

men as native donors and the energy for migration of electron trapped in an oxygen vacancy is very small ( $\sim 0.01$  eV), the activation energy in the extrinsic region may be less than that in the intrinsic region. When the formation of interstitial indiums is begun, the extrinsic region may disappear. Then the activation energy in the intrinsic region must have a larger value than that in the extrinsic region. Consequently, the electrical conduction in the intrinsic region contains the formation of new donor level ( $\text{In}_i^{\cdot}$ ) represented as Eq. (5). In the extrinsic region, it is believed from the viewpoint of the activation energy (0.24 eV) that electron carriers itinerate in the conduction band. Both  $\text{Zn}^{18}$  and  $\text{Sn}$ -doped  $\text{In}_2\text{O}_3$ <sup>15,19</sup> show increased conductivity as compared to undoped  $\text{In}_2\text{O}_3$ , but  $\text{Cd}$ -doped  $\text{In}_2\text{O}_3$  shows decreased conductivity compared to pure  $\text{In}_2\text{O}_3$  as shown in Figure 4. In other words, the  $\text{Cd}$ -dopant decreases the electrical conductivity. The increase in  $\text{CdO}$  mol % decreases the electrical conductivity. This result enables us to consider that the incorporated  $\text{Cd}$  inhibits the ionization of  $\text{In}_i^{\cdot}$  to  $\text{In}_i^+$ , and results in the decrease of the concentration of conduction electron and electrical conductivity with increasing  $\text{CdO}$  mol %.

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### References

1. L. C. Schmacher, S. Mamichi-Afara, and M. J. Dignam, *J. Electrochem. Soc.*, **133**, 716 (1986).
2. D. Laser, *J. Appl. Phys.*, **52**, 5179 (1981).
3. K. Otsuka, T. Yasui, and A. Morikawa, *Bull. Chem. Soc. Jpn.*, **55**(6), 1768 (1982).
4. S. H. Lee, G. Heo, K. H. Kim, and J. S. Choi, *Int. J. Chem. Kinetics*, **19**(1), 1 (1987).
5. Z. Ovadyahu, B. Ovrin, and H. W. Kraner, *J. Electrochem. Soc.*, **130**(4), 917 (1983).
6. J. H. W. de Wit, *J. Sol. Sta. Chem.*, **8**, 142 (1973).
7. J. H. W. de Wit, *ibid.*, **13**, 192 (1975).
8. Y. Kanai, *Jpn. J. Appl. Phys.*, **24**(5), L361 (1985).
9. W. R. Runyan, "Semiconductor Measurements and Instrumentation", McGraw-Hill Co., New York, p.65, 1975.
10. J. F. McCan and J. O. M. Bockris, *J. Electrochem. Soc.*, **128**, 1719 (1981).
11. R. L. Weiher and B. G. Dick, *J. Appl. Phys.*, **35**(12), 3511 (1964).
12. A. K. Vijh, *J. Phys. Chem. Solids*, **29**, 2233 (1969).
13. I. Hamberg and C. G. Granqvist, *J. Appl. Phys.*, **60**(11), R123 (1986).
14. J. H. W. de Wit, G. van Unen, and M. Lahey, *J. Phys. Chem. Solids*, **38**, 819 (1977).
15. J. L. Bates, C. W. Griffin, D. D. Marchant, and J. E. Granier, *Am. Ceram. Soc. Bull.*, **65**(4), 673 (1986).
16. A. Gupta, P. Gupta, and V. K. Srivastava, *Thin Solid Films*, **123**, 325 (1985).
17. C. A. Pan and T. P. Ma, *Appl. Phys. Lett.*, **37**(163), 714 (1980).
18. R. L. Weiher, *J. Appl. Phys.*, **33**(9), 2834 (1962).
19. Y. Kanai, *Jpn. J. Appl. Phys.*, **23**(1), L12 (1984).
20. C. A. Pan and T. P. Ma, *J. Electrochem. Soc.*, **128**(9), 1953 (1981).

