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## Crystal Structure of Dehydrated Partially Ag<sup>+</sup>-Exchanged Zeolite A, Ag<sub>4.6</sub>Na<sub>7.4</sub>-A, Treated with Hydrogen at 350°C

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The crystal structure of Ag<sub>4.6</sub>Na<sub>7.4</sub>-A, dehydrated, treated with H<sub>2</sub>, and evacuated, all at 350°C, has been determined by single crystal x-ray diffraction methods in the cubic space group *Pm3m* at 24(1)°C; *a* = 12.208(2)Å. The structure was refined to the final error indices *R*<sub>1</sub> = 0.088 and *R*<sub>2</sub> (weighted) = 0.069 using 194 independent reflections for which *I*<sub>o</sub> > 3σ(*I*<sub>o</sub>). On threefold axes near the centers of 6-oxygen rings, 7.4 Na<sup>+</sup> ions and 0.6 Ag<sup>+</sup> ions are found. Two non-equivalent 8-ring Ag<sup>+</sup> ions are found off the 8-ring planes, each containing about 0.6 Ag<sup>+</sup> ions. Three non-equivalent Ag atom positions are found in the large cavity, each containing about 0.6 Ag atoms. This crystallographic analysis may be interpreted to indicate that 0.6 (Ag<sub>6</sub>)<sup>0</sup> clusters are present in each large cavity. This cluster may be viewed as a nearly linear trisilver molecule (Ag<sub>3</sub>)<sup>0</sup> (bond lengths, 2.92 and 2.94 Å; angle, 153°) stabilized by the coordination of each atom to a Ag<sup>+</sup> ion at 3.30, 3.33, and 3.43 Å, respectively. In addition, one of the silver atoms approaches all of the 0(1) oxygens of a 4-ring at 2.76Å. Altogether 7.4 Na<sup>+</sup> ions, 1.8 Ag<sup>+</sup> ions, and 1.8 Ag atoms are located per unit cell. The remaining 1.0 Ag<sup>+</sup> ion has been reduced and has migrated out of the zeolite framework to form silver crystallites on the surface of the zeolite single crystal.

### Introduction

The structures of metal clusters are of great interest because of their pronounced catalytic activity.

Ag<sup>+</sup> ions in zeolite A are autoreduced upon dehydration to form uncharged silver clusters, the molecules Ag<sub>6</sub>, each within a cube of eight Ag<sup>+</sup> ions, each near the plane of a 6-oxygen

ring.<sup>1,2</sup> The number of silver clusters in 7 separate crystallographic determinations has been found to depend upon the dehydration time and temperature.<sup>2</sup> Hermerschmidt and Haul also identified these clusters in dehydrated Ag<sup>+</sup>-exchanged zeolite A using epr spectroscopy.<sup>3</sup> These clusters, of (Ag<sub>6</sub>)<sup>0</sup> stabilized by coordination to 8 Ag<sup>+</sup> ions, may also be viewed

as (Ag<sub>14</sub>)<sup>8+</sup>.

Silver ion can also be reduced interzeolitically by the introduction of specific reducing agents. Tsutsumi and Takahashi found that Ag<sup>+</sup> ions in zeolite Y can be reduced to bulk clusters of Ag<sup>0</sup> by treatment with alcohol and alkyl benzenes.<sup>4</sup> Ag<sup>+</sup> ions in Ag-A, Ag-Y, Ag-mordenite, and Ag-chabazite can also be reduced by treatment with hydrogen.<sup>5,7</sup> Beyer, Jacobs, and Uytterhoeven reported that the silver clusters (Ag<sub>3</sub>)<sup>+</sup> and (Ag<sub>6</sub>)<sup>+</sup> are formed at temperatures up to 150°C, but that silver crystallites external to the zeolite are created at higher temperatures (350°C) in Ag-Y and Ag-mordenite treated with H<sub>2</sub>.<sup>6</sup> Hydrogen uptake by Ag-chabazite produced (Ag<sub>4</sub>)<sup>2+</sup> and (Ag<sub>5</sub>)<sup>+</sup> clusters according to epr measurements.<sup>5</sup> The reduction in Ag-mordenite was similar to that in Ag-chabazite and also led to the intermediate formation of charged clusters.<sup>5</sup> Ag<sup>+</sup> ions in zeolite A can be easily reduced by H<sub>2</sub> and the reduced Ag atoms or clusters can be readily reoxidized to Ag<sup>+</sup> by O<sub>2</sub>.<sup>7</sup>

