The Journal of Adhesion

Role of Amines in Adhesion of Polybutadiene to Glass Substrates. II. Reactions of Amines with Trimethoxysilanol and/or Fumed Silica

Y. Eckstein[ab]; P. Dreyfuss[a]

[a] Institute of Polymer Science, The University of Akron, Akron, Ohio, U.S.A. [b] Owens/Corning Fiberglas, Technical Center, Granville, OH, U.S.A.

PLEASE SCROLL DOWN FOR ARTICLE

Role of Amines in Adhesion of Polybutadiene to Glass Substrates. II. Reactions of Amines with Trimethoxysilanol and/or Fumed Silica

Y. ECKSTEIN† and P. DREYFUSS

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325, U.S.A.

This paper is part of a larger investigation of the role of amines in the adhesion of polybutadiene to glass substrates. It describes near infrared, infrared and nuclear magnetic resonance spectroscopy studies of the interaction of amines with silanol groups usually under ambient conditions but sometimes when heated in air. Additional supporting evidence was obtained from gas liquid chromatography, mass spectrometry and elemental analyses. In order to assure a sufficiently high concentration of silanol groups, triethylsilanol and fused silica were used as models for the glass surface. The mechanism of interaction of aliphatic amines and of the aminosilane was different from that of aromatic amines. Most notably, reaction of aliphatic amines with carbon dioxide in the air and/or dissolved/adsorbed in/on the silanol occurred almost instantaneously, whereas the corresponding reaction of the aromatic amines with carbon dioxide was not observed under the experimental conditions used. The carbamates formed underwent further reactions much more rapidly than either the simple aromatic amines or the unmodified aliphatic amines.

INTRODUCTION

The goal of this study is to define the role of amines in general, and of 3-aminopropyltriethoxysilane in particular, in the mechanism of adhesion of elastomers to inorganic substrates. The first paper in the series described reactions of amines during peroxide curing of polybutadiene and the effect of

---

† Present address: Owens/Corning Fiberglas, Technical Center Granville, OH 43023, U.S.A.

low concentrations of amines (comparable to the peroxide concentration) on mechanical properties of the elastomer.[1] When aromatic amines or piperazine were added to the elastomer, maximum stress at break and minimum swelling ratios were observed when the number of alkoxide radicals generated was equal to the number of hydrogen atoms on the nitrogen of the amines. The greatest effect of aliphatic amines also occurred when the concentration of primary amino groups was equal to the concentration of peroxide; but the behavior was more complex than that of the aromatic amines and piperazine. These effects were attributed to the formation of chemical bonds between the amines and the polybutadiene. This paper examines model reactions aimed at better defining reactions that occur between amines or aminosilanes and a glass surface.

It is generally agreed that chemical bonds, in the form of a polysiloxane coating, form when silanol groups in a glass surface react with a triethoxy-silane under appropriate conditions. However, reactions between amines and the inorganic substrate are also possible. A 1971 infrared study by Kaas and Kardos[2] indicated not only that on treatment with 3-aminopropyltrimethoxy-silane the silanol groups on fused silica undergo condensation as expected but also that hydrogen bonds are formed between the amino groups of the silane compound and the surface hydroxyls. Protonated amine groups were also suggested in a more recent study of the structure of films formed when 3-aminopropyltrimethoxysilane is absorbed into alumina[3] or on the surface of sapphire crystals.[4] Hence a study of reactions of amines with triethylsilanol and/or fused silica was included in this project. The present study supports the earlier conclusions that reactions do occur and shows that the mechanism of interaction between amines and silanol groups is strongly influenced by the structure of the amine; in particular, aliphatic amines behave quite differently from aromatic amines. Absorption of carbon dioxide by aliphatic amines appears to be catalyzed by silanols and the adducts formed are more reactive than the uncomplexed amines.

EXPERIMENTAL

Materials

Many of the materials used were described in Part I of this series.[1] Cab-O-Sil,® Grade M5 Fumed Silica from Cabot Corporation, was used as received. Triethylsilanol and the Cab-O-Sil were used as model compounds of a glass surface. Additional silanes included 3-aminopropyldiethyethoxy-silane, $NH_2(CH_2)_3Si(OEt)Me_2$, and 3-aminopropyldiethylmethylsilane, $NH_2(CH_2)_3SiMeEt_2$, from Petrarch Systems, Inc. These silanes were selected for study because they are not capable of undergoing the polysiloxane forming

condensation reaction that occurs readily with 3-aminopropyltriethoxysilane, $NH_2(CH_2)_3Si(OEt)_3$. n-Propylamine from Eastman was distilled before use. 1,12-Dodecane-diamine, 97%, (M.P. 62–65°C) and pyrrolidine, 99% (b.p. 87–88°C), both from Aldrich Chemical Co. were used as received. Carbon tetrachloride, Spectroanalyzed grade, and picric acid, Reagent ACS grade, from Fisher Scientific Co. were used as received. CO_2 was used as powdered dry ice. Deuterium oxide, 99.7% minimum isotopic purity, was obtained from Merck-Sharp and Dohme of Canada Limited.

Preparation of aliphatic amine precipitates

These salts were prepared by mixing equal volumes of the amine and silanol (S) and heating gently at 50°C. After an hour or so a white precipitate formed. The solid was filtered off, washed with acetone to remove any remaining amine or silanol, and dried. Alternatively, the precipitates were prepared by mixing the amine with Cab-O-Sil and heating in an open vessel covered with a Teflon sheet. Usually within 18–48 hr significant quantities of the amine salt collected on the sheet and solidified on cooling. It was collected, washed and dried.