## Reaction of Triethylsilyl Radical with Sulfides, a Laser Flash Photolysis Study

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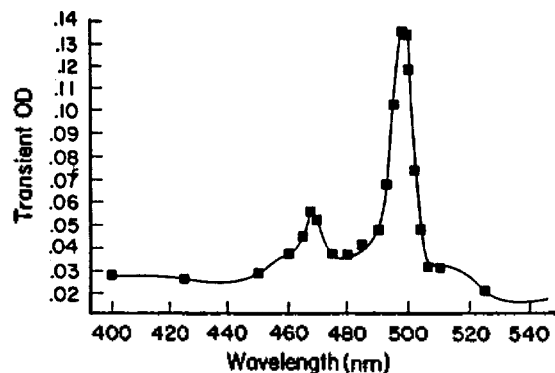
Triethylsilyl radical was generated by laser flash photolysis of a 1:1 (v/v) solution of triethylsilane and di-*tert*-butyl peroxide. The silicon centered radical was reacted with sulfides to give carbon centered radicals by displacement at sulfur. The carbon radicals were readily detected by their transient absorption spectra. The absolute rate of reaction of triethylsilyl radical with 9-fluorenylphenylsulfide, di-*n*-butylsulfide, di-*sec*-butyl sulfide, di-*tert*-butyl sulfide and di-*n*-butyl disulfide are  $2.40 \pm 0.12 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ ,  $11.21 \pm 0.89 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ ,  $8.79 \pm 0.73 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ ,  $3.29 \pm 0.18 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ , and  $3.41 \pm 0.09 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ , respectively.

### Introduction

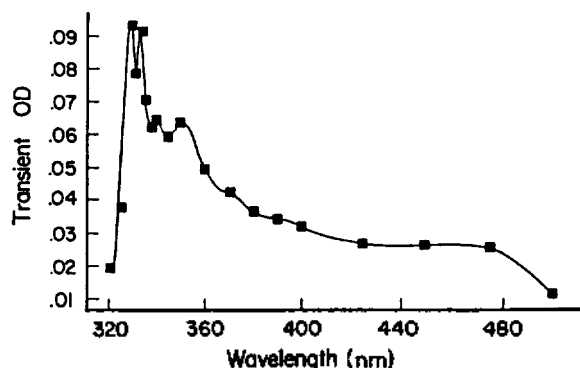
Silicon and tin centered radicals rapidly abstract halogen atoms from alkyl halides to generate carbon centered radicals.<sup>2</sup> This approach has been used numerous times to gene-

rate organic radicals for study by EPR or laser flash photolysis, or for use in organic synthesis. One of the more common approaches is to photolyze a solution of di-*tert*-butyl peroxide (DTBP) and triethylsilane containing a halogen atom donor RX. Under these conditions R· can be can be

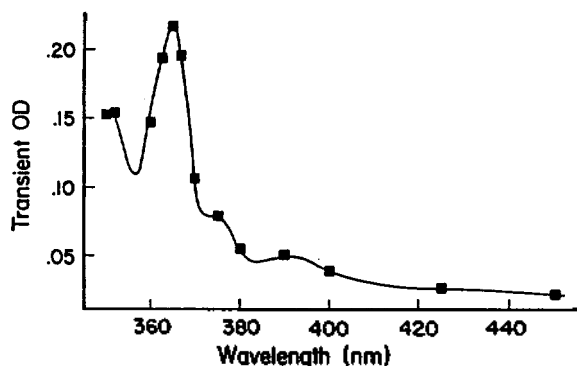




**Figure 1.** The transient absorption spectrum of 9-fluorenyl produced by laser flash photolysis of 1/1 triethylsilane/DTBP containing 9-fluorenylphenylsulfide.

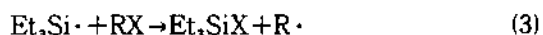
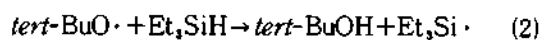
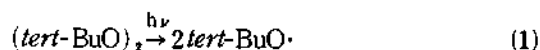


**Figure 2.** The transient absorption spectrum of benzhydryl produced by laser flash photolysis of 1/1 triethylsilane/DTBP containing 3.

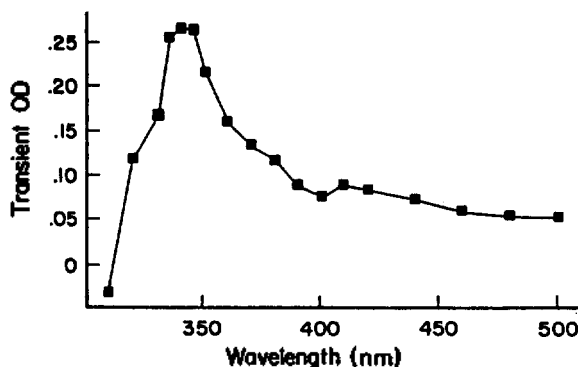


**Figure 3.** The transient absorption spectrum of 1-naphthylmethyl produced by laser flash photolysis of 1/1 triethylsilane/DTBP containing 4.

generated via reaction 1-3.



