

SILANES AND OTHER COUPLING AGENTS

VOLUME 2

Editor: K.L. Mittal

Silanes and Other Coupling Agents, Volume 2



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Preface

This book embodies the proceedings of the Second International Symposium on Silanes and Other Adhesion Promoters held under the auspices of C4 Technologies, Inc., in Newark, New Jersey, October 21–23, 1998. The premier symposium on this topic with the title ‘Silanes and Other Coupling Agents’ was held in honor of the 75th birthday of Dr Edwin P. Plueddemann in Midland, Michigan, April 3–5, 1991, the proceedings of which have been properly documented [1]. Apropos, the title of the second symposium was slightly different from that of the first event, but to main consistency, we have adopted the same title for this volume as its predecessor.

Silanes are the most popular and widely used coupling agents (or adhesion promoters) to promote adhesion between dissimilar materials in a variety of situations, e.g. coating technology, adhesive bonding, reinforced composites, etc. The availability of modern surface analysis techniques has been a boon in unravelling the mechanism(s) by which coupling agents perform. Since the first symposium on this topic, there had been a tremendous R&D activity in developing new and more effective adhesion promoters and in understanding and optimizing the performance of available coupling agents. So it was deemed necessary and timely to hold the second symposium on this topic.

The technical program for the symposium contained 36 papers and reflected both overviews and original research contributions and the presenters hailed from academia, industry and other research laboratories. Many different aspects of coupling agents were discussed, and both fundamental and applied aspects were accorded due coverage. In addition to formal presentations, there were brisk and lively discussions throughout the symposium, and this event provided an opportunity for cross-pollination of ideas in the broad arena of adhesion promoters.

Now turning to the present volume, it contains a total of 18 papers. It must be recorded for posterity that all manuscripts were subjected to rigorous peer review and were suitably revised before inclusion in this volume. So this book is not merely a collection of unreviewed papers, rather it contains information which has passed peer scrutiny. The book is divided into two parts as follows: Part 1. Silane Coupling Agents; and Part 2: Non-silane Coupling Agents/Adhesion Promoters. The topics covered include: silane adhesion promoters for hydrosilylation cure systems; sterically hindered silanes; study of silanes hydrolysis; adsorption of silanes on different substrates; interaction of water with silane films studied by

neutron reflection; characterization of glass fiber sizings; silanes as dispersion promoters; corrosion protection of metals by silanes; surface 'intelligraft' as a new class of adhesion promoters; hydroxymethylated resorcinol, sol-gels, and β -diketone functionalised polymers as adhesion promoters; and plasma deposition of silanes.

I sincerely hope this book reflecting the latest developments in the field of coupling agents will be useful to everyone interested in promoting adhesion between different materials for a host of applications.

Acknowledgements

First, it is a great pleasure for me to acknowledge my friend and colleague, Dr Robert H. Lacombe, for helping with the organization of this symposium. The reviewers provided much valuable comments and they are thanked for their time and effort. The interest, enthusiasm and contribution of authors is gratefully acknowledged. Appreciation is expressed to the staff of VSP (publisher) for giving this book a bodily form.

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Part 1

Silane Coupling Agents



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Novel silane adhesion promoters for hydrosilylation cure systems

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Abstract—Hydrosilylation offers a convenient, low-temperature, addition cure that is widely exploited in silicone sealants, adhesives and elastomers, and increasingly so in other polymer systems. One significant drawback of this cure system is the absence of polar groups, such as silanols, for reaction with hydroxylated oxide surfaces, which can result in poor adhesion. Numerous functional silanes have been proposed to improve matters. Preferably, these silanes should be incorporated as integral adhesion promoters rather than applied separately as primers. Cure and development of adhesion are interdependent phenomena in such mixed systems with compatibility and relative reaction rate considerations being paramount in product formulations.

We have found calculated solubility parameters to be an effective guide to the design of optimum combinations of wholly compatible cross-linkers and partially compatible adhesion promoters to enhance the adhesion of both silicones and hydrocarbon polymers such as poly(isobutylene). Adducts of tetraethoxysilane with unsaturated alcohols were found to be particularly effective. The tetraalkoxy substitution provides the most reactive functionality for bonding to hydroxylated substrates such as glass, aluminum and stainless steel. The unsaturation permits linkage to the polymer matrix and the partial compatibility is believed to allow an interpenetrating interfacial network to develop.

Keywords: Silane; hydrosilylation; silicones; poly(isobutylene); solubility parameter.

1. INTRODUCTION

One of the most useful ways of cross-linking poly(dimethylsiloxane) (PDMS) polymers to produce elastomers, sealants, adhesives and coatings is the hydrosilylation reaction where a silicon hydride group adds to an unsaturated group, generally vinyl or allyl, using a noble metal catalyst, typically a platinum complex. This approach has found widespread commercial use because of the following advantages:

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1. One-part and two-part systems are possible.
2. Fast, controllable cure rate.
3. Reaction can be accelerated by heat.
4. No volatile by-products are produced.
5. Deep section/confined cure capability.
6. Good bond stability.

The general drawbacks of this approach, of which only the last is the subject of the present investigation, include:

7. Catalyst easily inhibited/poisoned.
8. Interfering side reactions.
9. Properties very stoichiometry dependent.
10. Poor adhesion without priming or other adhesion promotion scheme.

Curable poly(isobutylene) (PIB) is a class of cross-linked polymer that offers some interesting parallels to PDMS coupled with some intriguing differences. The use of hydrosilylation cure technology should confer similar cure control and processability as PDMS. This approach requires alkenyl functional PIB and a variety of such species have been described in the patent literature, for example, telechelic allyl terminated PIB [1]. The surface energy of PIB, deriving like PDMS from its pendent methyl groups, is also quite close to PDMS. However, due mostly to the more compact, constrained hydrocarbon backbone, it has much reduced gas permeability compared to PDMS. Also with a higher solubility parameter than PDMS it should offer more compatibility with organic materials, for example, the resultant sealant should probably be readily paintable by conventional solvent-based coatings. Some quantitative comparisons of PIB and PDMS along with low density poly(ethylene) (LDPE) and poly(tetrafluoroethylene) (PTFE) are given in Table 1. Characteristic pressure (p^*) is probably the least familiar property: it comes from Flory's equation-of-state and is a measure of intermolecular energy per unit volume. A perusal of this table readily helps understand the attractiveness of PIB in applications such as insulated glass sealants.