Preparation of adducts of amines and carbon dioxide

Powdered excess dry ice was added to neat liquid amine in a test tube and stirred with a spatula to achieve a uniform mixture. Heat was evolved and a white cloud formed above the amine. The liquid quickly became a uniform white powder. The powder was dried on a filter paper, usually in air but sometimes in a vacuum oven. The method of drying did not seem to affect the properties of the product.

Preparation of picrates

Picrates were formed from the various compounds following the procedure given in Shriner and Fuson.[5]

Near-infrared studies

Near-infrared spectra of neat compounds, of compounds diluted with CCl_4 or of reaction products in CCl_4 were recorded using a Cary 17 Spectrophotometer. Reaction mixtures were prepared at room temperature by adding the required amount of amine or amine containing silane and silanol to CCl_4 in a volumetric flask. Usually equimolar quantities of each reagent at a concentration of $\sim 10^{-3}$ mol per 10 ml CCl_4 (0.1 M) were used and the spectra were recorded within 2–6 hr of mixing the reagents. On standing the amines react with CCl_4 and dark brown solutions are formed.[6,7]

Y. ECKSTEIN AND P. DREYFUSS

Infrared studies

Infrared spectra were recorded on a Perkin Elmer 521 Grating Infrared Spectrophotometer or on a Perkin Elmer 337 Grating Infrared Spectrometer. The state of the material being examined determined whether a silver chloride cell, a gas cell with 10 cm path length and sodium chloride windows, a KBr pellet, or a cell consisting of sodium chloride windows alone was selected as sample holder.

NMR studies

^{1}H NMR spectra of neat compounds or of reaction products in CCl_4 or D_2O were obtained with the aid of a Varian T-60 NMR Spectrometer. ^{13}C NMR spectra were recorded on a Varian Associates CFT-20. The instrumental conditions were PW = 19 μsec, SW = 4000 Hz, PD = 1.0 sec, AT = 0.5 sec, T = $+27°$C.

Other studies

Gas liquid chromatograms were obtained using a Hewlett Packard 5150 Chromatograph fitted with an SE 30 column, a flame ionization detector and a Perkin-Elmer Model 149B printing integrator. The injection port temperature was 220°C. The program used for separating components consisted of 4 min at 60°C followed by heating at 60°C/min to 100°C and then 8 min at 160°C. The mass spectrum of the solid formed by reacting triethylsilanol and 1,4-diaminobutane was recorded on a Finnegan Mass Spectrometer Model 1015S-L. Melting points were taken in capillary tubes in a MEL-TEMP Laboratory Device. Analyses were performed by Galbraith Laboratories, Inc.

RESULTS

Aromatic amines

Phenylenediamine (PDA) was reacted with triethylsilanol (S) in CCl_4 and the reaction products were examined by near-infrared spectroscopy. PDA is solid at room temperature and is only slightly soluble in CCl_4. However, upon addition of the silanol, the amine dissolved and a small amount of water soluble white precipitate formed. Near-infrared spectra of the amine and of the silanol alone and of the mixture of PDA and S are presented in Figure 1. After addition of the S, all the spectral bands showed broadening; the —NH$_2$ band at about 1.48 μm was shifted to longer wavelength; and large quantities of water (broad band at about 1.87 μm) formed. Broadening of spectral bands
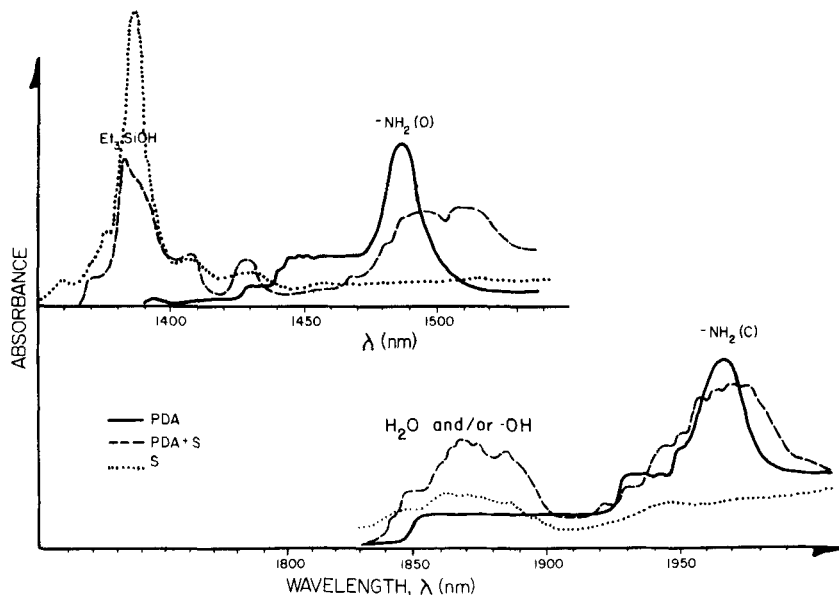
FIGURE 1   Near infrared spectra of m-phenylenediame (PDA) alone, of triethylsilanol (S) and of a mixture of PDA and S. All compounds were dissolved in CCl_4.

suggests the presence of hydrogen bonds, while the shift of the $-NH_2$ band to lower energies (longer wavelength) is characteristic of an NH_3R^+ type species.

