

men as native donors and the energy for migration of electron trapped in an oxygen vacancy is very small (~ 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 (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 Zn^{18} and Sn -doped In_2O_3 ^{15,19} show increased conductivity as compared to undoped In_2O_3 , but Cd -doped In_2O_3 shows decreased conductivity compared to pure In_2O_3 as shown in Figure 4. In other words, the Cd -dopant decreases the electrical conductivity. The increase in CdO mol % decreases the electrical conductivity. This result enables us to consider that the incorporated Cd inhibits the ionization of In_i^x to In_i^{\cdot} , and results in the decrease of the concentration of conduction electron and electrical conductivity with increasing 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. Ovrzyn, 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. Vijn, *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.² This approach has been used numerous times to gener-

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

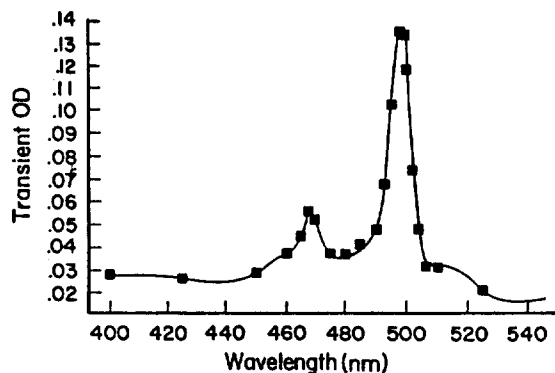


Figure 1. The transient absorption spectrum of 9-fluorenyl produced by laser flash photolysis of 1/1 triethylsilane/DTBP containing 9-fluorenylphenylsulfide.

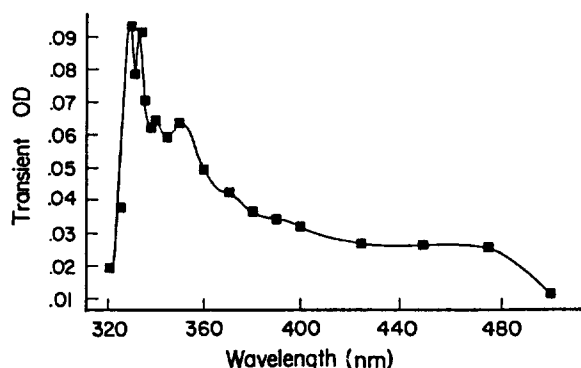


Figure 2. The transient absorption spectrum of benzhydryl produced by laser flash photolysis of 1/1 triethylsilane/DTBP containing 3.

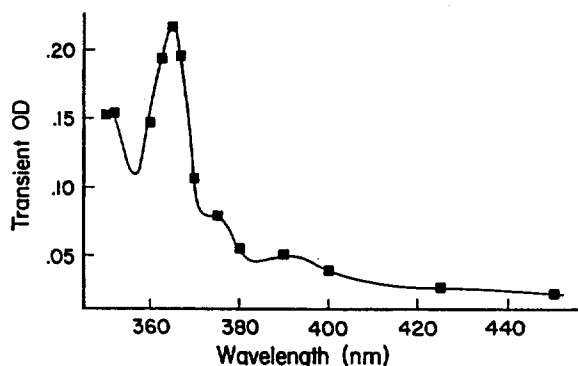
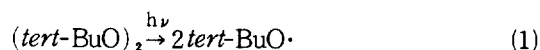


Figure 3. The transient absorption spectrum of 1-naphthylmethyl produced by laser flash photolysis of 1/1 triethylsilane/DTBP containing 4.

generated via reaction¹⁻³.



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

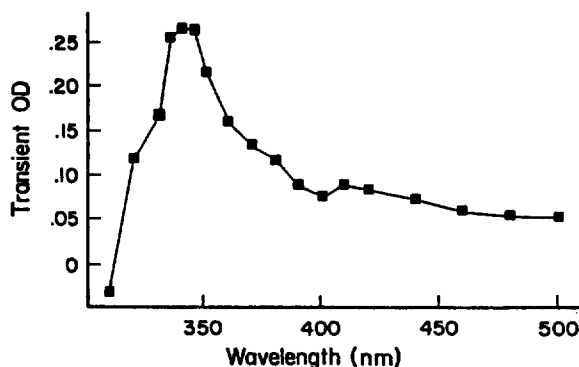
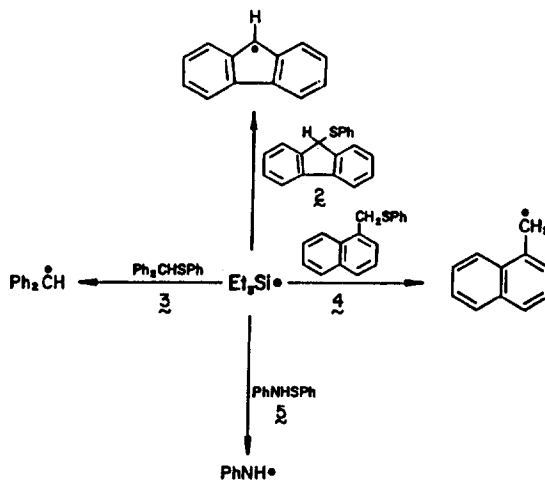