Table 1.
Relevant fundamental polymer properties

	PDMS	PIB	LDPE	PTFE
Critical surface tension of wetting {mN/m}	24	27	33	18
Water contact angle {deg}	101	102	94	108
Solubility parameter {(cal/cm ³) ^{1/2} }	7.5	7.9	8.0	6.2
Glass transition temperature {K}	146	197	148	390
Characteristic pressure {J/cm ³ }	341	448	485	362 ^a
Oxygen permeability {cm ³ (STP) cm·cm ⁻² ·s ⁻¹ (cm Hg) ⁻¹ × 10 ¹⁰ }	605	1.0	2.9	4.2

^a Data for perfluorohexane.

The solubility parameter (δ) is the square root of the cohesive energy density (CED) defined in Equation 1:

$$\text{CED} = \frac{\text{energy of vaporization } (\Delta E_v)}{\text{molar volume } (V)} \quad (1)$$

The cohesive energy density is a measure of intermolecular forces and as such is related not only to solubility but also to surface tension, boiling point, glass transition temperature, etc. Both the energy of vaporization and the molar volume can be calculated to a first approximation by the summation of atomic and group contributions. A variety of such approaches are available, the simplest and the one we chose to use is the one introduced by Fedors [2].

2. ADHESION FUNDAMENTALS

Adhesion is a complex, multidisciplinary subject in which the nature of the interfacial region between the curing polymer matrix and the substrate to which it is applied is one very important aspect of the problem. It should be possible to improve adhesion both by increasing the strength of individual molecular interactions across an interface and by increasing the number of them. In this regard polymers such as PIB and PDMS have contradictory properties. Their low surface energies reflect low intermolecular forces dominated by weak London dispersion forces, however, the same property implies good wetting of most substrates that should maximize the interfacial contact achieved.

Table 2 is adapted from the one given by Good [3]. Shafrin and Zisman [4] have shown that aliphatic hydrocarbon and fluorocarbon groups have the lowest London dispersion forces among polymeric materials, so clearly we have an inherent disadvantage with PDMS and PIB. PIB even lacks the partially polar siloxane backbone so it is likely to be an even greater challenge than PDMS. Chemical reactivity with the substrate must be provided in some way to move into the high strength intermolecular interactions listed in the top of Table 2. Many substrates including glass and many metals are hydroxylated so the reaction of

Table 2.
Strengths of interactions at interfaces

Interaction type	Bond energy range (kJ/mol)
Ionic	600–1000
Covalent	60–700
Metallic	100–350
Strong H bonds (involving F)	up to 40
Other H bonds	10–25
Dipole–dipole	4–20
Dipole–induced dipole	1–2
London dispersion forces	0.1–40

silanols with surface hydroxyls is a very attractive method of providing covalent interaction, albeit reversible and sensitive to extremes of pH, in organosilicon sealants, adhesives and coatings. For example, when the substrate is glass or quartz the resulting Si—O—Si bonds have a bond energy of *circa* 450 kJ/mol. Such silanols are often part of the cross-linking reaction, for example with acetoxy cure materials, but they are not part of the hydrosilylation cure materials which accounts in large measure for the adhesion problems associated with them. Alkoxysilyl functionality is the usual way in which this capability is provided to silane coupling agents and primers and it should be expected that adhesion promoters added to PDMS and PIB materials would also be based on similar entities.

Likewise, one would anticipate a chemical linkage to the matrix polymer. Unsaturation in the adhesion promoter would provide this, although in some cases good adhesion can be obtained without any evident reaction with the polymer. Alkoxysilyl groups do, of course, react with each other as well as with the substrate and if the network thereby produced interpenetrates with the polymer adequately good adhesion will ensue because chemical bonds will have to be broken to separate the interpenetrating network (IPN) linked both to the substrate and threaded through the matrix polymer even though no actual bonding between the IPN and the matrix has occurred. The existence of such IPNs has been demonstrated with silane coupling agents when used as an adhesion priming layer between various substrates [5] and could exist with integral adhesion promoters where the promoter is added to one of the bulk phases and functions by diffusion to the relevant interface. Such an approach would involve a delicate solubility parameter balance. We would want the adhesion promoter to have some solubility in the matrix to enable an IPN to form but it should not be too soluble that it has no drive to separate into the interfacial phase. This is one of the main reasons why we anticipated solubility parameter calculations would be helpful.

The practical need is not simply improved adhesion but faster adhesion at low temperature. This requires more hydrolytically reactive monomers to react with each other as well as with the substrate in the surface region and also unsaturation to tie into the polymer matrix. Since reactivity of $R_xSi(OR)_{4-x}$ increases as x decreases [6], materials such as $(CH_2=CHR^1O)_xSi(OR)_{4-x}$ will have the best chance of success. R^1 could be chosen, guided by solubility parameter considerations, for use in PDMS and PIB systems. For example, when R^1 is $(CH_2)_9$, and x is unity we have undecenylxytriethoxysilane (UTES, also named undecylenylxytriethoxy-silane) which has considerable utility in both PDMS [7] and PIB. Not only does it have reactivity to both glass or metal substrates and vinyl functional PDMS or allyl functional PIB but it is also a relatively small molecule capable of diffusion into the interfacial region from the bulk of the material. The calculated solubility parameters of PDMS, PIB and UTES are 7.4, 7.7 and $8.2 \text{ (cal/cm}^3)^{1/2}$ respectively. A rule of thumb suggests being between about a half and one solubility parameter unit from the polymer matrix provides a balance of enough compatibility for dispersion in the polymer together with sufficient drive to

concentrate in the interfacial region, so UTES has the potential to be effective in both PDMS and PIB systems.

3. EXPERIMENTAL

3.1. Formulations

We have used a variety of formulations in our studies. A minimal formulation must contain a functional polymer, cross-linker A, cross-linking Pt catalyst, catalyst inhibitor, and adhesion promoter. Diluents such as plasticizers, other catalysts (for example, to enhance the condensation reaction with the substrate) and various fillers may also be present. For the initial evaluations reported here we mostly used unfilled systems. It is usual to have the vinyl or allyl unsaturation on the primary polymer chain with the SiH functionality on the lower molecular weight cross-linkers. The general reaction is:



where y is usually zero (vinyl) or unity (allyl) but can be greater, for example, four (hexenyl).