Aliphatic amines and silanes containing n-propylamino groups

Triethylsilanol (S) was reacted with n-propylamine (PA), 1,4-diaminobutane (AB), 3-aminopropyltriethoxysilane (AS), 3-aminopropyldiethylethoxysilane (AMEOS) and 3-aminopropyldiethylmethylsilane (AEMS). Additional experiments were carried out with Cab-O-Sil and some of the same aliphatic amine containing compounds.

Upon addition of S to PA, AB, AS, AMEOS or AEMS a white cloud appeared above the solution. The cloud gave a basic reaction with wet litmus paper and was similar in appearance to the cloud that forms from ammonia and hydrochloric acid. Heat was evolved in all cases and the reaction was more vigorous with the aliphatic amines than with the silanes. Attempts were made to isolate any gaseous products and the products isolated were studied by infrared, nuclear magnetic resonance and mass spectroscopy and by gas liquid chromatography. Indications from the various methods for the presence of materials other than starting materials were contradictory and inconclusive. At present, we believe that the cloud contains a mixture of products possibly

including ammonia, cyclic compounds, amine and ethanol and certainly
including carbon dioxide and an amine derivative. The exact composition of
the cloud varies with the starting reagents. For example, Young *et al.* have
shown that polymerized AS, and presumably by analogy the monomer since
the monomer almost always contains some oligomers, is not completely stable
and releases ammonia at both room and elevated temperature;[8] also we have
found ethanol in the vapors above a mixture of AS and S.

    The solution   Figure 2 shows the near infrared spectra of neat AS and of
solutions of AS + S and of AS + S in CCl_4. The general features of the spectra
are common to all the aliphatic amines and aminosilanes studied. As seen in
the spectra, addition of the silanol resulted in broadening of all spectral bands
and a slight shift to longer wavelengths of the NH_2-group peak at about
1.525 μm (1525 nm). The doublet at about 2.0 μm (2000 nm) is also
characteristic of the NH_2-group, and its spectral distribution varies with the
relative concentrations of AS and S in the reaction mixture. Dependence of the
spectral bands on concentration and broadening of the spectral bands is
characteristic of the presence of hydrogen bonds.[9] The shift of the 1.525 μm
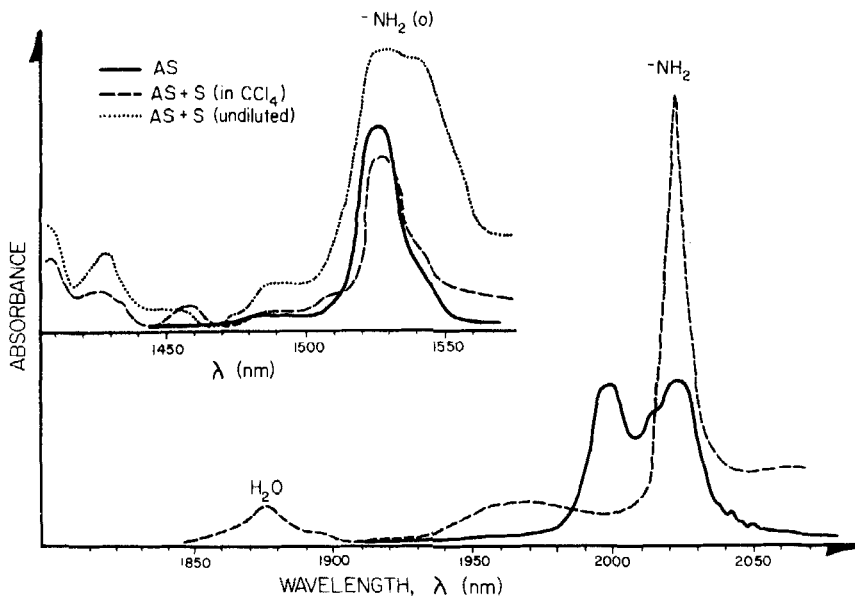band to lower energies indicates the presence of protonated amine.

FIGURE 2   Near infrared spectra of neat 3-aminopropyltriethoxysilane (AS) and of mixtures of
AS and triethoxysilanol (S) both neat and diluted with CCl_4. The spectrum of AS + S undiluted is
not shown in the 1900 to 2050 nm region because it absorbs very strongly in this region.

The intensities of peaks for the initial compounds and for the reaction products are summarized in Table I. The intensity, I, was calculated from the relationship $I = A/C$, where A denotes the absorbance and C the molar concentration of the compounds responsible for the specific band. Upon addition of the silanol to any of the aminosilanes or amines a small decrease in intensity of the NH— peak at about 1.525 μm and a larger decrease in the intensity of the —OH peak of the silanol at 1.383 μm were observed. If the aminosilane contained ethoxy groups, ethanol, with a peak maximum at 1.408 μm, was among the reaction products. The magnitude of the decrease of the intensities of the 1.525 μm and 1.383 μm peaks seems to be dependent on the initial concentration of the silanol. Usually, small amounts of H_2O are also found among the reaction products.