Gellens and Schoonheydt studied Ag<sup>+</sup>-faujasite type zeolites by reflectance spectroscopy.<sup>8</sup> Ag<sup>+</sup>-faujasites are autoreduced by dehydration to form uncharged silver clusters and charged di- and trisilver clusters in low-Al zeolites, but only the charged di- and trisilver clusters in high-Al zeolites. They also found, independent of the Si/Al ratio, that reduction with hydrogen forms Ag atoms, uncharged Ag clusters, and inside or outside the zeolite, Ag microcrystallites.<sup>8</sup>

Recently, Ozin *et al.* by fluorescence emission and excitation, by diffuse optical reflectance, and by epr spectroscopies, identified (Ag<sub>3</sub>)<sup>2+</sup>, (Ag<sub>5</sub>)<sup>2+</sup>, and (Ag<sub>5</sub>)<sup>4+</sup> clusters in Ag, Na-Y zeolite, and concluded that they were on the walls of the super cages.<sup>9</sup>

When fully Ag<sup>+</sup>-exchanged zeolite A is evacuated and treated with H<sub>2</sub>, the zeolite loses its crystalline diffraction pattern.<sup>10</sup> This work was done, therefore, with incompletely Ag<sup>+</sup>-exchanged zeolite A. It was done to learn whether new silver clusters, or known clusters with unknown structure, could be synthesized, and, if so, to determine their structures by single-crystal x-ray diffraction techniques.

## Experimental

Complete Ag<sup>+</sup>-exchange of zeolite 4A single crystals was accomplished by a static method. Two grams of zeolite 4A (Union Carbide, Lot no: 494107701161) were allowed to exchange at 24°C with 0.1N AgNO<sub>3</sub> of which concentration is a 7-fold excess of exchangeable Ag<sup>+</sup> ions and the solution was agitated periodically. Each day, the supernatant solution was decanted and a fresh aliquot of 0.1N AgNO<sub>3</sub> was added. After 8 days, the zeolite was filtered and dried. Samples of Ag<sub>12</sub>-A and Na<sub>12</sub>-A were mixed in a 1:2 mole ratio (neglecting water contents). To this mixture were added a few large single crystals of zeolite 4A which had been prepared by Charnell's method,<sup>11</sup> with enough water to submerge all solid particles so that at equilibrium the composition of the large crystals would be Ag<sub>4</sub>Na<sub>8</sub>-A. After 5 days, the water was allowed to evaporate in air at room temperature.

A cubic single crystal 80 μm on an edge are selected and lodged in fine glass capillary. The clear colorless hydrated partially Ag<sup>+</sup>-exchanged crystal was dehydrated for 58 hours at 350°C and 2 × 10<sup>-6</sup> torr. The crystal was treated with ca 320 torr of H<sub>2</sub> gas at 350°C for 3 hours, evacuated at 350°C for 2.5 hours, and sealed off in its capillary by torch. Microscopic examination showed that the crystal color had become charcoal black.

The diffraction intensities were then collected at 24°C. The cubic space group *Pm3m* (no systematic absences) was used instead of *Fm3c* throughout this work for reasons discussed previously.<sup>12,13,14</sup> Diffraction data were collected a Syntex P1 4-circle computer-controlled diffractometer, equipped with a pulse-height analyzer and a graphite monochromator, using Mo K<sub>α</sub> radiation (K<sub>α1</sub>, λ = 0.70930 Å, K<sub>α2</sub> λ = 0.71359 Å). The unit cell constant, as determined by a least-squares refinement of 15 intense reflections for which 20° < 2θ < 24° is 12.208(2) Å at 24°C.