Figure 4. The transient absorption spectrum of anilino radical produced by laser flash photolysis of 1/1 triethylsilane/DTBP containing 5.

RX that are easily prepared and handled.³ Although there are several absolute rate constants reported for reaction of 1 with halogen donors⁴ 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·) reported elsewhere.⁵ 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.⁶⁻⁸



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).

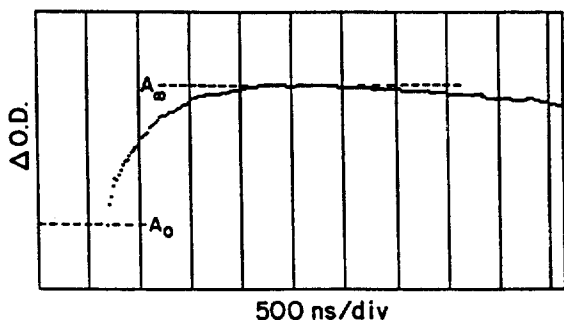


Figure 5. The formation of FIH· following laser flash photolysis of 1/1 triethylsilane/DTBP containing 2.

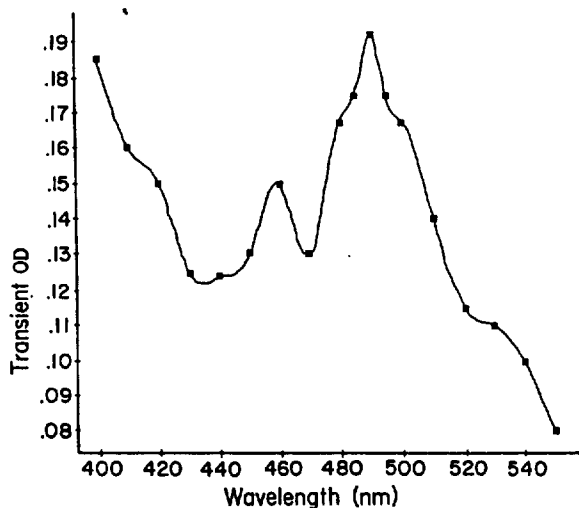
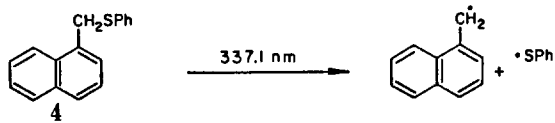


Figure 6. The transient absorption spectrum of 9-thiophenylfluorenyl radical, obtained by laser flash photolysis of DTBP containing 9-fluorenylphenylsulfide.



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_{∞} is the maximum in the transient absorption of FIH following the laser pulse. The value of A_{∞} 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.⁴ 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.

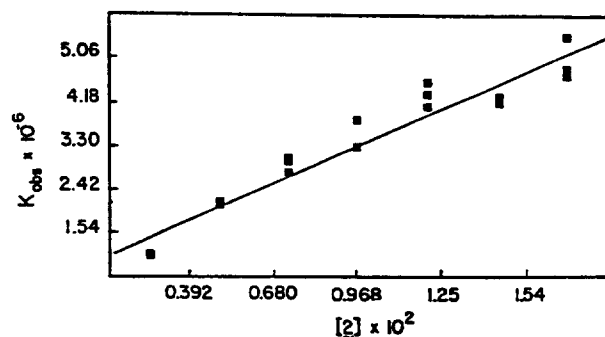
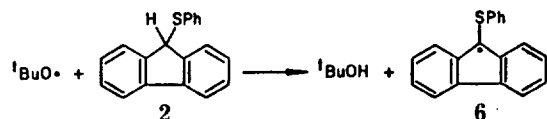


Figure 7. A plot of k_{obs} versus concentration of 9-fluorenylphenylsulfide obtained for its reaction with triethylsilyl (see text).