Heating the reaction mixture of AS and S to 55°C and 95°C caused a continuous increase with temperature in the height of the ethanol peak at 1.408 μm and a continuous decrease with temperature in the height of the silanol peak at 1.383 μm. The NH_2-peak at 1.525 μm decreased only slightly. (See Figure 3.) These results suggest that heat is driving the following reaction

TABLE I

Near-infrared spectra of amines alone and of amines plus silanol mixtures

Reaction mixture[a]	Intensities			
	NH_2 $\sim$1.5 μm	$\equiv$SiOH 1.383 μm	EtOH[b] 1.408 μm	H_2O 1.87 μm
S	—	0.97	—	—
PA	0.47	—	—	—
AB	1.06	—	—	—
AS	0.80	—	—	—
AMEOS	0.68	—	0.27	—
AEMS	0.44	—	—	—
PA + S	0.43	0.44	—	traces
AB + S	0.95	0.3	—	—
AS + S	0.69	0.62	0.21	traces
AMEOS + S	0.54	0.73	0.41	traces
AMEOS + 2S	0.49	0.575	0.15	0.06
AMEOS + 3S	0.41	0.53	0.1	0.03
AEMS + S	0.41	0.72	—	0.04

[a] S = Et_3SiOH, PA = $CH_3CH_2CH_2NH_2$, AB = $NH_2(CH_2)_4NH_2$, AS = $NH_2(CH_2)_3Si(OEt)_3$, AMEOS = $NH_2(CH_2)_3Si(OEt)Me_2$, AEMS = $NH_2(CH_2)_3SiMeEt_2$. The reaction mixture was prepared in CCl_4 from equimolar concentrations of the amine and of the silanol. 2S or 3S indicate that the concentration of S was twice or three times that of AS.
[b] The intensities were calculated relative to the concentration of silanol.
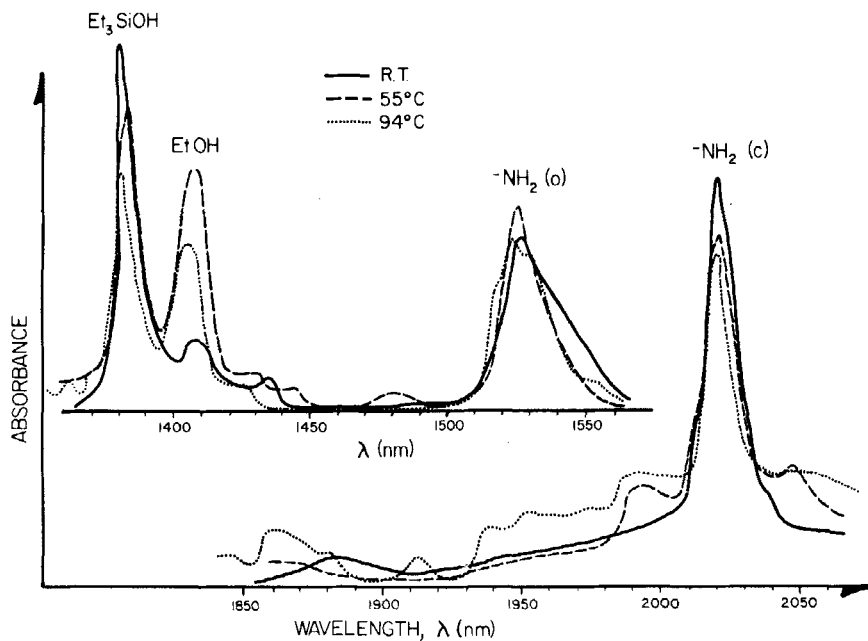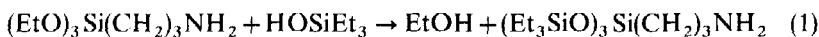
FIGURE 3   Effect of heating on near infrared spectra of reaction mixtures of 3-aminopropyl-triethoxysilane (AS) and triethoxysilanol (S).

between AS and S to the right:

$$(EtO)_3 Si(CH_2)_3 NH_2 + HOSiEt_3 \rightarrow EtOH + (Et_3SiO)_3 Si(CH_2)_3 NH_2 \quad (1)$$

Alternatively, a mixture of symmetrical and unsymmetrical siloxanes and polysiloxanes may form. Gas liquid chromatography of the reaction mixture of AS and S, measured 24 hr after mixing, showed the disappearance of a peak at a retention time of 10.2 min, characteristic of AS. A large peak at long retention time, ~ 24 min, appeared. This is consistent with formation of the condensation product indicated in Eq. (1).

Precipitates   Addition of S to AB resulted also in the formation of a white precipitate, which had the characteristics of a salt; namely, the precipitate dissolved in water and did not dissolve in most organic liquids. Further investigation showed that a similar precipitate could be obtained on gently heating a mixture of AB and Cab-O-Sil. Liquid droplets collected on the Teflon sheet covering the vessel containing the mixture and solidified on cooling. The evidence to be presented below indicates that the two solids were identical. Similar solids were collected above mixtures of Cab-O-Sil with 1,12-

diaminododecane or with AS (a liquid). Unlike the AB salt, the products from 1,12-diaminododecane and AS did not dissolve in water. Therefore, further efforts to characterize the salts formed when amines interacted with —SiOH groups were concentrated on the products from AB.