Data collection was done by methods described previously,<sup>15</sup> except that only one unique region of reciprocal space was examined at a scan rate (ω) of 1° min<sup>-1</sup> in 2θ. Standard deviations were assigned to individual reflections according to the

TABLE 1: Positional, Thermal,\* and Occupancy Parameters

	Wyckoff position	x	y	z	β <sub>11</sub> or B	β <sub>22</sub>	β <sub>33</sub>	β <sub>12</sub>	β <sub>13</sub>	β <sub>23</sub>	Occupancy constrained	factor <sup>d</sup> varied
(Si, Al)	24(k)	0	1824(4)	3701(4)	41(4)	36(4)	24(4)	0	0	12(8)	24.0 <sup>e</sup>	
0(1)	12(h)	0	2145(17)	5000	79(20)	97(21)	50(18)	0	0	0	12.0	
0(2)	12(i)	0	2931(9)	2931(9)	64(16)	43(9)	43(9)	0	0	83(25)	12.0	
0(3)	24(m)	1129(6)	1129(6)	3365(9)	58(6)	58(6)	83(12)	38(21)	-17(14)	-17(14)	24.0	
Na(1)	8(g)	2093(9)	2093(9)	2093(9)	164(12)	164(12)	164(12)	257(26)	257(26)	257(26)	7.39(3)	7.31(7)
Ag(1)	8(g)	2093(9)	2093(9)	2093(9)	164(12)	164(12)	164(12)	257(26)	257(26)	257(26)	0.61(3)	0.69(7)
Ag(2)	24(m)	1027(52)	4108(39)	4108(39)	3.7(16)						0.61(3)	0.67(14)
Ag(3)	24(m)	493(84)	4347(53)	4347(53)	12.9(46)						0.61(3)	0.35(13)
Ag(4)	24(m)	2638(27)	4249(18)	4249(18)	-0.4(9)						0.61(3)	0.82(8)
Ag(5)	8(g)	3651(29)	3651(29)	3651(29)	296(53)	296(53)	296(53)	-226(88)	-226(88)	-226(88)	0.61(3)	0.33(5)
Ag(6)	12(j)	2256(23)	2256(23)	5000	29(19)	29(19)	59(46)	40(53)	0	0	0.61(3)	0.65(6)

\* Positional and anisotropic thermal parameters are given × 10<sup>4</sup>. Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter. The anisotropic temperature factor = exp[-β<sub>11</sub>h<sup>2</sup> + β<sub>22</sub>k<sup>2</sup> + β<sub>33</sub>l<sup>2</sup> + β<sub>12</sub>hk + β<sub>13</sub>hl + β<sub>23</sub>kl]. <sup>b</sup> Root mean square displacements can be calculated from β<sub>ii</sub> values using the formula μ<sub>i</sub> = 0.225a(β<sub>ii</sub>)<sup>1/2</sup>. Also, β<sub>ii</sub> = 4a<sup>2</sup>β<sub>ii</sub>. <sup>c</sup> Isotropic thermal parameter in units of Å. <sup>d</sup> Occupancy factors are given as the number of atoms or ions per unit cell. <sup>e</sup> Occupancy for (Si) = 12; occupancy for (Al) = 12. <sup>f</sup> This physically unacceptable value was increased 10 in the preparation of Figure 1.

formula.

$$\sigma(I) = [\omega^2(CT + B_1 + B_2) + (\rho I)^2]^{-\frac{1}{2}}$$

where  $\omega$  is the scan rate, CT is the total integrated count,  $B_1$  and  $B_2$  are the background counts, and the intensity  $I = \omega(CT - B_1 - B_2)$ . A value of 0.02 was assigned to the empirical parameter  $\rho$  to account for the empirically observed reduced reliability of the more intense reflections.<sup>16</sup> The intensities were corrected for Lorentz and polarization effects<sup>17</sup>; the contribution of the monochromatic crystal was calculated assuming it to be half-perfect and half-mosaic in character. An absorption correction was judged to be negligible ( $\mu = 1.72 \text{ mm}^{-1}$ ) and was not applied.<sup>17</sup>

All 870 reflections for which  $2\theta < 70^\circ$  were collected by counter methods. Of these, only the 194 for which  $I_o > 3\sigma(I_o)$  were used for structure solution and refinement.

### Structure Determination

Full-matrix least-squares refinement was initiated using the atomic parameters of the framework atoms (Si, Al, O(1), O(2), and O(3)) and of the threefold-axis  $\text{Na}^+$  ions in dehydrated  $\text{Na}_{12}\text{-A}$ .<sup>18</sup> Anisotropic refinement of these converged to the error indices

$$R_1 = \sum |F_o - |F_c|| / \sum F_o = 0.16$$

$$R_2 = [\sum w(F_o - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.17$$

A subsequent difference Fourier synthesis revealed four peaks ( $1.9$  to  $2.6 \text{ e}\text{\AA}^{-3}$  in height,  $\text{esd} = 0.2 \text{ e}\text{\AA}^{-3}$ ) at  $(0.21, 0.21, 0.5)$ ,  $(0.26, 0.42, 0.42)$ ,  $(0.37, 0.37, 0.37)$ , and  $(0.09, 0.41, 0.41)$ , all of which were stable in least-squares refinement. Simultaneous positional, occupancy, and anisotropic thermal parameter refinement converged with  $R_1 = 0.081$  and  $R_2 = 0.064$ .

