

ORGANOSILICON COMPOUNDS. XCII.*

THE EFFECT OF STRUCTURE OF SOME ORGANOSILICON THIOLS ON THE RATE OF THEIR ADDITION TO PHENYL ISOCYANATE

J. HETFLEJŠ, L. SVOBODA, M. JAKOUBKOVÁ and V. CHVALOVSKÝ

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, Prague-Suchbátol 2*

Received November 23rd, 1971

A kinetic study was made of the addition of alkylsilyl-substituted thiols $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{SH}$ ($n = 1-4$) and siloxysilyl-substituted thiols $[(\text{CH}_3)_3\text{SiO}]_{3-n}(\text{CH}_3)_n\text{SiCH}_2\text{SH}$ ($n = 1-3$) to phenyl isocyanate catalysed with triethylamine. It was found that the reaction is first order in the reactants and the catalyst. In harmony with the proposed mechanism, the reactivity of the trimethylsilyl-substituted thiols decreased with decreasing influence of the +I effect of trimethylsilyl group. An enhanced reactivity of the siloxysilyl-substituted thiols is discussed in terms of possible interaction of the tertiary amine with the silicon atom.

As a continuation of our study of the effect of structure on the reactivity of organofunctional derivatives of silicon¹, in the present work we have examined the relationship between the structure and the reactivity of some silyl-substituted thiols in their addition to phenyl isocyanate catalysed with triethylamine. This study was initiated by two circumstances: 1. Although in so far few works devoted to the addition of thiols to aryl isocyanates the kinetic course of the reaction²⁻⁴, the effects of reaction products³, solvent polarity⁴, and the basicity of a tertiary amine were established and the role of steric factors was recognized, it is still difficult to evaluate the role of electronic structure of substituents⁴. 2. In so far the only work concerned with the addition of silyl-substituted thiols to phenyl isocyanate, Mironov and Pogonkina found⁵ that the relative reactivity of the thiols $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{Si}(\text{CH}_2)_n\text{SH}$ ($n = 1-3$) (determined by the method of competition reactions and related to 1-butanethiol) increases with increasing distance between the substituent and the reaction centre (curve 3, Fig. 1). This reactivity order, which was unexpected and was at variance with widely accepted views about transmission of polar effects through aliphatic chain⁶, has not been explained. An enhanced reactivity of (3-thiopropyl)diethylmethylsilane ($n = 3$) ($k_{\text{rel}} = 4.85$) was even more surprising, since in a study of the addition of analogous silyl-substituted alcohols to phenyl isocyanate it was observed that the inductive effect of trimethylsilyl group in position 3 to hydroxyl group practically did not influence the reaction centre^{1,5}.

As model compounds, we have chosen a series of trimethylsilyl-substituted alkanthiols of the type $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{SH}$ ($n = 1-4$), with the aim of reducing the influence of steric effect of the substituent on the reactivity of studied compounds. Trimethylsilyl group, which is less sterically demanding than tert-butyl group⁷, has

* Part XCI: This Journal 37, 3885 (1972).

great positive inductive effect⁸. In view of a potential use of silyl-substituted thiols as cross-linking agents in producing silicone polymers⁹ it was also of interest to determine the reactivity of the thiomethyl group bonded to siloxane polymer units of varying functionality. For this purpose we prepared a series of trimethylsilyloxy-substituted thiols of the type $[(\text{CH}_3)_3\text{SiO}]_n(\text{CH}_3)_{3-n}\text{SiCH}_2\text{SH}$ ($n = 1-3$). To evaluate the influence of the catalytic activity of reaction products as well as to ascertain whether the mechanism of the reaction is dependent on the structure of studied compounds, in contradistinction to the Soviet authors⁵, we have followed the reaction kinetically, measuring the consumption of phenyl isocyanate with the use of the titrimetric method suggested by Stagg¹⁰.

EXPERIMENTAL

Purity of all compounds was checked by gas chromatography. Temperature data are uncorrected.