In certain cases, halides are inconvenient precursors to free radicals, particularly when  $RX$  is too labile to isolate or it reacts on mixing with triethylsilane. Hart has encountered this problem in his synthetic work on free radical cyclizations and found that aryl sulfides are convenient substitutes for

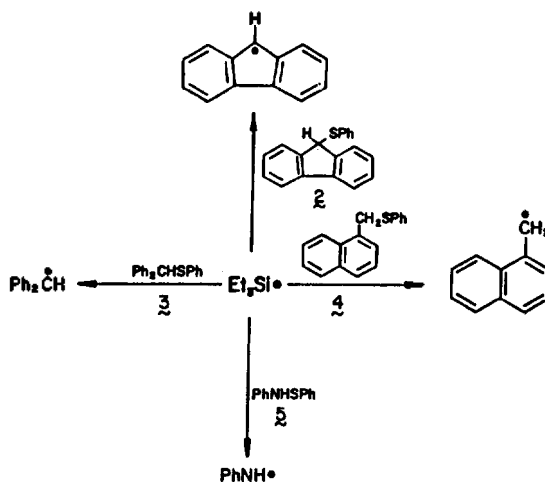


**Figure 4.** The transient absorption spectrum of anilino radical produced by laser flash photolysis of 1/1 triethylsilane/DTBP containing 5.

$RX$  that are easily prepared and handled.<sup>3</sup> Although there are several absolute rate constants reported for reaction of 1 with halogen donors<sup>4</sup> no such data have been reported for sulfides. This has prompted our study of the absolute reactivity of triethylsilyl with various sulfides. This will allow a comparison of the reactivity of triethyl silyl with sulfides and the more traditionally used halide substrates.

## Results and Discussion

Laser flash photolysis (337.1 nm) of a solution of 1/1 triethylsilane/DTBP (v/v) containing 9-fluorenylphenylsulfide 2 gives the transient absorption spectrum of Figure 1. This spectrum is identical to that of the 9-fluorenyl radical (FIH $\cdot$ ) reported elsewhere.<sup>5</sup> In a similar fashion, flash photolysis of 1/1 triethylsilane/DTBP containing 3, 4, and 5 gives the transient spectra (Figures 2-4) of the benzhydryl radical, 1-naphthylmethyl radical and anilino radical respectively. The spectra are in good agreement with those previously reported for these radicals.<sup>6-8</sup>



Control experiments with 2-5 in benzene demonstrated that direct laser excitation of these compounds does not produce detectable transient absorbance of the corresponding radicals. The quantum yield for process (4) must be low, but is not necessarily zero. Any radical formed in this reaction would appear "instantaneously" on these time scales and would not interfere with the kinetic analysis (vide infra).



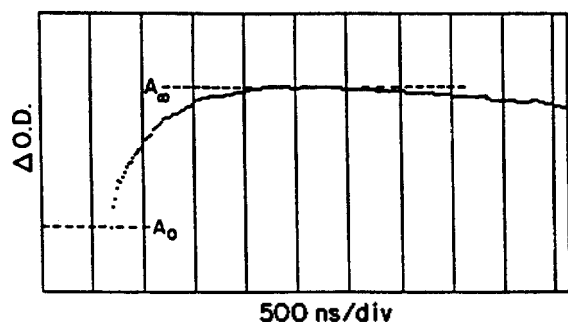


Figure 5. The formation of FIH· following laser flash photolysis of 1/1 triethylsilane/DTBP containing 2.

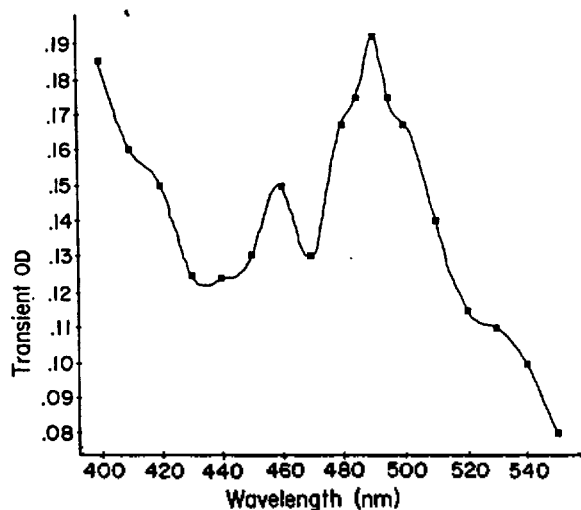
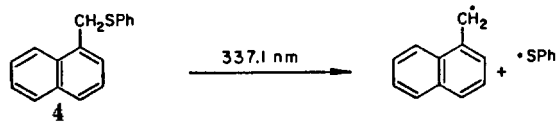


Figure 6. The transient absorption spectrum of 9-thiophenylfluorenyl radical, obtained by laser flash photolysis of DTBP containing 9-fluorenylphenylsulfide.