The near infrared and ^{1}H NMR spectra of the precipitate from S and AB indicated that the compound did not contain any groups derived from the S. Other properties are compared in Table II with those of the starting material and some plausible products.[10–14] The carbon dioxide adduct was selected for comparison because AB is known to absorb CO_2,[10,12,14] although properties of the adduct are not reported. Pyrrolidine, $\overline{CH_2CH_2CH_2CH_2NH}$, and its derivatives were selected for comparison because it has been reported that heating the dihydrochloride of AB below 150°C gives pyrrolidine.[10,12] Since —SiOH groups are known to be acidic and the near infrared studies indicate that an ammonium type salt is formed when AB and S are mixed, a similar reaction could be possible. Moreover, pyrrolidine is formed during some methods of synthesis of AB.[12]

The infrared spectra of the salts obtained from AB in the presence of S or Cab-O-Sil were different from that of AB but closely resembled that of the carbon dioxide adduct of AB. (Compare Figures 4 and 5.) The salient features of the IR spectra of the salts consist of a singlet at 3325 cm^{-1} instead of the doublet in the free amine, a broad strong "ammonium band"[15] in the range 3200 to 1800 cm$^-$, and a weak amide-like shoulder at 1620 cm^{-1}. (See Figure 4.)

TABLE II

Comparison of properties of salt of AB with properties of known materials

Property	Material				
	Salt	AB	AB·CO_2	Pyrrolidine	Pyrrolidine·CO_2
M.P., °C	sublimes 167	27	sublimes 167	a	67–75
Picrate	y, d257	y, d265^b	y, 256	y, 112^b	y, 112^b
		y, d263^c		y, 112^d	
		y, 250–55^d			
Elemental analysis					
%C	45.84^b	54.50^e	45.44^e	67.55^e	52.16^e
%H	9.61^b	13.72^e	9.15^e	12.75^e	7.88^e
%N	21.40^b	31.78^e	21.20^e	19.69^e	12.17^e
%O	23.01^b	—	24.21^e	—	27.79^e
%Si	0.38^b	—	—	—	—

^{a} A liquid with B.P. = 87–88°C.
^{b} Observed.
^{c} Ref. 7.
^{d} Ref. 11.
^{e} Calculated for AB, AB·CO_2, Pyrrolidine, and Pyrrolidine·CO using the formulas $C_4H_{12}N_2$, $C_5H_{12}N_2O_2$, C_4H_9N and $C_5H_9NO_2$, respectively.
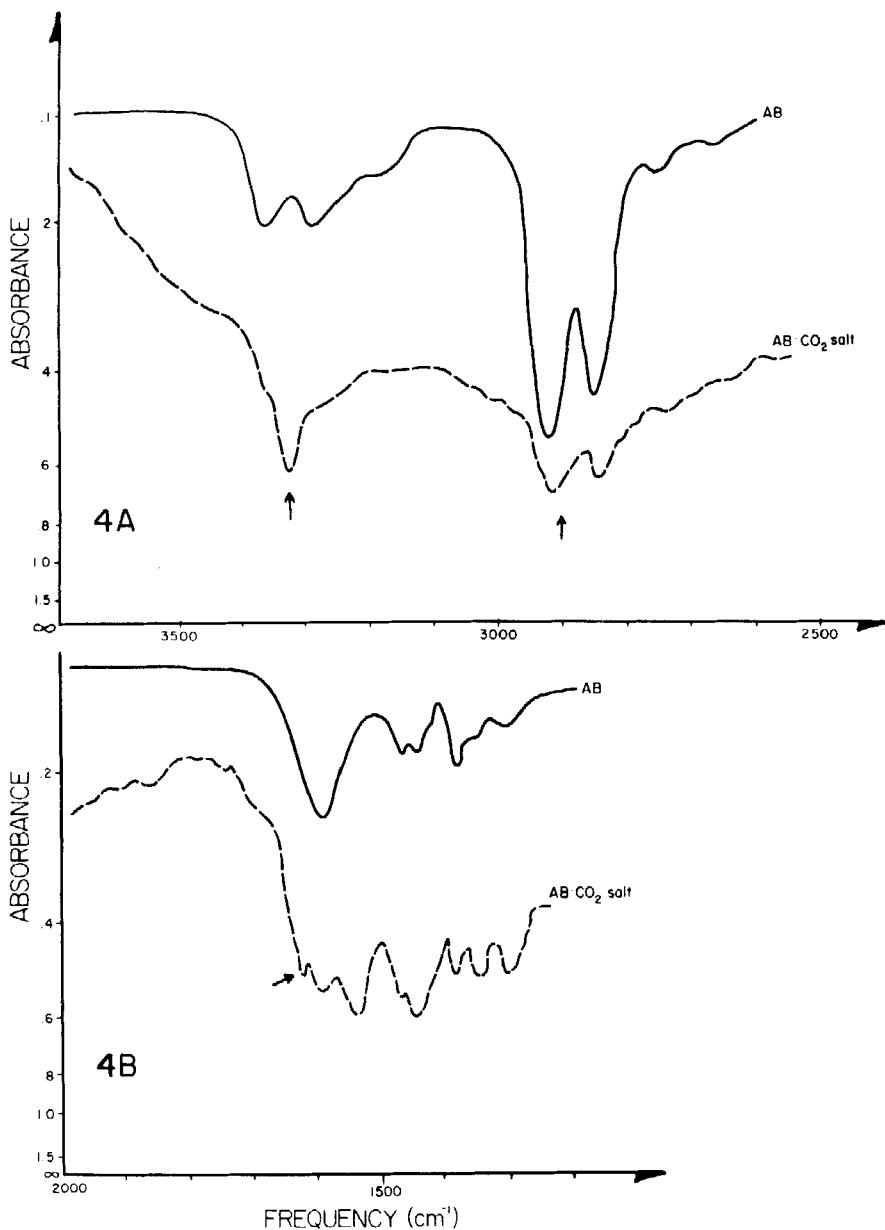
FIGURE 4 Two regions of the infrared spectra of 1,4-diaminobutane (AB) and of its adduct with carbon dioxide (AB · CO_2) taken neat between windows on the Perkin Elmer 521 Grating Infrared Spectrophotometer. Figure 4A shows the change from the doublet to the singlet on formation of the adduct as well as the broad "ammonium band". Figure 4B shows the carbonyl peak. The regions in question are marked with arrows.
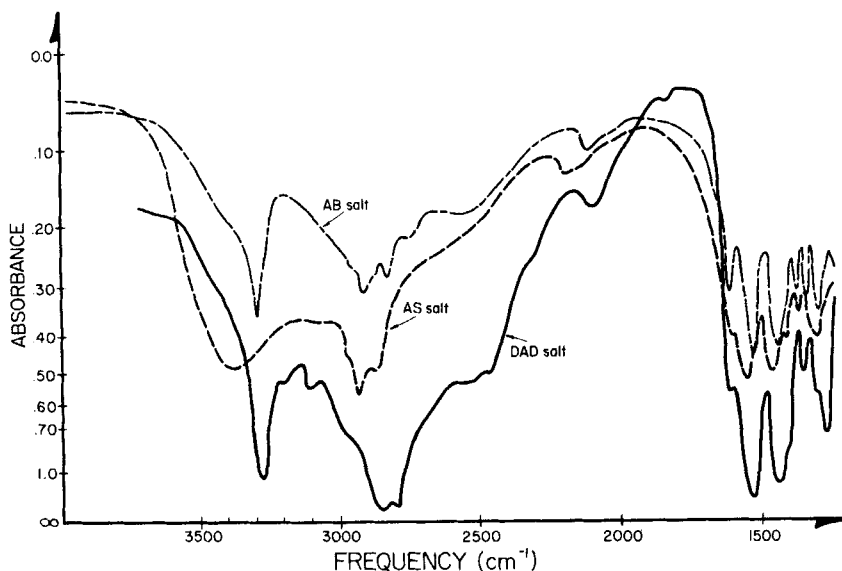
FIGURE 5 Comparison of infrared spectra of amine salts taken in KBr pellets on the Perkin Elmer 337 Grating Infrared Spectrometer. AB, AS, and DAD are 1,4-diaminobutane, 3-propylaminotriethoxysilane and 1,12-diaminoduodecane, respectively.