For evaluation of adhesion promoters in PDMS a common formulation consisted of vinyl functional PDMS of 2 Pa·s viscosity (Dow Corning), cross-linker A at a SiH : vinyl ratio of 1.25 : 1, Pt catalyst with methyl-vinylcyclsiloxanes as inhibitor, adhesion promoter, and tetrabutyl titanate to catalyze the condensation reaction of the adhesion promoter with the substrate. For evaluation of adhesion promoters in PIB, the usual formulation contained allyl functional PIB (Kaneka-Fuji), the plasticizer KP-32 (Kaneka-Fuji), a variety of cross-linkers at a SiH : allyl ratio of 2 : 1, Pt catalyst with 2-methyl-3-butyne-2-ol inhibitor, and adhesion promoter. The PDMS cross-linker (cross-linker A) proved to be poorly compatible with the PIB. Cross-linkers with calculated solubility parameter more closely matching PIB (cross-linkers B and C) were better as can be seen from Table 3. Note, however, that the best adhesion results (see Results section) were obtained with a 50/50 mixture of cross-linkers A and B. This suggests it is important to have adequate cross-linker both in the bulk and in the interfacial region. In this context note also that the unsaturation of the adhesion promoter is probably complexing with the Pt catalyst

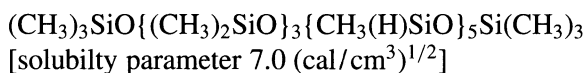
Table 3.

PIB/cross-linker formulation evaluation

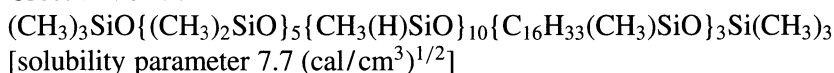
Cross-linker	Appearance	Wet-out (on glass)	Cure		Tack	Hardness (Durometer Shore A)
			(RT)	(70°C)		
A	Cloudy	Poor	Fair	Good	Slight	23
B	Clear	Good	Good	Good	None	25
C	Clear	Good	Fair	Good	Slight	28

ensuring an increased catalyst concentration in the interfacial region also [8]. The compositions of these cross-linkers are:

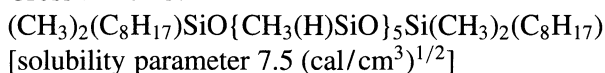
Cross-linker A:



Cross-linker B:

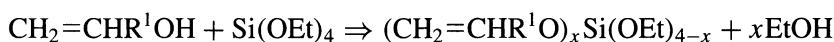


Cross-linker C:



3.2. Synthesis

Unsaturated alkoxy silane adducts suitable for investigation as potential adhesion promoters were conveniently prepared by the transesterification reaction of tetraalkoxy silanes with unsaturated alcohols. For example:



The reaction is usually carried out in batch mode between 100°C and 120°C for *circa* three hours followed by nitrogen purging at atmospheric pressure to remove the ethanol produced. Mono adduct stoichiometry is used but dimer and trimer adducts as well as unreacted tetraethoxy silane are usually present in the product. For example, in the UTES case where R^1 is $(\text{CH}_2)_9$, the typical composition is 45% mono adduct, 20% dimer adduct, 5% trimer adduct and 30% unreacted

Table 4.

Adhesion of PDMS compositions containing various unsaturated tetraalkoxy silane adducts

Unsaturated alcohol	Adduct solubility parameter $\{(\text{cal/cm}^3)^{1/2}\}$	Functional group separation ^a	Relative RT adhesion effectiveness ^b (%)	
			1 day	7 day
None (TEOS control)	7.87	—	0	55
4-penten-2-ol	7.95	3	60	60
4-penten-1-ol	8.06	4	60	60
10-undecen-1-ol	8.20	10	80	100
Allyl(EO) ₄ OH	8.56	11	60	80
Allyldiglycol carbonate	8.74	10	75	100
2-hydroxyethyl acrylate	8.76	5	60	100
1-phenyl-3-buten-1-ol	8.79	3	60	60

^a The number of atoms separating the alkene group from the triethoxysilyl group.

^b The relative RT adhesion effectiveness was based on adhesion to five substrates after cure at room temperature for one or seven days. The effectiveness would be 100% if the composition failed cohesively (CF) from all substrates.

tetraethoxysilane. A considerable variety of such molecules have been prepared and investigated, some of which are shown in Table 4. These are similarly distributions of composition. It is recognized that the by-products may have an impact on the performance of the adhesion promoter but the purification and testing of pure adducts has not yet been carried out.

3.3. Adhesion testing

Formulations were prepared by simply blending the desired components and de-airing for at least 10 minutes under vacuum. This was very effective in removing bubbles from the PDMS compositions but usually had little effect on the more viscous, less gas permeable PIB compositions. Portions of these compositions were drawn down at 200 μm wet thickness onto the substrates of interest. These included glass microscope slides, bare aluminum, milled aluminum, copper, and stainless steel. Not all these substrates were used every time. Prior to applying the coatings to the substrates, the substrates were solvent washed (MIBK or IPA) and allowed to air dry. Coatings were cured at room temperature and at 70°C for 30 min and 120°C for 90 min. Adhesion was checked initially and after 1, 3 and 7 additional days of room temperature cure. Hydrolytic stability of the bond was sometimes assessed by immersing the coated substrates in deionized water, typically for seven days at 70°C, and then retesting the adhesion. In addition adhesion was also sometimes evaluated on a variety of plastics substrates.

Adhesion was assessed by scratching the cured coatings with the blade of a metal spatula (scratch test) to determine whether the coating could be removed without leaving a residue on the surface (interfacial failure, IF) or whether failure occurred within the coating layer, resulting in at least a portion of the coating material in the test area adhering to the substrate (cohesive failure, CF). Coatings exhibiting cohesive failure were further tested to determine if the residue on the substrate and the adjacent coating material could be removed by rubbing with a finger. If the coating could be removed in this manner, the pressure required to remove the coating was rated as slight (wipes easy, WE), medium (WM) or high (wipes with difficulty, WD). These abbreviations in parentheses are those used in the Tables. This rapid, qualitative, subjective test proved adequate for our purposes. Some quantitative tensile testing of joints formed by cross-lapping of two similar substrates with the coating between them was done in some cases but provided no extra information on the performance trends we were seeking.