The occupancy at Na(1) on the threefold axis refined to 10.2  $\text{Na}^+$  ions, although the number of ions at this position cannot exceed 8.0. Considering the relative scattering powers of  $\text{Ag}^+$  and  $\text{Na}^+$ , this indicates that some  $\text{Ag}^+$  ions (*ca* 0.6) occupy this predominantly  $\text{Na}^+$  (*ca* 7.4) position. Attempts to refine two nonequivalent threefold-axis positions did not succeed, so they were refined with identical positional parameters with the constraint in least-squares<sup>17</sup> that the total number of ions be 8.0. The thermal ellipsoids of Ag(2) became very elongated in subsequent least-squares refinements, indicating the presence of two nonequivalent  $\text{Ag}^+$  ions at that position. These were refined at  $(0.12, 0.41, 0.41)$  and  $(0.05, 0.43, 0.43)$  (Table 1).

The refined occupancies given in the last column of Table 1 were all within  $3\sigma$  of 0.6 except that at Ag(5) which appears to be too small. The environment about Ag(5) suggests that it should not be located directly on a threefold axis, and its incorrect placement on that symmetry element could explain its unusual thermal ellipsoid and its low occupancy parameter. Unfortunately, attempts to refine Ag(5) at nearby positions of lower symmetry led to divergence; it had been found on that axis on the original Fourier function, and must therefore at least be quite close to it. It appeared possible, therefore, that all 6 occupancies could be equal.

An acceptable geometry could be calculated for a  $(\text{Ag}_6)^{3+}$  silver cluster (see Figure 1), thereby explaining the nearly equal occupancies, by filling positions of partial occupancy in an ap-

propriate manner. Accordingly, the occupancy numbers of these silver positions were constrained to follow that of Ag(1) (which had been in turn constrained to sum, with that of Na(1), to 8.0). Anisotropic refinement of all but Ag(2), Ag(3), and Ag(4), which were refined isotropically, converged to the final error indices  $R_1 = 0.088$  and  $R_2 = 0.069$ .

The final difference function was featureless except for one peak  $6.4(7) \text{ e}\text{\AA}^{-3}$  in height at the center of the unit cell ( $\text{esd} = 0.1 \text{ e}\text{\AA}^{-3}$  at a general position and therefore  $\text{esd} = 0.1\sqrt{48} \sim 0.7$  at this position<sup>19</sup>).

The final structural parameters are presented in Table 1. Interatomic distances and angles are given in Table 2. The goodness-of-fit,  $[\sum w(F_o - |F_c|)^2 / \sum (m - s)]^{1/2}$  is 2.77;  $m(194)$  is the number of observations, and  $s(42)$  is the number of variables in least-squares. All shifts in the final cycle of refinement were less than 0.5% of their corresponding  $\text{esd}$ 's.

The full-matrix least-squares program<sup>17</sup> used in all structure determinations minimized  $\sum w(\Delta|F|)^2$ ; the weight ( $w$ ) of an observation was the reciprocal square of  $\sigma$ , its standard deviation. Atomic scattering factors<sup>20,21</sup> for  $\text{Na}^+$ ,  $\text{Ag}^+$ ,  $\text{O}^-$ , and  $(\text{Si}, \text{Al})^{1-75+}$  were used. The function describing  $(\text{Si}, \text{Al})^{1-75+}$  is the mean of the  $\text{Si}^0$ ,  $\text{Si}^{4+}$ ,  $\text{Al}^0$ , and  $\text{Al}^{3+}$  functions. All scattering factors were modified to account for the real component ( $f'$ ) of the anomalous dispersion correction.<sup>22,23</sup>

