maximum described by the formula $[3\ C_6H_4(OH)_2] \cdot M$, where M is the inert gas atom. The gas retention ability of the clathrates seems to be unaffected by the mechanical stress and localized heating attendant upon vigorous grinding. Tests designed to simulate the thermal stress of storage at elevated temperatures reinforce the notion that these are robust materials with excellent gas retention. Based on Powell's crystallographic results[8] for similar systems, we calculate that 260 $cm^3$ of crystalline material will contain one mole of gas. Using the ideal gas law, the pressure of gas in the clathrate is found to be *94 atm* at 25 °C. Clathrates of this type thus provide an extremely efficient way to deliver gases in a solid matrix with no special precautions required to handle them.

## References

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