As can be seen in Figure 5, the infrared spectra of the solids obtained from 1,12-diaminododecane and AS showed similar features. Also, as with the AB salt (Table II) the melting temperatures of these other solids were substantially higher than those of the starting amines, 140°C compared to 64°C for the diamine and $d \sim 395°C$ for the AS. The melting behavior of the solids isolated from the AS and Cab-O-Sil mixture was the same as that of a carbon dioxide adduct prepared from the same silane. A solid was not isolated from the Teflon sheet above the PA and Cab-O-Sil mixture but it was demonstrated that PA also forms an adduct with carbon dioxide (M.P. = 70–72°C). The adduct from PA is soluble in water.

The carbonyl peak in the infrared spectrum of the salt from AB and S or Cab-O-Sil was not well resolved but in the ^{13}C NMR spectrum shown in Figure 6, the carbonyl peak was clearly visible. The ^{13}C NMR spectrum, in fact, revealed 2 carbonyl peaks, 4 kinds of C—N bonds and 4 kinds of C—C bonds. Comparison with spectra of the authentic compounds allowed one of the carbonyls, one C—N bond and one C—C bond to be attributed to the carbon dioxide adduct of AB. Another pair of bonds, one C—C and one C—N could be associated with AB itself. The carbon dioxide salt clearly is $\sim 67\%$ dissociated in D_2O. The other peaks could arise from a different amine, the structure of which is unknown at the present time. Those peaks definitely
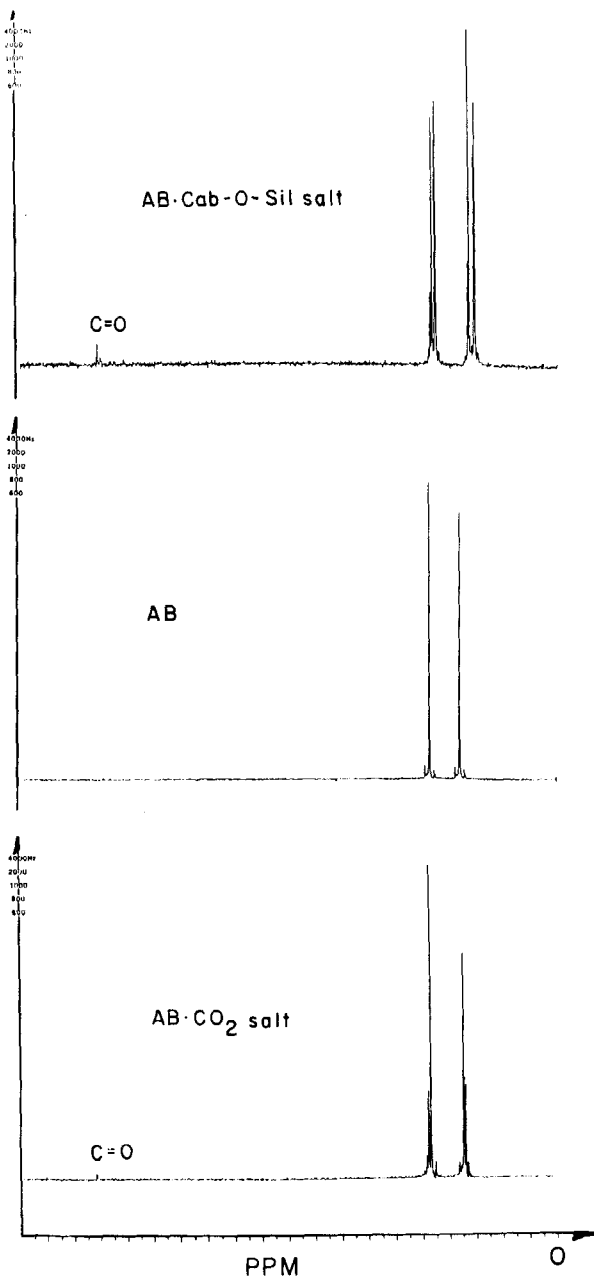
FIGURE 6 ^{13}C NMR spectra of AB, AB·CO$_2$ and the AB salt. 0 = transmitter frequency. TMS = 3.5 external ppm.