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
sec-Bu-S-sec-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

^aThis work, ^bRef. 4

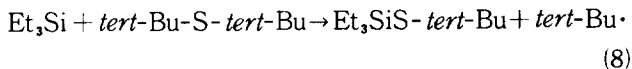
The spectra of radicals such as 6 are quite different from those of the corresponding hydrocarbon radicals and are quite easy to detect by flash photolysis.^{9a} We have generated 6 by photolysing solutions of 2 in DTBP alone (Figure 6), and this radical shows a λ_{max} at 490 nm, which is well separated from the sharp 500 nm maximum found for FIH·, but similar to the 490 nm λ_{max} reported for 9-chlorofluorenyl radical.^{9b} 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.⁴ 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.¹⁰ 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**.

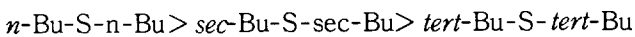
The reaction of **1** with dialkyl sulfides (reaction 8) gives alkyl radicals which lack a suitable chromophore to allow for their direct detection by laser flash photolysis.



The kinetics of this process were monitored via a Stern-Volmer approach using 9-fluorenylphenyl sulfide as a kinetic probe.⁴ In this experiment the yield of F1H· (formed by flash photolysis of Et₃SiH/DTBP) containing constant [**2**], was monitored as a function of added alkyl sulfide or disulfide. Under these conditions equation (9) will hold

$$\frac{\phi^0}{\phi} = 1 + k_q \tau [q] \quad (9)$$

where ϕ and ϕ^0 are the yields of F1H· in the presence and absence of alkyl sulfide respectively, k_q is the absolute rate constant of reaction (8), $[q]$ is the concentration of alkyl sulfide quencher, and τ is the lifetime of formation of triethylsilyl radical in the absence of sulfide quencher. The values of ϕ and ϕ^0 are given by $(A_\infty - A_0)$ (see Figure 5). Typical values of τ are in the range of 250–300 ns when [**2**] = 0.02 M. A typical plot of ϕ^0/ϕ versus di-*n*-butyldisulfide is given in Figure 8, and values of k_q are listed in Table 1. The reactivity trend for triethylsilyl radical is



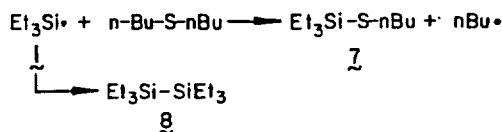
This trend is opposite to that of organic radical stability (primary < secondary < tertiary). Obviously there is a small steric effect to reaction (8) which offsets the effect of radical stability. The data suggest that the transition structure for reaction (8) is very early, with very little radical development on carbon, hence the small spread (on a factor of 3.4) in the observed rate constants. The absolute reactivity of triethylsilyl radicals with alkylsulfides is comparable to the rate of reaction of **1** with chlorides and much slower than the reaction of **1** with bromides or iodides.

Di-*n*-butyl disulfide reacts nearly 30 times more rapidly with **1** than do the dialkyl sulfides.



This is not a consequence of the relative bond strengths of C–S and S–S which are nearly identical (65 *versus* 64 Kcal/mol)¹¹. The longer bond length of S–S relative to C–S (2.05 *versus* 1.82 Å)¹¹ may lead to increased steric accessibility of the disulfide sulfur, which will accelerate the rate of homolytic displacement.

Chemical analysis of the DTBP, triethylsilane, di-*n*-butylsulfide system is in agreement with the proposed mechanism. Photolysis of 0.1M dibutylsulfide and 0.1M DTBP in triethylsilane gives a high yield (79%) of silyl sulfide **7** as required by the proposed mechanism. A small quantity of hexaethyldisilane **8** was also formed in the reaction. It was not possible to perform product studies of this type using benzylic sulfides due to the light sensitivity of both the reactants and the expected reaction products.



Conclusions

The absolute kinetics of reaction of triethylsilyl radical with various sulfides can be readily monitored by laser flash photolysis. The absolute rate constants for reaction are comparable to the corresponding alkyl chlorides and much slower than the corresponding bromides. This implies that sulfides can be used as convenient precursors for radical generation when the halide is intractable. The kinetics of the reaction are more sensitive to steric effects than to the stability of the radical reaction product which implies a transition state with more sulfur-silicon bond making than carbon-sulfur bond breaking.