The formation of 9-fluorenyl radical is not instantaneous (Figure 5). The formation of FIH follows first order kinetics to give  $k_{obs}$  according to (5)

$$\ln \left( \frac{A_{\infty}}{A_{\infty} - A_t} \right) = k_{obs} t \quad (5)$$

where  $A_{\infty}$  is the maximum in the transient absorption of FIH following the laser pulse. The value of  $A_{\infty}$  is taken at the plateau region of Figure 5 prior to the start of FIH decay. Because the pseudo first order rate of formation of FIH is very much faster than its subsequent radical-radical decay, the two processes can be analyzed separately.<sup>4</sup>  $A_t$  is the absorption at time  $t$ .

There is no evidence for reaction of *tert*-butoxy radical with 2 as per equation (6) to give 6 under the conditions employed in this work.

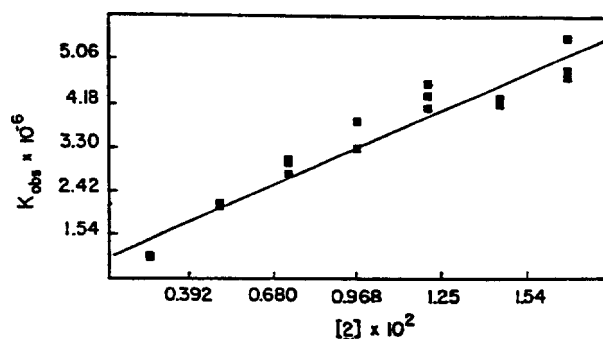
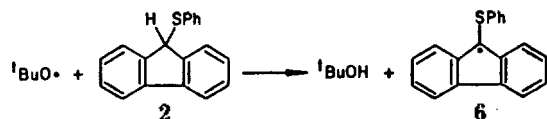


Figure 7. A plot of  $k_{obs}$  versus concentration of 9-fluorenylphenylsulfide obtained for its reaction with triethylsilyl (see text).

Table 1. The Absolute Rate Constants of Reaction of Triethylsilyl Radical with Various Quenchers

| Reagent                            | $k_q (M^{-1}s^{-1})$        | Ref. |
|------------------------------------|-----------------------------|------|
| 9-bromofluorene                    | $1.27 \pm .13 \times 10^9$  | a    |
| 9-fluorenylphenylsulfide           | $2.40 \pm .12 \times 10^8$  | a    |
| <i>n</i> -Bu-S- <i>n</i> Bu        | $11.21 \pm .89 \times 10^6$ | a    |
| <i>sec</i> -Bu-S- <i>sec</i> -Bu   | $8.79 \pm .73 \times 10^6$  | a    |
| <i>tert</i> -Bu-S- <i>tert</i> -Bu | $3.29 \pm .18 \times 10^6$  | a    |
| <i>n</i> -Bu-S-S- <i>n</i> Bu      | $3.41 \pm .09 \times 10^8$  | a    |
| <i>n</i> -Bu-Br                    | $5.4 \pm 0.1 \times 10^8$   | b    |
| <i>tert</i> -Bu-Br                 | $1.1 \pm 0.5 \times 10^9$   | b    |
| <i>n</i> -Bu-Cl                    | $3.1 \pm 1.4 \times 10^5$   | b    |
| <i>tert</i> -Bu-Cl                 | $2.5 \pm 0.2 \times 10^6$   | b    |