cannot be attributed to pyrrolidine, a likely side product,[12] since they are at different fields from those that arise from the authentic compounds. Whatever the unknown structure, it arises in the course of preparation or isolation of the salt, because the same sample of diamine was used to prepare the CO_2 adduct used for comparison.

From all the above data we conclude that the salt isolated from AB plus S or AB plus Cab-O-Sil was a 1:1 carbon dioxide adduct of AB, probably having the structure:
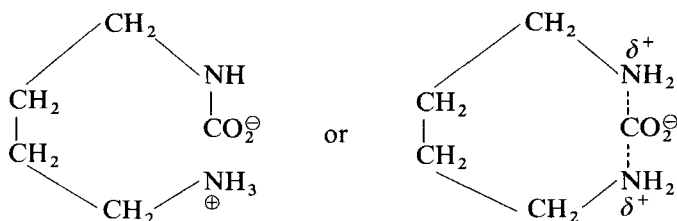

Fragments observed by mass spectrometry were in agreement with the proposed composition. The other solids are linear carbamates of the structure $RNHCO_2H$ or $RNHCO_2^\ominus H_3O^\oplus$.[11]

It is noteworthy that the same AB salt forms when AB is heated in air or when AB stands in an open vessel in air, but its formation is much slower in the absence of —SiOH groups or added dry ice.

DISCUSSION

Aromatic amines

The reaction of aromatic amines such as PDA with —SiOH groups either in a silanol or on the surface of glass results in the formation of silanes, protonated amine, hydrogen bonds and comparatively large quantities of water. Overall the results can be accounted for by the following reactions, which involve the formation of a donor-acceptor type intermediate, I:


(2)
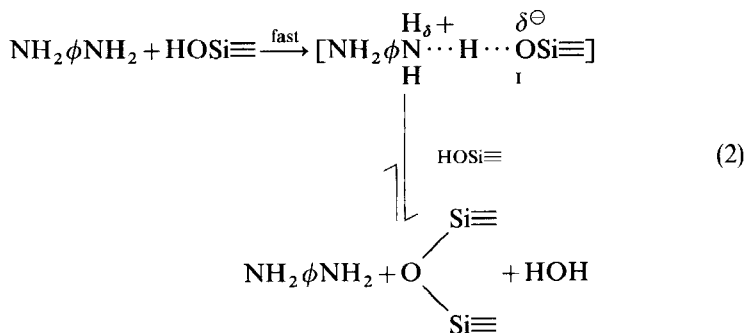
Since, upon addition of S, no change in concentration of the $-NH_2$ group was observed, it seems that the role of the amine is to catalyze the condensation of the silanol. This catalytic effect can be explained in the following way. At the initial stages a dynamic equilibrium between the $-NH_2$ groups on the amine and the $-SiOH$ groups takes place:

$$\equiv SiOH + NH_2R \leftrightarrow \equiv SiO^{\ominus} + NH_3^{\oplus}R \tag{2a}$$
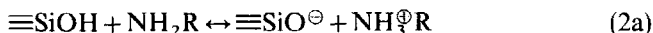
As a result the solution or surface contains negatively charged $\equiv SiO^{\ominus}$ groups, which may react with another $-SiOH$ group:

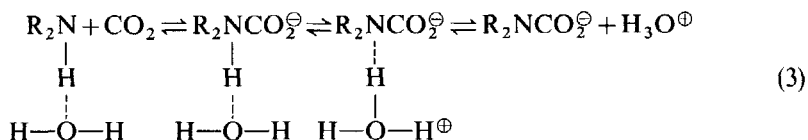$$\equiv SiO^{\ominus} + HOSi\equiv \rightarrow \equiv SiOSi\equiv + OH^{\ominus} \tag{2b}$$

Then the $OH^{\ominus}$ reacts with the protonated amine to the extent needed to satisfy the equilibrium required by the concentration of ions in the solution:

$$RNH_3^{\oplus} + OH^{\ominus} \rightarrow RNH_2 + HOH \tag{2c}$$
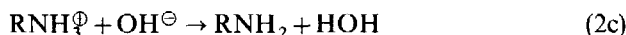
These reactions probably occur with all amines but are dominant only with aromatic amines and certain cyclic amines like piperazine.