Compounds Studied

n-Butanethiol (*I*) (b.p. 93–96°C, n_D^{25} 1.4401; lit.¹¹ n_D^{25} 1.44014) was prepared in the usual way¹². Trimethylsilyl-methanethiol (*II*) was obtained in 56% by reaction of (thiocyanomethyl)-trimethylsilane with propylmagnesium bromide¹³; b.p. 114–114.5°C, n_D^{20} 1.4492 (lit.¹³ b.p. 116.3°C, n_D^{20} 1.4500). (2-Trimethylsilyl)ethanethiol (*III*) was prepared¹⁴ by a radical addition of thioacetic acid to vinyltrimethylsilane and subsequent methanolysis of the formed 2-(S-thioacetoxy)ethyltrimethylsilane. The product had b.p. 49–50°C/28 Torr and n_D^{20} 1.4542 (lit.¹⁵ gives b.p. 62–63°C/43 Torr and n_D^{20} 1.4540).

(3-Trimethylsilyl)propanethiol (*IV*). To 125 ml of KHS solution in 96% aqueous ethanol (obtained from 30 g (0.375 mol) of KOH and gaseous hydrogen sulphide) were added with stirring 20 ml (17 g, 0.115 mol) of (3-chloropropyl)trimethylsilane¹⁶ over a 30 min period and then the reaction mixture was kept at mild reflux for another 2 h, with permanent introduction of stream of hydrogen sulphide. Then the content was acidified with conc. HCl and the ethanol was removed by distillation through a short column. The organic layer was separated and the residue was washed with three 50 ml portions of ether. After removal of the ether, the condensed extract and the organic layer were combined and the so obtained crude thiol was dried over calcium oxide and distilled from Hickman flask. The yield was 7.32 g (42.9%). The product had b.p. 162–166°C, n_D^{20} 1.4550 (lit.¹³ gives b.p. 164.2°C/751 Torr, n_D^{20} 1.4539).

(4-Trimethylsilyl)butanethiol (*V*). To a refluxed mixture of 40 ml (29.6 g, 0.22 mol) of 3-butenyltrimethylsilane¹⁷ and 0.1 g of recrystallized azo-bis-isobutyronitrile was slowly added with stirring a mixture of 13 ml (13.9 g, 0.183 mol) of pure thioacetic acid (obtained by distillation of commercial product (Lachema, Brno) as the fraction boiling 87–93°C, n_D^{20} 1.4645 (lit.¹⁸ n_D^{20} 1.4648)) and 0.1 g of the radical initiator. After the addition was complete, the reaction mixture was refluxed for another 3 h. Distillation through a 20 TP column afforded 29.8 g (79%) of 4-(S-thioacetoxy)-butyltrimethylsilane, b.p. 68°C/5 Torr, n_D^{20} 1.4648. For $\text{Si}_1\text{C}_9\text{H}_{20}\text{O}_1\text{S}$ (240.4) calculated: 52.58% C, 9.86% H; found: 52.63% C, 9.69% H. A mixture of 28.8 g (0.141 mol) of 4-(S-thioacetoxy)butyltrimethylsilane, 0.05 g of sodium metal and 28 ml (0.70 mol) of anhydrous methanol was heated under nitrogen for 4 h to the boiling point. After removal of the methanol the mixture was distilled under reduced pressure through a 20 TP column to give 11.1 g (48%) of (4-trimethylsilyl)butanethiol, b.p. 95°C/25 Torr, n_D^{20} 1.4562. For $\text{Si}_1\text{C}_8\text{H}_{18}\text{S}$ (162.4) calculated: 51.78% C, 11.18% H; found: 51.78% C, 11.01% H.

(*Trimethylsilyloxydimethylsilyl*)methanethiol (VI) was prepared by a modified procedure to the synthesis reported by Cooper¹⁹. Sodium (18.4 g, 0.76 mol) was dissolved in 250 ml of anhydrous methanol and then hydrogen sulphide was introduced into the mixture for 2 h. Then a solution of 150 g (0.76 mol) of (chloromethyl)pentamethyldisiloxane²⁰ in 300 ml of light petroleum was slowly added with stirring and maintaining the mixture under an atmosphere of hydrogen sulphide. After heating the reaction mixture to 50°C for 5 h, the salts were removed by filtration, the filtrate was made neutral, and the organic layer was separated and dried over anhydrous magnesium sulphate. Distillation through a 20TP column yielded 11.6 g (76.5%, lit.¹⁹ 51%) of the product; b.p. 161–162°C, n_D^{20} 1.4312 (lit.¹⁹ n_D^{20} 1.4308).