### Discussion

The silver species at Ag(1), Ag(2), and Ag(3) are located near framework oxygens and may be considered to be  $\text{Ag}^+$  ions. Ag(2) and Ag(3) approach O(2) oxygens of 2 different 8-rings most closely at  $2.51(5) \text{ \AA}$  and  $2.52(10) \text{ \AA}$ , respectively. Ag(1) is associated with a 6-ring and approaches 3 O(3) oxygens at  $2.28(1) \text{ \AA}$ . For comparison, the sum of the  $\text{Ag}^+$  and  $\text{O}^{2-}$  radii is  $2.58 \text{ \AA}$ .<sup>24</sup>

The silver species at Ag(4) and Ag(5) are located deep inside the large cavity. Their closest distances to framework oxygens are Ag(4)-O(2) =  $3.94(3) \text{ \AA}$  and Ag(5)-O(3) =  $4.37(4) \text{ \AA}$ . They may be placed within their equipoints of partial occupancy, however, if they are to have any near neighbors at all, rather close to  $\text{Ag}^+$  ions: Ag(4)-Ag(2) =  $3.33(6) \text{ \AA}$  and Ag(5)-Ag(1) =  $3.30(12) \text{ \AA}$  (see Figure 1). These 2 distances are too short to be unmoderated  $\text{Ag}^+-\text{Ag}^+$  contacts, and too long to be  $\text{Ag}^0-\text{Ag}^0$  bonds ( $\text{Ag}^0-\text{Ag}^0$  distance in silver metal is  $2.89 \text{ \AA}$ ). They may be considered to be  $\text{Ag}^0-\text{Ag}^+$  coordination distances; they are almost the same as those in  $(\text{Ag}^*)_6(\text{ag}_6)^0$  in the structure of dehydrated partially decomposed  $\text{Ag}_{12}\text{-A}$ .<sup>1,2</sup> These positions of partial occupancy may be filled to give, in addition to the above contacts, an Ag(4)-Ag(5) distance of  $2.94(4) \text{ \AA}$ , approximately the

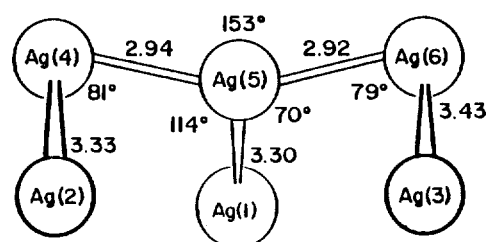


Figure 1. A schematic view of the  $(\text{Ag}_6)^{3+}$  cluster. Ag(5)-Ag(1) is approximately perpendicular to the plane of Ag(*i*), *i* = 2 to 6.

TABLE 2: Selected Interatomic Distances (Å) and Angles (Deg)<sup>a</sup>

(Si, Al)-O(1)	1.63(1)	O(1)-(Si, Al)-O(2)	111(3)
(Si, Al)-O(2)	1.64(4)	O(1)-(Si, Al)-O(3)	111(1)
(Si, Al)-O(3)	1.67(3)	O(2)-(Si, Al)-O(3)	106(1)
		O(3)-(Si, Al)-O(3)	111(3)
		(Si, Al)-O(1)-(Si, Al)	152(3)
		(Si, Al)-O(2)-(Si, Al)	160(2)
		(Si, Al)-O(3)-(Si, Al)	141(2)
Na(1)-O(3)	2.28(1)	O(3)-Na(1)-O(3)	116(1)
Ag(1)-O(3)	2.28(1)	O(3)-Ag(1)-O(3)	116(1)
Ag(2)-O(1)	3.01(4)	O(1)-Ag(6)-O(3)	59(1)
Ag(2)-O(2)	2.51(5)		
Ag(3)-O(1)	2.87(7)	Ag(4)-Ag(2)-O(2)	176(3)
Ag(3)-O(2)	2.52(10)	Ag(5)-Ag(1)-O(3)	101(3)
Ag(4)-O(1)	4.22(3)	Ag(6)-Ag(3)-O(2)	78(2)
Ag(4)-O(2)	3.94(3)		
Ag(5)-O(3)	4.37(4)	Ag(2)-Ag(4)-Ag(5)	81(1)
Ag(6)-O(1)	2.76(2)	Ag(4)-Ag(5)-Ag(6)	153(2)
Ag(6)-O(3)	2.79(2)	Ag(4)-Ag(5)-Ag(1)	114(2)
		Ag(1)-Ag(5)-Ag(6)	70(2)
		Ag(5)-Ag(6)-Ag(3)	79(2)
Ag(1)-Ag(5)	3.30(12)		
Ag(2)-Ag(4)	3.33(6)		
Ag(3)-Ag(6)	3.43(9)		
Ag(4)-Ag(5)	2.94(4)		
Ag(5)-Ag(6)	2.92(4)		