Experimental

Triethyl silane (Aldrich) and DTBP (Mallinkrodt) were used as received. Solutions were placed in 1 cm² cylindrical suprasil quartz cells and deoxygenated by bubbling with high purity nitrogen. The samples were irradiated with the pulses of a Molecron UV-22 Nitrogen laser (337.1 nm, 6 mj, 10 ns) which were passed through a beam splitting prism to be coincident with a 1000 Watt xenon arc lamp monitoring beam. In some cases a Lumonics TE-861-4 Excimer laser using a Xe, F₂, He gas mix (350 nm, -80 mj, 10 ns) was used as the excitation source. Suitable Ealing glass filters were placed between the sample and monochromator photomultiplier tube assembly to prevent laser radiation from impinging on the detector. The monitoring beam was focused on the slit of an Oriel Monochromator with approximately 1 mm front and rear slits. Signals were obtained with an IP 28 photomultiplier tube detector and were digitized by a Tektronix 7912 A/D converter. The experiment was controlled by an Apple IIe microcomputer which was also used for storage, processing, and hard copies of the data. Absorption spectra were obtained from flowed solutions. Kinetic studies were performed using static samples.

9-Fluorenylphenylsulfide (**2**), diphenylmethylphenylsulfide (**3**), 1-naphthyl methylphenylsulfide (**4**) and *N*-phenylbenzene-sulfenamide used in this study were prepared and purified by procedures described in the literature.¹²⁻¹⁵

Product analyses were performed by photolyzing degassed solutions sealed in pyrex tubes with a Rayonet Reactor using RPR-350 light sources. The products were analyzed on a Hewlett Packard 5830A G. C. using a 6 ft by 1/8" SE-30 column.

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References

1. Camille and Henry Dreyfus Teacher Scholar
2. H. Sakura, *Free Radicals Vol. II*, J. R. Kochi, ed., Wiley Interscience, New York, NY p. 741 (1973).
3. D. J. Hart and Y.-M. Tsai, *J. Am. Chem. Soc.*, **106**, 8209 (1984).
4. C. Chatgililoglu, K. U. Ingold, J. C. Scaiano, *J. Am. Chem. Soc.*, **104**, 5123 (1982).
5. D. Griller, L. Hadel, A. S. Nazran, M. S. Platz, D. C. Wong, T. G. Savino, and J. C. Scaiano, *J. Am. Chem. Soc.*, **106**, 2227 (1984).
6. A. Porter and E. Strachen, *Trans. Far. Soc.*, **54**, 1595

- (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 Co^{2+} ions and 4.5 Na^+ ions per unit cell lie at two crystallographically different 6-ring positions. 0.5 Na^+ ion lines 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°C (vapor pressure of I_2 is *ca.* 8.3 torr) within 30 minutes and 5 iodine molecules per unit cell at 80°C (vapor pressure of 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 4A^1 and a similar iodine complex in zeolite 5A^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 Na^+ ions¹. I_2 molecules, however, were involved in charge-transfer complexes with the framework 8-ring oxygens². No iodine- Ca^{2+} or iodine- Na^+ interaction was observed^{1,2}.

Several structures of Cl_2 and Br_2 sorption complexes of Ag^+ , Eu(II) , and Co(II) -exchanged zeolite A have been determined³⁻⁵. In the structure of a chlorine sorption complex of vacuum-dehydrated Eu(II) -exchanged zeolite A, chlorine gas is reported to have oxidized Eu(II) to Eu(IV)^4 . Chlorine gas has also oxidized hexasilver to AgCl as observed in the structure of a chlorine sorption complex of dehydrated, fully Ag^+ -exchanged zeolite A^3 . 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 Br_2 molecules interact to draw with 3.6 of the 8.0 6-ring Ag^+ ions into large cavity and 2.4 Br_2 molecules form charge transfer complexes with framework oxide ions ($\text{O-Br-Br} = 174(4)^\circ$).⁶ When 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 Co(II) ion in a bent manner. The chlorine molecule is equatorially basic with respect to the hard acid Co(II) and the dichlorine bond is lengthened by a large amount, approximately 0.5 \AA , upon complexation⁵.

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 4A , $\text{Na}_{12}\text{Si}_{12}\text{Al}_{12}\text{O}_{48} \cdot 27\text{H}_2\text{O}$, were prepared by a modi-