Bis(trimethylsiloxy)silylmethanethiol (VII) was prepared as compound VI, except that hexamethyldisiloxane was used in place of light petroleum and the reaction mixture was heated to 70°C for 5 h. The product had b.p. 95°C/13 Torr, n_D^{20} 1.4225 (34% yield). For $\text{Si}_3\text{C}_8\text{H}_{24}\text{O}_2\text{S}$ (268.5) calculated: 11.9% S; found: 11.6% S. An attempt at preparing this compound by the procedure used by Mironov and Pogonkina¹³ in the synthesis of alkylsilylalkanethiols has failed. No formation of the thiocyno derivative was observed on heating a solution of 30 g (0.1 mol) of bis(trimethylsiloxy)(chloromethyl)methylsilane and 38.5 g (0.4 mol) of KSCN in 250 ml of anhydrous methanol to 60°C for 10 h.

Tris(trimethylsiloxy)silylmethanethiol (VIII). A) Attempted alkylation of NaHS: Using the procedure described in the preparation of the bis-siloxy derivative, 6.72 g of the fraction boiling 112–120°C/12 Torr was obtained from 75 g (0.2 mol) tris(trimethylsiloxy)chloromethylsilane, which according to chromatographic analysis consisted of two compounds. A compound with the shorter elution time (on 14% silicone elastomer E-301 on Celite), which formed 65% of the mixture, corresponded according to elemental analysis to the desired product. For $\text{Si}_4\text{C}_{10}\text{H}_{30}\text{O}_3\text{S}$ (343.2) calculated: 35.18% C, 8.72% H; found: 35.28% C, 8.44% H. A compound with the longer retention time, which was contaminated by small amount of the other derivative, was not fully characterized. According to elemental analysis and m.w. it might be bis(trimethylsiloxy)bis-(thiomethyl)silane. For $\text{Si}_3\text{C}_8\text{H}_{24}\text{O}_2\text{S}_2$ (300.6) calculated: 31.97% C, 8.04% H; found: 32.64% C, 7.65% H. M.w. 310 was determined osmotically. B) Preparation by the xanthate method: To a mixture of 24.4 g (0.15 mol) of potassium ethylxanthate²¹ and 200 ml of dry acetone kept at mild reflux, 25.5 g (0.1 mol) of tris(trimethylsiloxy)chloromethylsilane were added with stirring over 0.5 h and the reaction mixture was refluxed for 10 h. The precipitate, potassium chloride, was removed by filtration, the acetone was evaporated under reduced pressure and to the solid residue, 30 ml of ethylenediamine were added and the reaction mixture was maintained at 30°C for 5 h. The content of the flask was left aside for 4 days, then it was shaken with 2×10 ml of water, the organic layer was separated and dried over sodium sulphate. A vacuum distillation afforded 3.5 g (10%) of the desired product, b.p. 112°C/12 Torr, n_D^{20} 1.4229, which was chromatographically pure and its retention time corresponded to the product obtained by the procedure A.

Reaction of Thiols VI–VIII with Phenyl Isocyanate

A thiol (1–2 g) was weighed to a drop-like flask, 5 ml of toluene solution of triethylamine (conc. $4 \cdot 10^{-2}$ M) and appropriate volume of toluene solution of phenyl isocyanate (conc. 0.25 M) were added, and the reaction mixture was after shaking allowed to stand at ambient temperature for 10 days. Then the toluene and the unreacted starting materials were partly evaporated in a stream of dry nitrogen at 40–50°C. The residual oily liquid was evaporated at 1 Torr and 50°C to constant weight, which took as a rule 35–50 h. The weight of the so obtained evaporation residue corresponded in all cases to the conversion of starting compounds to thiourethanes higher than 97%. The oily product was crystallized from toluene with 91–93% yield. Elemental analyses of the so prepared thiourethanes agreed with calculated data.