4. RESULTS

A considerable variety of unsaturated tetraalkoxysilane adducts of tetraethoxysilane with unsaturated alcohols were prepared and evaluated as potential adhesion promoters. Variants examined included mono- and dihydroxy primary, secondary, and tertiary alcohols containing alkyl, ether, acrylate and carbonate groups of various chain lengths and number of hydrosilylation reactive unsaturated groups. The

adhesion effectiveness of several of these is summed up in Table 4, including UTES which was prepared by reaction of 10-undecen-1-ol with tetraethoxysilane. In this table the relative adhesion effectiveness is the summation of the observed adhesion behavior with the five substrates (glass, bare aluminum, milled aluminum, copper, and stainless steel) after curing the coating for one and seven days at room temperature. 100% indicates cohesive failure on each of the five substrates, 0% would be interfacial failure on all five substrates. Such tests were carried out at other temperatures and times as stated earlier. Table 4 is a sampling of our data to illustrate the effects experienced. It shows that incorporation of hydrosilylation reactive unsaturation on the tetraalkoxysilane clearly affords enhanced adhesion effectiveness in this PDMS based composition. Other structural variations which impact the solubility parameter and separation of the hydrosilylation reactive unsaturation and the triethoxysilyl group also impact the adhesion effectiveness of the unsaturated tetraalkoxysilane adduct.

Adhesion data for PDMS compositions containing UTES for a broader variety of substrates are provided in Table 5. Cohesive failure was obtained on the inorganic and metallic substrates examined, even gold, after cure for one day at room temperature or 30 minutes at 70°C. Good adhesion is evident with only some of the plastics substrates examined. Table 5 also includes the effect of exposure to water; in this case the wet adhesion was evaluated after immersion in water for seven days at 70°C.

Table 5.

Adhesion of PDMS compositions containing UTES on various substrates

Substrate	Dry adhesion ^a		Wet adhesion ^b	
	RT cure	70°C cure	RT cure	70°C cure
Glass	CF	CF	CF	IF
Alumina	CF	CF	CF	CF
Bare aluminum	CF	CF	WM	IF
Bare aluminum ^c	CF	CF	CF	CF
Milled aluminum	CF	CF	CF	CF
Copper	CF	CF	CF	CF
Stainless steel	CF	CF	CF	CF
Gold plating	CF	CF	WD	WE
Epoxy (FR-4)	CF	CF	CF	CF
Polycarbonate	CF	CF	CF	CF
Nylon	IF	IF	IF	IF
PMMA	IF	IF	IF	IF

^a Measured after one day cure at RT or initially after 30 minutes cure at 70°C.

^b Measured after immersion in water for seven days at 70°C.

^c Composition additionally contained a portion of hexenyltriethoxysilane.

In this and the following tables, the abbreviations IF, CF, WE, WM and WD stand for interfacial failure, cohesive failure, 'wipes easy', 'wipes medium' and 'wipes with difficulty', respectively. The terms are explained more fully in the text.

Since the unsaturated tetraalkoxysilane adducts are based on a Si—O—C linkage which is less hydrolytically stable than the Si—C linkages in conventional coupling agents, there is a need to evaluate this aspect of adhesion performance. It can be seen from Table 5 that on some substrates, for example, copper and stainless steel, the adhesion is not compromised by water exposure but that it is with other substrates such as glass and bare aluminum. To help remedy the hydrolytic instability, the more conventional Si—C linked hydrosilylation reactive hexenyltriethoxysilane was added to the composition along with the UTES adhesion promoter with the intent to rely on the UTES for development of rapid adhesion and on the conventional adhesion promoter for robust, hydrolytically stable adhesion. This approach proved successful as demonstrated in Table 5.

Note also that the results in Table 5 show that this weakening of the adhesional bond on some of the substrates upon exposure to water is more pronounced with samples that have been cured at 70°C than with those cured at room temperature. While adhesion is generally regarded to improve with increasing cure temperature, the concentration of adhesion promoter at the interface may actually be higher after low temperature cure where the matrix molecular weight increases more slowly with time, helping to drive the adhesion promoter to the interface.

Examples of the effectiveness of UTES as an adhesion promoter in PIB are given in Table 6. Cohesive failure can be achieved at 120°C after seven days over a range of concentrations. The adduct of tetraethoxysilane and 4-penten-1-ol, where the hydrocarbon link between the alkoxyisilane and the hydrosilylation reactive vinyl group has been reduced from nine methylene units to three also performed most satisfactorily. This adhesion promoter, designated PTES, has a calculated solubility parameter of $8.06 \text{ (cal/cm}^3)^{1/2}$. Its performance in PIB is given in Table 7. It might be expected that its lower solubility parameter than UTES would make it more compatible with PIB and hence less effective. However, we suspect viscosity and other diffusion related complications. PIB has a steeper viscosity/temperature response than PDMS and diffusion will be much

Table 6.

Effect of UTES adhesion promoter in PIB formulations

Adhesion promoter conc. (%)	Cross-linker	Adhesion ratings			
		Glass	Milled aluminum	Bare aluminum	Stainless steel
0	A	IF	IF	WH	IF
0	B	IF	IF	IF	IF
1.5	A+B(50/50)	CF	CF	CF	CF
2.5	B	IF	CF	CF	IF
2.5	A	CF	CF	CF	CF
2.5	A+B(50/50)	CF	CF	CF	CF
2.5	A+B(70/30)	CF	WM	CF	CF
2.5	A+B(30/70)	CF	CF	CF	CF
5.0	A	CF	CF	CF	CF

Table 7.

Effect of PTES adhesion promoter on the adhesion behavior of PIB formulations

Substrate	Adhesion promoter conc. (%)	Adhesion ratings		
		1 day/7 day (RT cure)	1 day/7 day (70°C cure)	1 day/7 day (120°C cure)
Glass	2.5	CF/CF	WM/WM	CF/CF
Glass	5.0	CF/CF	WE/WE	CF/CF
Bare aluminum	2.5	CF/CF	WE/CF	CF/CF
Bare aluminum	5.0	CF/CF	CF/CF	CF/CF
Milled aluminum	2.5	CF/CF	CF/CF	CF/CF
Milled aluminum	5.0	CF/CF	CF/CF	CF/CF
Stainless steel	2.5	CF/CF	CF/CF	CF/CF
Stainless steel	5.0	CF/CF	CF/CF	CF/CF

more restricted at lower temperatures in PIB compared to PDMS. The smaller molecular size of PTES than UTES would facilitate its transport through the PIB matrix at lower temperatures. PIB also has a higher glass transition temperature and, consequently, lower free volume than PDMS which also affects diffusional behavior.