Aliphatic amines

The reaction of aliphatic amines with $-SiOH$ groups is more complex than the corresponding reaction with aromatic amines. The aliphatic amines can undergo all the reactions already described for aromatic amines but probably do so to a lesser extent. Several features of the reaction are different: (1) a white cloud forms above the solution immediately upon mixing an aliphatic amine and a compound containing $-SiOH$ groups, (2) heat is evolved, (3) the $-NH_2$ group concentration definitely decreases while that of the aromatic amine hardly changes, (4) only traces of water are present in the reaction products and (5) precipitates form. The main mechanism seems to proceed through an active intermediate formed at the earliest stage of the reaction. The evidence indicates that the active intermediate is an adduct of carbon dioxide and amine, a carbamate, probably formed as suggested in Caplow's mechanism:[11]

$$
\begin{array}{ccccccc}
R_2N + CO_2 & \rightleftharpoons & R_2NCO_2^{\ominus} & \rightleftharpoons & R_2NCO_2^{\ominus} & \rightleftharpoons & R_2NCO_2^{\ominus} + H_3O^{\oplus} \\
| & & | & & | & & \\
H & & H & & H & & \\
| & & | & & | & & \\
H-O-H & & H-O-H & & H-O-H^{\oplus} & &
\end{array} \tag{3}
$$

An $-SiOH$ group could facilitate formation of the required protonated amine in the first step but would not form part of the final salt because of subsequent siloxane formation as described above in the section on aromatic amines. It appears that $-SiOH$ groups or at least the silanol or silica facilitate the

formation of the CO_2 adduct of the amines also. It is possible they do so by formation of a reactive ammonium intermediate which dissolves readily in the silanol or complexes firmly with silica. It is also likely that the reaction proceeds so well because silicon compounds absorb large quantities of air including the CO_2. (We have observed that it is almost impossible to keep a sample of silicones degassed. After thorough degassing and storage on a high vacuum line, the silicones become resaturated with air within seconds after opening to the atmosphere.) Thus the silicon compounds may merely be serving as a medium for bringing substantial amounts of amine and of CO_2 into favorable contact for reaction.

Carbamate formation is probably facilitated also by other fillers containing —OH groups. Moreover, if the relative ease of formation of picrates from the carbon dioxide adducts compared to their ease of formation from amines is a valid indication of the general reactivity of carbamates, the presence of the amines in the form of carbamates greatly enhances their reactivity in subsequent reactions.

Finally, it should be mentioned that although no evidence for the formation of pyrrolidine in reactions involving AB and S or Cab-O-Sil was found, the formation of pyrrolidine during curing at elevated temperatures such as 150°C cannot be definitely excluded. These model studies were carried out mostly at room temperature and were always below 100°C.

Acknowledgements

References

1. Y. Eckstein and P. Dreyfuss, *J. Adhesion* **13**, 303 (1982).
2. R. L. Kass and J. L. Kardos, *Polym. Eng. and Sci.* **11**, 11 (1971).
3. C. S. Park, S. H. Lee and N. H. Sung, in *Polym. Sci. and Technol.*, *12B*, L. H. Lee, Ed. (Plenum Press, N.Y., 1980), p. 757.
4. F. J. Boerio, C. A. Gosselin and Y. W. Williams, *Abstracts 4th Annual Meeting of the Adhesion Society*, Savannah, Georgia, Feb. 23–25, 1981, p. 7.
5. R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds* (John Wiley & Sons, Inc., N.Y., 1948), p. 180.
6. F. M. Unger, *Dissertation Abstracts* **29B**, 2821-B (1969). Ph.D. Thesis, Georgetown University, 1968.
7. W. J. Lautenberger, *Dissertation Abstracts* **29B**, 140-B (1968). Ph.D. Thesis, University of Pennsylvania, 1967.
8. F. M. Young, T. G. Roskos and H. R. Radloff, SPI, 17th Conference, Section 14-C, 1 (1962).
9. R. T. Conley, in *Infrared Spectroscopy* (Allyn Bacon, Inc. Boston, 1966), p. 119.

10. Beilsteins, *Handbuch der Organischen Chemie*, 4)1), 264.
11. M. Caplow, *J. Am. Chem. Soc.* **90,** 6795 (1968).
12. *Berichte der Deutchen Chemischen Gesellschaft* **19,** 780 (1886), and **20,** 442 (1887).
13. *The Merck Index, 9th Edition*, M. Windholz, Ed. (Merck & Co., Inc., Rahway, N.J., 1976), No. 7802.
14. *Dictionary of Organic Compounds, 4th Edition*, J. R. A. Pollock and R. Stevens, Eds. (Oxford University Press, 1965), pp. 2809, 2827.
15. K. Nakanshi and P. H. Solomon, *Infrared Absorption Spectroscopy, 2nd Edition* (Holden-Day, Inc., San Francisco, 1977), pp. 33–44.