Kinetic Measurements

Chemicals. Acetone was dried by standing over a 4 Å molecular sieve for 2 days and distilled. Toluene was distilled from sodium, the content of water determined by Carl Fischer method amounted to $9 \cdot 10^{-3}$ mg H_2O/ml . Di-*n*-butylamine was dried in the usual manner² and distilled. Triethylamine was dried over solid potassium hydroxide pellets, boiled with small amount of phenyl isocyanate and then fractionated under nitrogen (b.p. 88°C, n_D^{20} 1.4005; lit.^{2,22} n_D^{20} 1.4003). Phenyl isocyanate was distilled under reduced pressure from P_2O_5 in a weak stream of nitrogen; the fraction boiling 56°C/20 Torr, n_D^{20} 1.5370 (lit.²³ 1.5370) was used in measurements. Studied thiols were stored over a 4 Å molecular sieve in a nitrogen atmosphere.

Procedure. The reaction vessels were 25 ml ground volumetric flasks. Each set consisted of 9 flasks. Each flask was charged with 5 ml of the solution of a thiol and triethylamine in toluene and the contents were warmed up to 25°C for 15 min, using a water bath the temperature of which was maintained constant within 0.05°C. Then 5 ml of the toluene solution of phenyl isocyanate were added to each flask, the contents were quickly shaken, and the flasks placed again in a water bath. In appropriate time intervals the flasks were removed from the bath and their content was introduced to 100 ml. titration flasks containing 25 ml of 0.053M solution of di-*n*-butylamine in acetone. The contents were stirred for 3–5 min, to effect the complete reaction of the residual phenylisocyanate with di-*n*-butylamine. The course of the studied reaction was followed on the basis of the consumption of phenyl isocyanate, which was determined by modified Stagg method². The unreacted di-*n*-butylamine was determined by titration with 0.3M hydrochloric acid on bromophenol blue as indicator. Before commencing the kinetic run the concentration of the dibutylamine solution was twice checked by titration. Two titrations were also made to determine a systematic error due to nonequivalency of molar amounts of the phenyl isocyanate and dibutylamine in time $t = 0$. The average value was then subtracted from the values found in the chosen time intervals. After this correction, the amount (in mol) of the hydrochloric acid consumed corresponded to the amount of the unreacted phenyl isocyanate. This procedure was repeated also after the completion of the kinetic run. The concentrations of the thiols, phenyl isocyanate, and triethylamine used in individual measurements are given in Table I. The value of the rate constant k_{rel} was calculated from experimental data with the use of the second-order rate equation derived for the equal concentration of the reactants (Eq. (1)),

$$k_{exp} = 1/t - x/c(c - x) \quad (1)$$

where c is the initial concentration of the thiol or of phenyl isocyanate and x is the concentration of these compounds in time t , since in majority of kinetic runs the concentrations of both reactants were the same within experimental errors. This relation was employed also in a few cases where the phenyl isocyanate concentration a was by about 10–15% higher than the thiol concentration b . On using the rate equation derived for different initial concentrations of reactants (Eq. (2))

$$k_{exp} = \frac{1}{t} \cdot \frac{2.303}{a - b} \log \frac{b(a - x)}{a(b - x)}, \quad (2)$$

we found that the error in determination of the initial concentrations resulted in a great increase of the relative error in the difference $a - b$ and by it also in the determination of the rate constant k_{exp} . With the use of statistical relations for the error of the function²⁴ we verified that also in these cases the relation (1) can be used to calculate k_{exp} , providing that the arithmetic mean of the initial concentrations of both compounds is taken as the concentration c . The rate constants obtained by the least-squares method are listed in Table I.

TABLE I
Addition of Thiols I—IX to Phenyl Isocyanate Catalysed by Triethylamine at $25 \pm 0.05^\circ\text{C}$