Noticeable in both Tables 6 and 7 is the suggestion that glass is a difficult substrate to adhere to for these PIB formulations. This was generally found to be the case, whereas for the PDMS formulations glass is usually one of the easier substrates to adhere to. The difference is surprising because in both cases the chemical link to the substrate, a Si—O—Si linkage, will be the same. We speculate that in the PDMS case either there is additional SiOH(glass)/Si—O—Si(polymer) polar interaction not possible with PIB or that the siloxane networks on both sides of the PDMS/glass interface permit some molecular alignments which maximize siloxane bond formation across the interface. There is also the implication in Table 7 that cure at 70°C is more difficult than at either room temperature or at 120°C. Temperature affects reactivity, solubility and diffusion rates of the various components of the formulations differently and such temperature variations are to be expected.

5. SUMMARY

A new class of silane adhesion promoters, adducts of tetraethoxysilane (TEOS) and unsaturated alcohols, have been shown to be particularly effective in improving the adhesion of hydrosilylation cure systems such as poly(dimethylsiloxane) (PDMS) and poly(isobutylene) (PIB) to hydroxylated surfaces such as glass and various metal oxide surfaces. The tetraalkoxy substitution provides the most reactive functionality for bonding to the substrate while the unsaturation permits reaction with the polymer matrix. There is a delicate balance between reactivity, solubility and diffusion rates of the various components of the formulations that determines the degree of adhesion improvement achieved. We have found that calculated

solubility parameter data obtained by the straightforward approach of Fedors provides a convenient guide for the design of useful adhesion promoters and cross-linking agents. This approach was also found to be effective in developing other adhesion promoters and additives for hydrosilylation cure systems not reported here. Only simple scratch test adhesion data are presented, although it should be mentioned that quantitative tensile testing yielded little more information.

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Sterically hindered silanes for waterborne systems: A model study of silane hydrolysis

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Abstract—The reactivity of silanes in waterborne systems was studied using model compounds. Vinyltrialkoxysilanes were used to investigate the effects of the leaving group on the rates of silane hydrolysis. The alkoxy groups were methoxy, ethoxy, 1-propoxy, 2-propoxy and 3-oxabutoxy. The base-catalyzed rates of hydrolysis for these silanes were measured under pseudo-first order conditions in an aqueous acetone solution at 22°C and in the presence of acetate buffer. The hydrolysis was catalyzed by the acetate anion. Steric and polar characteristics of the alkoxy leaving group affect the hydrolysis rates.

The hydrolysis rates of the vinylsilanes were compared with the gel contents of a series of silylated latex polymers. The latex polymers were copolymers of ethyl acrylate and 3-methacryloxypropyl-trialkoxysilanes. A trend between the hydrolysis rates of vinyltrialkoxysilanes and the gel content of the silylated latexes was observed. Lower gel content in the polymers occurs when the alkoxy silane monomer hydrolyzes more slowly.

Keywords: Hydrolysis kinetics; silane; base-catalyzed; steric effect; polar effect; Taft plot.

1. INTRODUCTION

Alkoxysilanes are used commonly as crosslinkers and adhesion promoters for numerous coating, adhesive and sealant formulations. They are often chosen because of their chemical reactivity, formulation flexibility and environmental stability. The alkoxysilyl group hydrolyzes to form silanols that condense to form crosslinks or react with surfaces to form chemical bonds. The condensation is initiated by exposure to moisture and catalysts.

The reactivity of the methoxysilyl group with water has limited the use of many alkoxysilanes in waterborne formulations. The methoxysilyl group prematurely hydrolyzes and condenses. These reactions reduce the shelf-life of the formulations to days or weeks and thereby make one-component waterborne formulations impractical. The current trend in the marketplace is towards water-based formulations

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because they comply with regulatory mandates and meet consumers' environmental and use requirements.

Recently, silanes that contain sterically hindered alkoxyisilyl groups have been successfully used in one-component waterborne formulations [1, 2]. The improved shelf-life of these formulations was achieved by restricting or eliminating the exposure of the alkoxyisilyl group to water. The approach was to isolate the silane in an organic phase and thereby minimize contact with water. Emulsions or organic polymer dispersions in which these silanes are partitioned into the organic phase provide effective barriers to water attack. The solubility of water in these organic phases is low. The stability of the formulations containing silanes can be improved further by slowing down the rate of water reaction with these silanes by using sterically hindered alkoxyisilyl groups. However, a balance must be reached whereby the silanes will be sufficiently stable to hydrolysis to allow preparation of an emulsion or a dispersion containing these silanes with a reasonable shelf-life, but the silanes will still hydrolyze upon application.

An understanding of the hydrolysis kinetics for these silanes would aid in the preparation of formulations with long shelf-lives and with sufficient reactivity to condense and react with surfaces upon application. Much is already known about the kinetics and mechanisms of alkoxyisilane hydrolysis [3]. The effects of alkyl substituents on the hydrolysis of trialkoxyisilanes in aqueous solutions have been reported previously [4]. Hydrolysis studies of alkoxyisilanes have also been done in mixtures of water and organic solvents [3]. In these studies it has been found that the reaction is first-order with respect to the silane. The order with respect to water was between one and six depending on the solvent and water concentration [5]. The structure of the alkoxy group also had a significant effect on the catalyzed hydrolysis of tetraalkoxyisilanes. Tetrakis-(2,6-dimethylheptoxy)silane was found to hydrolyze 17 times slower than tetraethoxyisilane [6]. Knowing the effects of the alkoxy groups on the hydrolysis of alkoxyisilanes would be useful in designing new materials for waterborne formulations.

This model study for investigating the reactions of alkoxyisilanes in waterborne formulations examines the hydrolysis of vinyltrialkoxyisilanes in an acetone and water mixture. The rates of hydrolysis were measured for trimethoxy-, triethoxy-, tripropoxy-, tri-2-propoxy-, and tris-(3-oxabutoxy)vinylsilanes. Vinylsilanes were chosen because they do not contain other reactive groups which would complicate the kinetic study. The reactions were carried out under pseudo-first order conditions where the concentration of water was much greater than the concentration of the silane.