<sup>a</sup>Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding value.

same as the Ag-Ag distance in silver metal, and that in the (Ag<sup>+</sup>)<sub>6</sub>(Ag<sup>0</sup>)<sub>6</sub> cluster,<sup>1,2</sup> 2.92(1) Å. Altogether, these distances indicate that Ag(4) and Ag(5) are occupied by silver atoms (see Figure 1).

The Ag(6) position is 2.76(2) Å from 2 O(1) oxygens and 2.79(2) Å from 2 at O(3). These distances are comparable to the corresponding 2.78 Å approaches of an Ag<sup>0</sup> atom in Ag<sub>6</sub>.<sup>1,2</sup> Furthermore, Ag(6)-Ag(5) and Ag(6)-Ag(3) distances of 2.92(4) and 3.43(9) Å, respectively, may be found, indicating that Ag(6)-Ag(5) is an atom-atom contact and Ag(6)-Ag(3) is an atom-ion contact. Therefore, Ag(6) is a silver atom position.

The number of silver atoms or ions at Ag(i), i = 1 to 6, are all about 0.6. This suggests that 0.6 clusters with stoichiometry 1:1:1:1:1:1 have formed per unit cell. This cluster, of 6 non-equivalent silvers in equal proportion, is (Ag<sub>6</sub>)<sup>3+</sup>. Although some delocalization of charge should cause the distinction between Ag<sup>+</sup> ions and Ag<sup>0</sup> atoms to be lost, the Ag-Ag bond lengths indicate that this distinction is quite clear, and that the cluster may accurately be viewed as a nearly linear (Ag<sub>3</sub>)<sup>0</sup> molecule (Ag(4)-Ag(5)-Ag(6) = 153°), each atom of which is coordinated to an Ag<sup>+</sup> ion at Ag(2), Ag(1), and Ag(3), respectively. See Figure 1.

On the threefold axes of the unit cell near the centers of the 6-ring planes, 7.4 Na<sup>+</sup> ions at Na(1) and 0.6 Ag<sup>+</sup> ions at Ag(1) are found. The single (Na, Ag)-O contact distance observed, 2.28(1) Å, must then be an appropriate average of the corresponding Na-O distance, 2.32(1) Å in Na-A,<sup>18</sup> and Ag-O, 2.25(2) Å in Ag<sub>12</sub>-A.<sup>1,2</sup> The Na(1), Ag(1) thermal ellipsoid is elongated normal to the 6-ring plane, consistent with this averaging.

It appeared from our previous work<sup>10</sup> that hydrogen treatment at 350°C had converted many Ag<sup>+</sup> ions to Ag<sup>0</sup> atoms by

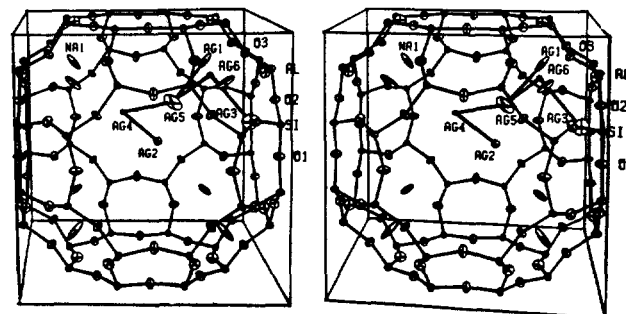
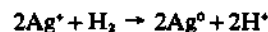


Figure 2. A stereoview<sup>17</sup> of the structure showing 1 (Ag<sub>6</sub>)<sup>3+</sup> cluster per unit cell. About 60% of the unit cells contain this cluster and 7 Na<sup>+</sup> ions. The remaining 40% would have 8 Na<sup>+</sup> ions and no cluster.