Thiol	$(\text{RSH}) \cdot 10^2$ mol/l	$(\text{C}_6\text{H}_5\text{NCO}) \cdot 10^2$ mol/l	$[(\text{C}_2\text{H}_5)_3\text{N}] \cdot 10^4$ mol/l	k_{exp} $\text{l mol}^{-1} \text{s}^{-1}$	k_2 $\text{mol}^{-2} \text{s}^{-1}$	k_{rel}
$\text{CH}_3(\text{CH}_2)_3\text{SH (I)}$	12.6	12.6	14.3	20.0	1.31 \pm 0.09	1
	12.4	12.0	20.3	24.9		
	12.5	12.0	40.6	53.1		
$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_2\text{SH (II)}$	11.4	12.0	6.5	11.8	1.79 \pm 0.10	1.37 \pm 0.17
	11.4	12.0	6.5	11.0		
	12.0	12.6	23.6	43.9		
$(\text{CH}_3)_3\text{Si}((\text{CH}_2)_2\text{SH (III)})$	12.1	12.1	12.4	15.0	1.26 \pm 0.05	0.96 \pm 0.10
$(\text{CH}_3)_3\text{Si}((\text{CH}_2)_3\text{SH (IV)})$	12.6	12.6	13.5	17.2	1.30 \pm 0.03	0.99 \pm 0.09
$(\text{CH}_3)_3\text{Si}((\text{CH}_2)_4\text{SH (V)})$	10.2	12.2	12.4	17.8	1.38 \pm 0.05	1.05 \pm 0.11
	11.2	12.2	24.9	33.3		
$[(\text{CH}_3)_3\text{SiO}](\text{CH}_2)_2\text{SiCH}_2\text{SH (VI)}$	10.7	12.1	22.4	55.5	2.18 \pm 0.04	1.66 \pm 0.14
	12.2	12.8	25.9	58.2		
$[(\text{CH}_3)_3\text{SiO}]_2(\text{CH}_3)_2\text{SiCH}_2\text{SH (VII)}$	12.3	12.4	23.6	54.0	2.25 \pm 0.04	1.72 \pm 0.15
	12.3	12.4	25.9	55.0		
$[(\text{CH}_3)_3\text{SiO}]_3\text{SiCH}_2\text{SH (VIII)}$	10.8	12.2	12.4	16.6	1.28 \pm 0.06	0.98 \pm 0.11
	12.0	12.2	24.9	30.6		

IR Measurements

Infrared spectra of studied compounds were recorded on a double beam Zeiss (Jena), Model UR-20, spectrophotometer in the regions $850\text{--}400\text{ cm}^{-1}$ (KBr prism), $1650\text{--}650\text{ cm}^{-1}$ (NaCl prism) and $4000\text{--}1600\text{ cm}^{-1}$ (LiF prism). The spectra of the compounds *in substantia* were measured in composed KBr cells, in the region around 2600 cm^{-1} in 0.6 cm thick NaCl cells. The spectra of binary mixtures thiol/triethylamine and ternary mixtures thiol/N,N-dimethylformamide/tetrachloromethane were measured in the same region in 0.1 cm thick NaCl cells.

RESULTS AND DISCUSSION

Before commencing a kinetic study of the reaction it was necessary to verify whether its course is not complicated by the formation of side products. As the additions of simple alkanethiols to phenyl isocyanate were already shown to give practically quantitative yields (in average 99%) of corresponding thiourethanes², we analysed products only in the case of trimethylsilyloxysilyl-substituted derivatives VI–VIII. We found that also here the thiourethanes are formed in high yields.

Another factor which would complicate the discussion of rate data in terms of structure effects is the fact that the experimental rate constant k_{exp} can be generally of the form³:

$$k_{\text{exp}} = k_0 + k_{\text{P}}(\text{product}) + k_{\text{BP}}(\text{base})(\text{product}) + k_{\text{B}}(\text{base}), \quad (3)$$

where k_0 is the rate constant of spontaneous reaction, k_{B} and k_{P} are rate constants of the reaction catalysed by the tertiary amine and the product, respectively, and k_{BP} is the rate constant of the base-product-catalysed reaction. Preliminary experiments showed that with studied thiols the spontaneous reaction rate was negligible. In this connection it is worthy of note that the rate constant k_0 was introduced to the relation (3) on the basis of the analogy with reactions of alcohols with phenyl isocyanate, although addition reactions of simple organic thiols have not yet been observed^{2–4} to occur under such mild conditions (the spontaneous reaction of thiols with phenyl isocyanate proceeds at relatively high temperatures²⁵). The effect of the product- and the base-product-catalysed reaction was eliminated by calculating k_{exp} only from the experimental data which fitted the second-order kinetic equation employed. In addition, we have found that in case of trimethylsilyloxysilyl-substituted thiols the addition of equimolar amounts of products at the beginning of the reaction changes the reaction rate only within experimental errors. Under these conditions k_{exp} can be therefore identified with the rate constant of the tertiary amine-catalysed reaction, k_{B} .