2. EXPERIMENTAL

2.1. Materials

Vinyltrimethoxysilane, vinyltriethoxysilane, vinyltri-2-propoxysilane, and vinyltris-(3-oxabutoxy)silane were obtained from Witco Corporation under the trade names

Silquest® A-171, Silquest® A-151, CoatOSil® 1706 and Silquest® A-172, respectively. Acetone and *n*-propanol were from Aldrich Chemical Company. Sodium acetate, acetic acid and potassium chloride were from Fisher Chemical Company.

Vinyltripropoxysilane was prepared by the transesterification of vinyltri-methoxysilane with *n*-propanol. To 225 g of vinyltrimethoxysilane was added 365.5 g of 1-propanol and 0.034 g of *p*-toluenesulfonic acid. The mixture was stirred and heated under nitrogen. Methanol was distilled from the reaction mixture through a Vigreux column and additional 1-propanol was added to maintain a constant volume level. The crude product was distilled to give 286.7 g of a clear, colorless liquid: b.p. 45–47°C (0.5 torr).

Stock solutions of acetate buffer were freshly prepared using sodium acetate and acetic acid. Potassium chloride was used to maintain the ionic strength of the final silane solutions at $\mu = 0.1$. The pH of the solution was measured with an Accumet 910 pH meter and a Fisher combination electrode.

2.2. Method for monitoring hydrolysis reactions

The hydrolysis of the silanes was monitored using proton nuclear magnetic resonance (^1H NMR) spectroscopy. The vinyltrialkoxysilane solutions were prepared by adding the silane, 5.0 g of acetone and 1.8 g of buffered water to a 10 ml volumetric flask. Additional acetone was added to the mark. The vinyltrialkoxysilane concentration was 0.009 M. The samples were placed in a 5-mm NMR tube with a 3-mm NMR tube insert containing acetone- d_6 . The temperature of the solutions was maintained at 295 K (22.0°C). Proton NMR spectra were taken on a Bruker ACP-300 or a Varian VXR-300 spectrometer. A 9.2-degree pulse width was used with an acquisition time of 2 s and a relaxation delay of 5 s. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (0.0 ppm). Spectra were taken at several time intervals from the initiation of the reaction.

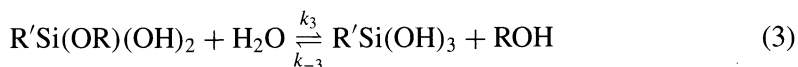
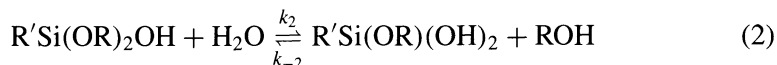
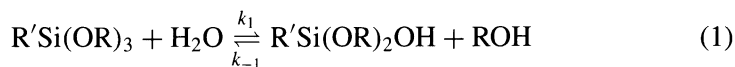
3. RESULTS AND DISCUSSION

3.1. Hydrolysis of hindered alkoxysilanes

The rates of hydrolysis of a series of vinyltrialkoxysilanes were determined by proton NMR spectroscopy. The alkoxy groups studied in the series included methoxy, ethoxy, propoxy, 2-propoxy and 3-oxabutoxy. The concentration of water in the silane–acetone solutions was 18 weight-volume percent. The solutions were buffered with an acetate buffer.

The hydrolysis of trifunctional silanes proceeds in a stepwise manner, as shown in Scheme 1 [7].

Each step of the hydrolysis reaction can be monitored independently using the NMR technique. The ^1H NMR spectra in the region $\delta = 3.25$ to 3.75 ppm are shown in Fig. 1 for the reaction solutions of vinyltrimethoxysilane at various times. The signal for the methoxy protons of the vinyltrimethoxysilane appears at $\delta = 3.564$ ppm. As the reaction proceeds, the peak intensity of vinyltrimethoxysilane



Scheme 1.

decreases and several new signals appear due to the formation of the reaction products methanol ($\delta = 3.34$ ppm), vinyltrimethoxysilanol ($\delta = 3.547$ ppm) and vinylmethoxysilanediol ($\delta = 3.527$ ppm). The integral of the protons that are due to the silanol and silanediol peaks remains very small throughout the reaction. The absence of any significant build-up of the silanol and silanediol intermediates indicates that the ratios of the rate constants k_1/k_2 and k_1/k_3 are small. The first step of the hydrolysis is, therefore, the slow step. Pratt and co-workers [7] found a similar result for the hydrolysis of phenyltris-(3-oxabutoxy)silane in aqueous solution. The ratio of k_1/k_2 in that study for specific acid catalysis was 2 to 3. The presence of the silanol and silanediol intermediates was not detected for the more sterically hindered alkoxysilane. The NMR data indicate that ratios of k_1/k_2 and k_1/k_3 are smaller for these alkoxysilanes and alkoxysilanol than for vinyltrimethoxysilane and vinylmethoxysilanol.

3.2. Base catalysis

The rate of hydrolysis of silane esters in mixtures of organic solvent and water may be expressed by Equation 4:

$$\begin{aligned} \frac{-d[\text{S}]}{dt} = & k_{\text{spn}}[\text{H}_2\text{O}]^n[\text{S}]^m + k_{\text{H}}[\text{H}^+][\text{H}_2\text{O}]^n[\text{S}]^m \\ & + k_{\text{HO}}[\text{HO}^-][\text{H}_2\text{O}]^n[\text{S}]^m + k_{\text{B}}[\text{B}][\text{H}_2\text{O}]^n[\text{S}]^m, \end{aligned} \quad (4)$$

where [S] is the concentration of the alkoxysilane and [B] is the concentration of the basic species that can accept a proton [2]. Previous work has also found that the order with respect to silane in these solvent systems was one [4]. By using a large excess of water relative to the silane, pseudo-first order conditions are achieved.