<sup>a</sup>This work, <sup>b</sup>Ref. 4

The spectra of radicals such as 6 are quite different from those of the corresponding hydrocarbon radicals and are quite easy to detect by flash photolysis.<sup>9a</sup> We have generated 6 by photolysing solutions of 2 in DTBP alone (Figure 6), and this radical shows a  $\lambda_{max}$  at 490 nm, which is well separated from the sharp 500 nm maximum found for FIH·, but similar to the 490 nm  $\lambda_{max}$  reported for 9-chlorofluorenyl radical.<sup>9b</sup> The complete absence of 6 under our conditions is not surprising. Scaiano has measured the absolute rate constant of reaction (2) to be  $5.7 \pm 0.6 \times 10^6 M^{-1}s^{-1}$  at 300K, thus the lifetime of *tert*-butoxy radical in the presence of 3.13 M triethylsilane (1:1  $Et_3SiH$ :DTBP) will be less than 56 ns.<sup>4</sup> Thus, even if the absolute rate constant of reaction (6) is as large as  $10^7 M^{-1}s^{-1}$ , then the pseudo first order rate constant for the formation of 6 in a solution containing as much as 0.1M 2 will be 18 times slower than the pseudo first order rate constant of formation of triethylsilyl radical.<sup>10</sup> The observed pseudo first order rate constant for the formation of FIH· is related to  $k_q$  the absolute rate of reaction (5) by equation (7),

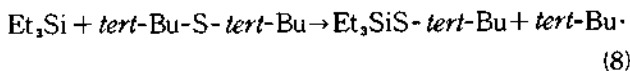
$$k_{obs} = k_o + k_q (9\text{-fluorenylphenylsulfide}) \quad (7)$$

where  $k_o$  represents all possible first order decay modes of triethylsilyl radical 1 in the absence of quencher. A plot of  $k_{obs}$  versus  $[2]$  from .005-.04M is linear. Two independent determinations of the quenching rate constant gave  $2.40 \pm 0.12 \times 10^8 M^{-1}s^{-1}$  (correlation coefficient = 0.943) and  $2.58 \pm 0.15 \times 10^8 M^{-1}s^{-1}$  (correlation coefficient 0.969) (Figure 7). This rate is about 5 times slower than the rate of reaction of 1 with 9-bromofluorene (Table 1) which we have measured in this work in a manner analogous to that used



with 2.

The reaction of **1** with dialkyl sulfides (reaction 8) gives alkyl radicals which lack a suitable chromophore to allow for their direct detection by laser flash photolysis.





- (1985).
7. L. M. Hadel, M. S. Platz, and J. C. Scaiano, *J. Am. Chem. Soc.*, **106**, 283 (1984).
  8. Porter, G. Land, *Trans. Far. Soc.* **59**, 2027 (1963).
  9. (a) Personal communication from D. Griller; (b) D. C. Wong, D. Griller, and J. C. Scaiano, *J. Am. Chem. Soc.* **103**, 5934 (1981).
  10. Typical rate constants for H atom abstraction reactions of *tert*-Butoxyl with ethers are  $10^6 \text{ M}^{-1} \text{ s}^{-1}$  (see V. Malatesta and J. C. Scaiano *J. Org. Chem.* **47**, 1455) (1982). The maximum concentration of 2 used in these experiments was 0.04M thus we feel that 18 represents a conservative lower limit.
  11. J. E. Huheey, *Inorganic Chemistry*, Harper and Row, New York, N.Y. p. 694-702 (1972).
  12. L. A. Paquette, W. D. Klobucar, and R. A. Snow, *Syn. Comm.* **6**, 575 (1976).
  13. G. Farnia, A. Ceccon, and P. Cesseli, *J. C. S. Perkin II* 1016 (1972).
  14. P. M. B. Bavin, *Can. J. Chem.* **38**, 917 (1960).
  15. H. Lecher, K. Koberle, W. Speer, and P. Stocklin, *Ber* **58**, 409 (1925).

## Iodine Sorption Complexes of Partially Cobalt(II) Exchanged Zeolite A. Two Crystal Structures of $\text{Co}_{3.5}\text{Na}_5\text{Si}_{12}\text{Al}_{12}\text{O}_{48} \cdot 2.5\text{I}_2$ and $\text{Co}_{3.5}\text{Na}_5\text{Si}_{12}\text{Al}_{12}\text{O}_{48} \cdot 5.0\text{I}_2$