Kinetic measurements were carried out at $25 \pm 0.05^\circ\text{C}$ with practically equimolar concentrations of both reactants (Table I). With all the studied compounds the reaction course was well described by the second-order equation at least to 60% conversion. The experimental data for higher conversions deviated from the calculated

curve in a non-systematic fashion. Table I further shows that in all cases k_{exp} is linearly dependent on the catalyst concentration. From kinetic viewpoint the reaction of the silyl-substituted thiols is analogous to the reaction of aliphatic thiols²⁻⁴; it is a third-order reaction, the first order in each reaction component. From the average values of the third-order rate constants k_3 and relative rate constants, k_{rel} , related to n-butanethiol as standard (Table I), it is further obvious that the employed procedure enabled to determine these quantities with sufficient accuracy.

The observed order of relative reactivities of trimethylsilyl-substituted thiols II-V differs from that found in a study of similar series of silylalkanethiols by Mironov and Pogonkina⁵ (compare curves 1 and 3 in Fig. 1). In this study relative rate constants were determined by the procedure based on the competition reaction with phenyl isocyanate of the couple n-butanethiol-a silyl-substituted thiol, the relative rate constants being calculated from the content of silicon in the mixture of products, obtained by evaporating unreacted starting compounds with successive crystallization of the products. The above-mentioned discrepancy might be due to the fact that to a perfect evaporation of the unreacted substances substantially longer time is needed than that used by the authors⁵. Especially the higher silyl-substituted thiols could contaminate the analysed sample, which would result in an increase of the content of silicon and thus account for increased values of the rate constants. In fact, we have found that, for instance, in the isolation of 3-trimethylsilylpropanethiocarbamate the constant weight of the sample is attained at 70°C and 2 Torr after 50 h, while the Russian authors used only 5 h at 70–80°C.

As follows from Fig. 1 and Table I, except trimethylsilylmethanethiol (I), the reactivity of the other thiols is within experimental errors comparable with the reactivity of the standard, n-butanethiol. A similar decrease of the reactivity with increasing number of the methylene groups between the substituent and the reaction centre was already observed in a study of the reactivity of trimethylsilyl-substituted alcohols in their uncatalysed reaction with phenyl isocyanate^{1,5} (curve 2 in Fig. 1, cf.⁵). This trend was ascribed to a progressive decrease of the nucleophilicity of the reaction

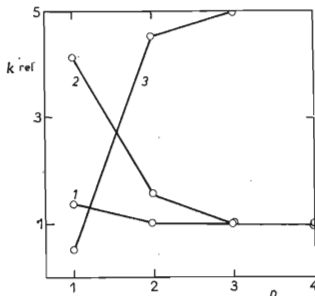
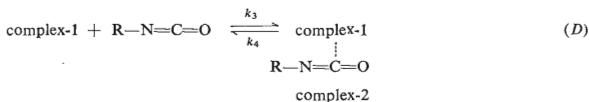
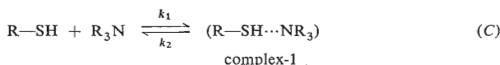
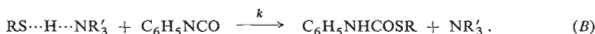
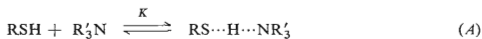


FIG. 1

Relative Rate Constants k_{rel} of the Addition of Thiols $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{SH}$ (1), Alcohols $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OH}$ (2) and Thiols $(\text{C}_2\text{H}_5)_2\text{CH}_2\text{Si}(\text{CH}_2)_n\text{SH}$ (3) to Phenyl Isocyanate

The values of k_{rel} for the alcohols are related to n-butanol, those for the thiols to n-butanethiol.