The hydrolysis of vinyltrimethoxysilane was carried out in the acetone-water solvent system. The solvent contained acetic acid and sodium acetate to buffer the aqueous acetone. The ionic strength was maintained at $\mu = 0.1$ with potassium chloride. Because the reaction was carried out in aqueous acetone, pH^* was used to determine the final acetic acid and acetate anion concentrations. pH^* is the negative logarithm of the hydronium ion concentration in aqueous acetone. It is determined by the equation:

$$\text{pH}^* = \text{pH}_{\text{obsd}} - \delta, \quad (5)$$

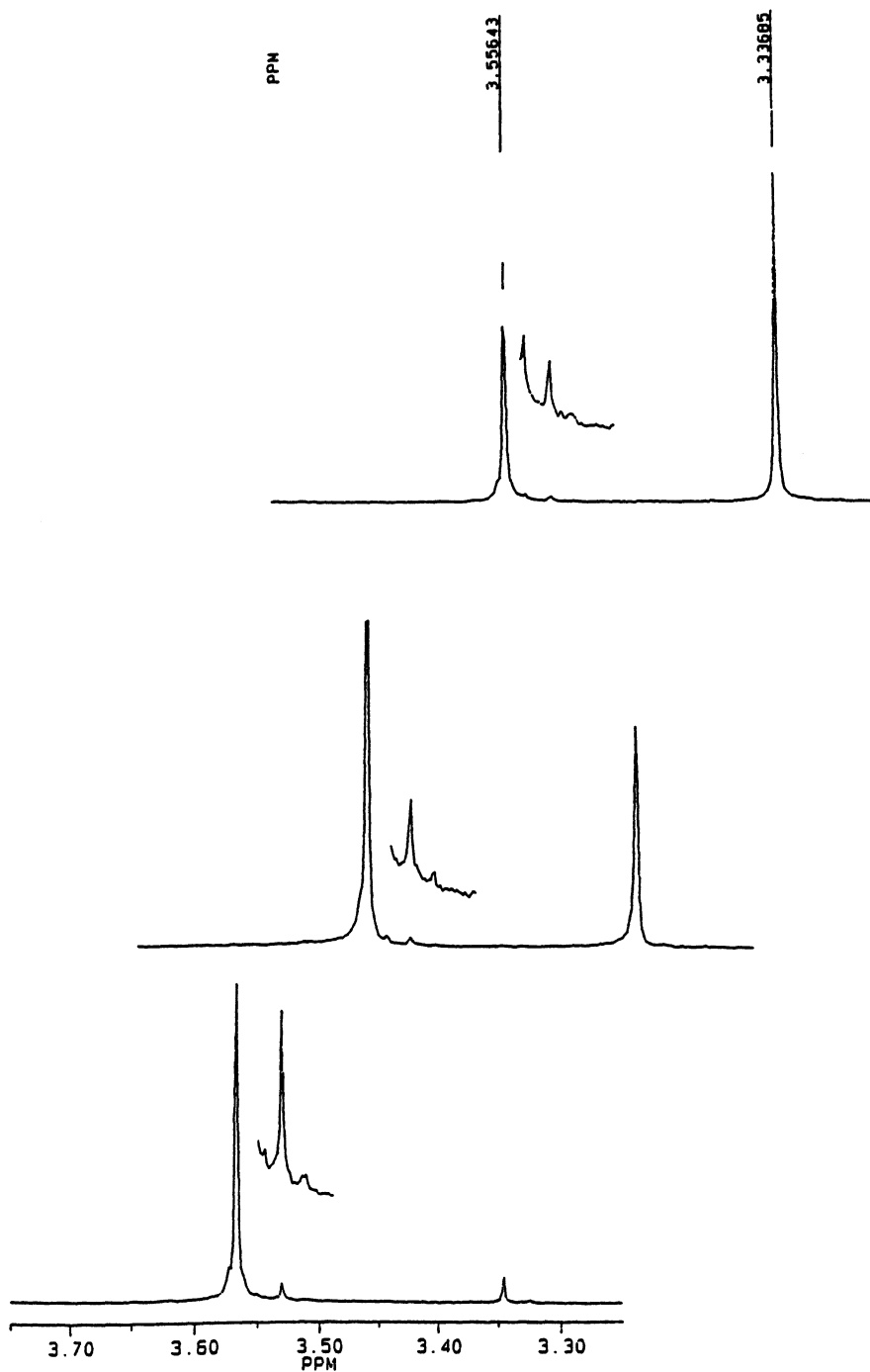


Figure 1. NMR spectra of vinyltrimethoxysilane in an aqueous acetone solution taken at various reaction times.

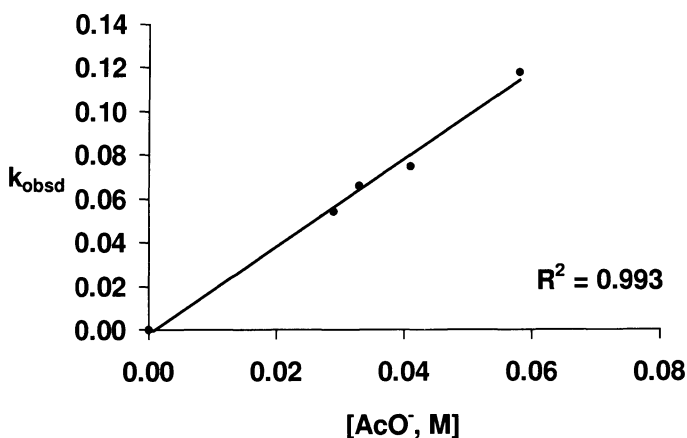


Figure 2. A plot of the observed rate constant versus acetate anion concentration for the hydrolysis reaction of vinyltrimethoxysilane.

where pH_{obsd} is the ordinary pH reading from the pH meter using a combination electrode and δ is a correction factor. The correction factor was -0.21 [8]. The acetic acid and acetate anion concentrations were corrected using the pH^* , the weights of sodium acetate and acetic acid used in preparing the solutions and the $\text{p}K_a$ for acetic acid. The $\text{p}K_a$ for acetic acid is 7.0 in 18 weight-volume percent water in acetone [8].