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Two crystal structures of iodine sorption complexes of dehydrated partially Co(II)-exchanged zeolite A,  $\text{Co}_{3.5}\text{Na}_5\text{-A} \cdot x\text{I}_2$ ,  $x = 2.5$  and  $5.0$ , have been determined by single crystal X-ray diffraction techniques. Both structures were solved and refined in cubic space group,  $Pm\bar{3}m$  at  $21(1)^\circ\text{C}$ . The structures of  $\text{Co}_{3.5}\text{Na}_5\text{-A} \cdot 2.5\text{I}_2$  ( $a = 12.173(1) \text{ \AA}$ ) and  $\text{Co}_{3.5}\text{Na}_5\text{-A} \cdot 5.0\text{I}_2$  ( $a = 12.130(1) \text{ \AA}$ ) were refined to the final error indices,  $R_1 = 0.081$  and  $R_2 = 0.077$  with 261 reflections and  $R_1 = 0.103$  and  $R_2 = 0.112$  with 225 reflections, respectively, for which  $I > 3\sigma(I)$ . In both structures,  $3.5 \text{ Co}^{2+}$  ions and  $4.5 \text{ Na}^+$  ions per unit cell lie at two crystallographically different 6-ring positions.  $0.5 \text{ Na}^+$  ion lies in an 8-oxygen ring plane. Dehydrated  $\text{Co}_{3.5}\text{Na}_5\text{-A}$  sorbs 2.5 iodine molecules per unit cell at  $70^\circ\text{C}$  (vapor pressure of  $\text{I}_2$  is ca. 8.3 torr) within 30 minutes and 5 iodine molecules per unit cell at  $80^\circ\text{C}$  (vapor pressure of  $\text{I}_2$  is ca. 14.3 torr) within 24 hours. Each iodine molecule makes a close approach, along its axis to framework oxygen atom with  $\text{I-I-O} = 175^\circ$ .

### Introduction

The crystal structures of a bromine complex in synthetic zeolite  $4\text{A}^1$  and a similar iodine complex in zeolite  $5\text{A}^2$  have been reported. In each of these sorption complexes, it was found that approximately six dihalogen molecules were sorbed per unit cell; 6 bromine molecules in  $\text{Na}_{12}\text{-A}^1$  and 5.65 iodine molecules in  $\text{Ca}_4\text{Na}_4\text{-A}^2$ . The bromine molecules did not interact with the anionic framework or with the  $\text{Na}^+$  ions<sup>1</sup>.  $\text{I}_2$  molecules, however, were involved in charge-transfer complexes with the framework 8-ring oxygens<sup>2</sup>. No iodine- $\text{Ca}^{2+}$  or iodine- $\text{Na}^+$  interaction was observed<sup>1,2</sup>.

Several structures of  $\text{Cl}_2$  and  $\text{Br}_2$  sorption complexes of  $\text{Ag}^+$ ,  $\text{Eu(II)}$ , and  $\text{Co(II)}$ -exchanged zeolite A have been determined<sup>3-5</sup>. In the structure of a chlorine sorption complex of vacuum-dehydrated  $\text{Eu(II)}$ -exchanged zeolite A, chlorine gas is reported to have oxidized  $\text{Eu(II)}$  to  $\text{Eu(IV)}$ <sup>4</sup>. Chlorine gas has also oxidized hexasilver to  $\text{AgCl}$  as observed in the structure of a chlorine sorption complex of dehydrated, fully  $\text{Ag}^+$ -exchanged zeolite A<sup>3</sup>. Additional six molecules per unit

cell are sorbed, which form charge transfer complexes with framework oxygens ( $\text{O-Cl-Cl} = 166(2)^\circ$ ). 6 bromine molecules are sorbed in the dehydrated  $\text{Ag}_{12}\text{-A}$ ; 3.6  $\text{Br}_2$  molecules interact to draw with 3.6 of the 8.0 6-ring  $\text{Ag}^+$  ions into large cavity and 2.4  $\text{Br}_2$  molecules form charge transfer complexes with framework oxide ions ( $\text{O-Br-Br} = 174(4)^\circ$ ).<sup>6</sup> When  $\text{Cl}_2$  gas was sorbed onto a single-crystal of vacuum-dehydrated  $\text{Co}_4\text{Na}_4\text{-A}$ , the chlorine molecules were coordinated to the  $\text{Co(II)}$  ion in a bent manner. The chlorine molecule is equatorially basic with respect to the hard acid  $\text{Co(II)}$  and the dichlorine bond is lengthened by a large amount, approximately  $0.5 \text{ \AA}$ , upon complexation<sup>5</sup>.

This work was undertaken to further investigate the sorption properties of zeolite A and to determine the positions of the sorbed iodine molecules.

### Experimental Section

Single crystals of the synthetic molecular sieve sodium zeolite  $4\text{A}$ ,  $\text{Na}_{12}\text{Si}_{12}\text{Al}_{12}\text{O}_{48} \cdot 27\text{H}_2\text{O}$ , were prepared by a modi-