centre with decreasing action of the +I effect of the trimethylsilyl group. In contrast to the alcohols, with the thiols the activating effect of the trimethylsilyl group is less pronounced [$k_{rel}((CH_3)_3SiCH_2OH) = 4.15$ (with respect to *n*-butanol¹), $k_{rel}((CH_3)_3SiCH_2SH) = 1.37$; $k_{rel}((CH_3)_3SiCH_2CH_2OH) = 1.60$ (lit.¹), $k_{rel}((CH_3)_3SiCH_2CH_2SH) = 0.96$]. It seems probable that this fact is the consequence of different mechanisms of the two reactions. While the reaction of alcohols with phenyl isocyanate is obviously an one-step process^{2,6}, we believe that the reaction of thiols proceeds in two stages (A, B):



$$\frac{d[RNHCOSR]}{dt} = \frac{k_1 k_3 k_5 [R_3N/R-NCO] [R-SH]^2}{(k_2 + k_3[R-NCO]) (k_4 + k_5[R-SH])} \quad (4)$$

In a study of the reaction of thiols with isocyanate Iwakura and Okada⁴ suggested the mechanism involving three steps, the last being rate determining (Eqs (C)–(E)). The evidence offered by the authors in support of this mechanism is not however convincing. On assuming steady-state concentration of intermediate products, the authors derived the rate equation (4). In order to bring the observed first order in the reaction components to agreement with the derived rate equation, the authors further assumed that $k_2 \gg k_3[R-NCO]$ and $k_4 \ll k_5[R-SH]$. Under these conditions, however, the equation (E) cannot be rate determining, as assumed by the authors, since the rate constant for this step does not appear in the expression for the experimental rate constant k_{exp} ($k_{exp} = k_1 k_3 / k_2$). For this reason also the statement of the authors⁴ that the observed increase of the reaction rate with increasing ionising power of the solvent indicates that the rate-determining step is represented by equation (E) is questionable.

The two-step mechanism suggested in the present work is in harmony with the observed first order in reaction components. The equilibrium formation of the complexes

between amines and thiols in the first step of the reaction is not improbable, because such complexes were already observed by Gordy and Stanford²⁷. The second, rate-determining step involves a nucleophilic attack on the electron-deficient carbon atom of phenyl isocyanate by the sulphur atom and the transfer of the hydrogen of the S—H bond on the neighbouring, more basic nitrogen atom. At present it cannot be decided whether and to what extent these processes are synchronous. The observed decrease of the reactivity with increasing distance between the silyl group (which by its strong +I effect increases electron density on the reaction centre) and the reaction centre indicates that, similarly to the reaction of alcohols, also here the nucleophilicity of the reaction centre (the sulphur atom) is the predominant factor. In view of the greater polarisability of the sulphur in comparison with the oxygen it could be expected that substituent effects will affect the reactivity of the thiols more than the reactivity of analogous alcohols. This should have manifested itself in a deeper decrease of the reactivity along the former series. The observed decrease of the selectivity of the reaction of the thiols is then the result of the equilibrium (A) which levels off the action of substituents.

It is obvious that for the verification of this assumption the knowledge of the values of k and K for the studied series would be of great interest. With regard to the fact that the rate constant k can be obtained only indirectly, we made an attempt to determine the values of K for the formation of the complexes between thiols III—X and triethylamine. For this purpose we first attempted to employ the method of Gordy and Stanford²⁷, who on the basis of the frequency and intensity change of the $\nu(\text{S—H})$ vibration determined equilibrium constants K for a series of purely organic thiols. This attempt has failed, however. The following of $\nu(\text{S—H})$ was made difficult by the proper absorption of triethylamine in this region and also by a relatively low intensity of the absorption band of this vibration. When the intensity was increased by using cells of greater thickness there occurred undesired overlap of this band with neighboring, much more intense bands corresponding to $\nu(\text{C—H})$. On the basis of the spectra of the studied compounds *in substantia* it can be only concluded that the position of the $\nu(\text{S—H})$ band practically does not depend on the structure of the thiols and compares well with the position of the corresponding band in *n*-butanethiol (2575 cm^{-1}). Similar difficulty has been also encountered in an attempt to determine differences in the acidity of the S—H group of these compounds by evaluating their proton-donor properties toward *N,N*-dimethylformamide. In this case we followed the work of Salinger and West²⁸, who by means of IR frequency shifts of $\nu(\text{S—H})$, induced by the added base, evaluated the acidity of some silanethiols and organic thiols. We have found that the frequency shift $\Delta\nu(\text{S—H})$ for the studied series lies within the range of $18\text{--}26 \text{ cm}^{-1}$ (Salinger and West²⁸ report for $(\text{CH}_3)_3\text{CSH}$ value $23 \pm 3 \text{ cm}^{-1}$). The observed changes in the $\Delta\nu$ values do not exceed much the experimental error in frequency determination, which makes their discussion in terms of structure effects impossible.