The relative importance of each term in Equation 4 was determined by varying the ratio of acetic acid to acetate anion and plotting the observed rate versus the concentration of the acetate anion, as shown in Fig. 2. The pH^* of the aqueous acetone solutions ranged from 6.74 to 7.36 due to the varying ratio of acetic acid and sodium acetate. The slope of the plot represents the second-order rate constant, k_B . The intercept near zero indicates that the terms in Equation 4 due to the spontaneous (k_{spont}), hydronium ion (k_H) and hydroxide anion (k_{OH}) catalyzed rates are very small under the conditions of the experiments. Although these reactions are specific acid- and general base-catalyzed [7], the term due to the acetate anion catalyzed rate, $k_B[\text{B}][\text{H}_2\text{O}]^n[\text{S}]^m$ dominates the rate equation. General acid catalysis for the hydrolysis reaction was not found. Plotting the observed rate constant versus the concentration of acetic acid showed no correlation. The observed rate of reaction was found to be dependent only upon the acetate anion concentration. Under these conditions, Equation 4 may be simplified to

$$\frac{-d[\text{S}]}{dt} = k_{\text{obsd}}[\text{S}], \quad (6)$$

where $k_{\text{obsd}} = k_B[\text{B}]$. Integrating Equation 6 gives

$$\ln[\text{S}] = -k_{\text{obsd}}t + \ln[\text{S}_0], \quad (7)$$

where t is the reaction time and $[\text{S}_0]$ is the initial concentration of the silane.

The observed rate constants for the hydrolysis of the vinyltrialkoxysilanes were obtained from the slopes of $\ln[\text{S}]$ versus time plots. The correlation coefficients

Table 1.

The base-catalyzed rate constants for the hydrolysis of vinylsilanes in aqueous acetone at 22 °C

Silane	k_B ($M^{-1} s^{-1}$)
Vinyltrimethoxysilane	5.2×10^{-4}
Vinyltriethoxysilane	2.6×10^{-5}
Vinyltripropoxysilane	7.9×10^{-6}
Vinyltri-2-propoxysilane	7.6×10^{-7}
Vinyltris-(3-oxabutoxy)silane	2.6×10^{-4}

The base catalyst was acetate anion and pH* was equal to 7.13.

were generally greater than $r^2 = 0.98$. The second-order rate constants (k_B) were obtained from the slopes of the plots of k_{obsd} versus acetate anion concentration. The results are reported in Table 1.

The rates of hydrolysis of the vinyltrialkoxysilanes are affected strongly by the alkoxy groups that are attached to the silicon atom. Vinyltrimethoxysilane was found to hydrolyze 675 times faster than vinyltri-2-propoxysilane. The steric and inductive effects of the alkoxy groups contribute to the overall rate of hydrolysis. However, determining the quantitative contribution of each effect is not straightforward because polar substituent constants (σ^*) and steric substituent constants (E_s) do not exist for alkoxy groups.

3.3. Polar effects

The Taft equation is often used to make an estimate of the magnitude of these polar and steric effects on chemical reactions [9]. The Taft equation is [9]

$$\log k/k_0 = \rho \Sigma \sigma^* + s \Sigma E_s, \quad (8)$$

where σ^* and E_s are the polar and steric substituent constants, respectively. ρ and s are coefficients that measure the contribution of the polar and steric effects, respectively.

Ballinger and Long were able to correlate the acid ionization constants for a series of primary alcohols with the polar substituent constants of the R groups attached to primary alcohols, RCH_2OH , using a Taft equation [10]. The correlation between the polar substituent constant and the pK_a values for a series of primary alcohols was

$$pK_a = 1.4\sigma^*, \quad (9)$$

where σ^* is the polar substituent constant for the R group. Using a similar approach, the polar substituent constants can be used to define a new constant for the alkoxy group $R^I R^II R^III CO-$, where the R's represent hydrogen or an alkyl group attached to the carboxy group. The new polar substituent constant, $\sigma^{*'}$, can be calculated by simply adding the individual polar substituent constants for the R

groups surrounding the carbinoxy group, as shown in Equation 10.

$$\sigma^{*'} = \sigma_R^{*I} + \sigma_R^{*II} + \sigma_R^{*III}, \quad (10)$$

where σ_R^{*I} , σ_R^{*II} and σ_R^{*III} represent the individual polar substituent constants for R^I , R^{II} and R^{III} , respectively, that was determined previously by Taft [11, 12]. The polar substituent constants for the alkoxy groups used in this study were calculated using Equation 10. Using this approach, the polar substituent constant for the 1,1-dimethylethoxy group, $(CH_3)_2CH-$, is zero. Therefore, the reference reaction for silane hydrolysis will be the hydrolysis of vinyl tris-(1,1-dimethylethoxy)silane.

3.4. Steric effects

Since the reference reaction is the hydrolysis of vinyl tris-(1,1-dimethylethoxy)silane, the steric substituent constant for the 1,1-dimethylethoxy group is set at zero. However, steric substituent constants do not exist for the other alkoxy groups. Steric substituent constants exist only for alkyl groups. The steric bulk of the alkoxy groups, $RO-$, can be estimated by using $R'CH_2-$ groups. Although oxygen with its lone pair of electrons is sterically more bulky than the methylene group, this difference should lead to a constant error. The error introduced by assuming the same steric bulk for the oxygen atom and the methylene group will affect the steric bulk of all the alkoxy groups to the same extent. Therefore, this constant error essentially will be eliminated because all the hydrolysis rate constants are normalized to the referenced reaction, the hydrolysis of vinyl tris-(1,1-dimethylethoxy)silane. The coefficient in the Taft equation is, therefore, a good estimate of the influences of steric bulk on reaction rate. Because the alkoxy group of the reference reaction is 1,1-dimethylethoxy, rather than the more commonly used hydroxy, an adjustment in the steric factors E_s was made. (The constant E_s for the $H-CH_2-$ group is zero. The $H-CH_2-$ is a model of the steric bulk for $H-O-$). The adjustments in the steric substituent constants E_s are made using the equation:

$$E'_s = E_s + 1.74. \quad (11)$$

The redefined polar and steric substituent constants for the alkoxy groups used in this study are given in Table 2.

Table 2.

The redefined steric and polar substituent constants for the alkoxy groups used to correlate the rate constants for silane hydrolysis with the Taft equation

Alkoxy group, $R^I R^{II} R^{III} CO-$	Steric substituent constant, E'_s	Polar substituent constant, $\sigma^{*'} $
CH_3O-	1.67	1.47
CH_3CH_2O-	1.38	0.980
$CH_3CH_2CH_2O-$	1.35	0.88
$CH_3OCH_2CH_2O-$	1.34	1.58
$(CH_3)_2CHO-$	0.81	0.49