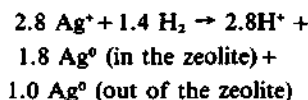
TABLE 3: Deviations(Å) of Atoms from the (111) Plane at 0(3)

Na(1)	0.46
Ag(1)	0.46
Ag(5)	3.76
O(2)	0.17

the reaction



The approximate unit cell composition determined here, (Ag<sup>+</sup>)<sub>1.4</sub>(Na<sup>+</sup>)<sub>7.4</sub>(H<sup>+</sup>)<sub>2.8</sub>Ag<sub>1.8</sub>-A, indicates that the following reaction has occurred.



In summary, in the structure of Ag<sub>4.6</sub>Na<sub>7.4</sub>-A, dehydrated, treated with H<sub>2</sub>, and evacuated, all at 350°C, 0.6(Ag<sub>6</sub>)<sup>3+</sup> clusters may be present per unit cell. This cluster may be viewed as a trisilver molecule in the large cavity of the zeolite, stabilized by coordination to 3 Ag<sup>+</sup> ions (and the oxygens of 1 4-ring). On threefold axes near 6-rings (Table 3), 7.4 Na<sup>+</sup> and 0.6 Ag<sup>+</sup> ions are found. Also, 0.6 Ag<sup>+</sup> ions at Ag(2) and 0.6 at Ag(3) are associated with the oxygens of 2 different 8-rings.

Altogether approximately 7.4 Na<sup>+</sup> ions and 3.6 silver species are located per unit cell. The remaining 1.0 Ag<sup>+</sup> ion per unit cell has been reduced and has migrated out of the zeolite framework to form small silver crystallites on the surface of the zeolite single crystal, accounting for its charcoal black color.

**Acknowledgement.** This work was supported by National Science Foundation (NSF-INT83-16234) and also by the Korean Science and Engineering Foundation.

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## Kinetics of the Photochemically Generated *t*-Butoxy Radical Reactions with Phosphine(PH<sub>3</sub>)\*

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The gas phase reactions of the photochemically generated *t*-butoxy radicals with phosphine (PH<sub>3</sub>) were studied in the temperature range of 35–80°C. We found the significant differences between high temperature thermal reactions and low temperature photo reactions. In comparison with the reactions of *t*-butoxy radicals with other hydrogen donors, some possible mechanistic suggestions were made for the explanation of the results.

### Introduction

In the last two decades our knowledge of phosphorus compounds has expanded so rapidly that it now constitutes a major branch of chemistry.<sup>1</sup>

In many ways phosphorus rivals carbon in its structural versatility, the general variety of its compounds, and its biochemical importance.

The presence of unoccupied low energy d-orbitals makes them participate in bonding and form hybridized orbitals which have special spatial orientations. The ready availability of d-orbitals in the phosphorus accounts for many of their differences in chemistry compared to nitrogen.

Phosphorus usually forms either three, four, or five covalent linkages to other atoms and a handful of one, two, and six-connected compounds are also known. In a few special cases, the phosphorus atom may form some kind of direct chemical linkage with as many as ten neighbors.<sup>1</sup>

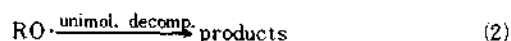
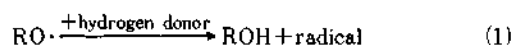
The intimate involvement of phosphorus compounds in living processes is now well recognized and modern biochemistry is dominated by phosphate esters such as ATP and DNA.

Phosphorus compounds have also been detected as minor constituents of the atmospheres of Jupiter and Saturn.<sup>2</sup> It has been proposed that the Great Red Spot on Jupiter may be due to red phosphorus formed as a final product of the photodissociation of phosphine by Prinn and Lewis.

Thus, to supply some informations for this interesting chemistry of phosphorus compounds, we have studied the reactions of phosphine with *t*-butoxy radicals in the gas phase.

Among alkoxy radicals, *t*-butoxy radical reactions have been the most extensively studied. Alkoxy radicals themselves are also known to be one of the most important intermediates in biological systems, atmospheric reactions, and etc.

Most of the alkoxy radical reactions have been studied by competition methods.<sup>3,14</sup> In the presence of hydrogen donors, alkoxy radicals may have two competitive pathways; the hydrogen abstraction reaction and self-decomposition.



Consequently, the distribution of final products are determined by the relative rate constants for two reaction routes.

In the liquid and gas phase, the relative rate constants for

\*This work has been supported by a Grant from Korea Science and Engineering Foundation (KSEF) (1984-1985).