The rate constants for the reaction of trimethylsiloxy derivatives VI—VIII are presented in Table I. The reason for the increased reactivity of the first two members is not yet clear. It is known that compounds of the type $\text{R}_{4-n}\text{SiX}_n$ ($n = 1\text{--}4$, $\text{X} = \text{Cl, Br, J, CH}_3\text{O}$) are capable of interacting with nitrogen-containing bases to form complexes with pentavalent silicon. This ability decreases with increasing number of organic groups R and is usually difficult to prove by spectroscopic and physico-chemical

methods in derivatives with two or more organic groups. Even in this case, however, the possibility of kinetic manifestation of such an interaction cannot be ruled out. As this interaction should increase the electron density at the silicon, it could account for the above mentioned finding. The decreased reactivity of tris(trimethylsiloxy)derivative VIII could then be due to the steric effect of the three bulky trimethylsiloxy groups, which makes both the above interaction and the attack by sulphur atom more difficult.

REFERENCES

1. Pola J., Bažant V., Chvalovský V.: This Journal 37, 3885 (1972).
2. Dyer E., Glenn J. F.: J. Am. Chem. Soc. 79, 366 (1957).
3. Dyer E., Glenn J. F.: J. Org. Chem. 26, 2919 (1961).
4. Išakura J., Okada H.: Can. J. Chem. 38, 2418 (1960).
5. Mironov V. F., Pogonkina N. A.: Izv. Akad. Nauk SSSR, Otd. Chim. Nauk 1960, 1998.
6. Exner O.: Chem. listy 53, 1302 (1959).
7. Dale J.: Chem. Ber. 94, 2821 (1961).
8. Mai L. A.: Izv. Akad. Nauk Latv. SSSR, Ser. Chim. 1968, 253.
9. Bažant V., Čermák J., Dvořák M., Hetflejš J., Mareš F., Chvalovský V.: BDR Offen. 2 008 426 (1970).
10. Stagg H. E.: Analyst 71, 557 (1946).
11. Mathias S.: J. Am. Chem. Soc. 72, 1897 (1950).
12. Zinner H.: Chem. Ber. 86, 825 (1953).
13. Mironov V. F., Pogonkina N. A.: Izv. Akad. Nauk SSSR, Otd. Chim. Nauk 1956, 707.
14. Gornowicz G. A., Ryan J. W., Speier J. L.: J. Org. Chem. 33, 2918 (1968).
15. Mironov V. F., Pogonkina N. A.: Izv. Akad. Nauk SSSR, Otd. Chim. Nauk 1959, 85.
16. Mironov V. F.: Dokl. Akad. Nauk SSSR 108, 266 (1956).
17. Hauser C. R., Hauce C. R.: J. Am. Chem. Soc. 74, 5091 (1952).
18. Sommer L. H., McKay F. P., Steward O. W., Campbell P. G.: J. Am. Chem. Soc. 79, 2764 (1957).
19. Cooper G. D.: J. Am. Chem. Soc. 76, 2500 (1954).
20. Andrianov K. A., Mindlin Ja., Leznov N. S.: Dokl. Akad. Nauk SSSR 94, 873 (1954).
21. Price C. R., Stacy G. W. in Organic Syntheses, Col. Vol. III, p. 667 (1955).
22. *Handbook of Chemistry and Physics* (C. D. Hodgman, Ed.) 30th Ed. Chemical Rubber Publishing Co., Cleveland 1961.
23. Krumpholtz M.: Thesis. Czechoslovak Academy of Sciences, Prague 1969.
24. Jakovlev K. P.: *Matematické zpracování výsledků měření*. Published by SNTL, Prague 1958.
25. Petersen S.: Ann. 562, 205 (1949).
26. Entelis S. G., Nesterov O. V.: Uspechi Chim. 35, 2178 (1966).
27. Gordy W., Stanford S. C.: J. Am. Chem. Soc. 62, 497 (1940).
28. Salinger R. M., West R.: J. Organometal. Chem. 11, 631 (1968).

Translated by the author (J. H.).