

## THE REACTIONS OF ORGANOMETALLIC COMPOUNDS INVOLVING SILICON

### Reactions of Triphenyl-, Diphenylmethyl-, and Phenyl dimethylsilyl potassium with Fluorene in Tetrahydrofuran

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Triphenylsilyl potassium ( $\text{Ph}_3\text{SiK}$ ), diphenylmethylsilyl potassium ( $\text{Ph}_2\text{MeSiK}$ ), and phenyl dimethylsilyl potassium ( $\text{PhMe}_2\text{SiK}$ ) react very rapidly with fluorene in tetrahydrofuran (THF). The reactions can be followed at low temperatures using a stop-flow technique. The thermodynamic constants of activation was calculated for the reactions of organosilyl potassium ( $\text{R}_3\text{SiK}$ ) with fluorene for  $-50^\circ$ . The results were compared with the corresponding reactions of organosilyllithium ( $\text{R}_3\text{SiLi}$ ), and organosilylsodium ( $\text{R}_3\text{SiNa}$ ) with fluorene, also calculated for  $-50^\circ$ . The bimolecular rate constant  $k$  increases with the increase in radius of cation. The sequence for the  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values,  $\text{R}_3\text{SiNa} < \text{R}_3\text{SiK} < \text{R}_3\text{SiLi}$ , parallels that for the  $A$  factor. The electronic spectra of  $\text{R}_3\text{SiK}$  and 9-fluorenyl potassium were determined at temperature varying from  $+20$  to  $-80^\circ$ . The special results are in full agreement with the kinetic results, that  $\text{R}_3\text{SiK}$  compounds exist as contact ion pairs in THF and the cation plays an important role in determining the rate of these reactions.

#### INTRODUCTION

The reactions of substituted silyllithium and silylsodium with fluorene [1,2] in THF have been investigated. It was observed that the bimolecular rate constant  $k$  was higher in the case of  $\text{R}_3\text{SiNa}$ , compared with the corresponding reactions of  $\text{R}_3\text{SiLi}$ . The relative reactivity of  $\text{R}_3\text{SiLi}$  and  $\text{R}_3\text{SiNa}$  have been discussed in terms of the degree of solvation attained by these reagents in the initial and the transition states. The reactions of  $\text{R}_3\text{SiK}$  with fluorene in THF are now investigated and the results are presented in this paper.

#### EXPERIMENTAL

**Materials.** Fluorene [3], tetrahydrofuran [4] and hexaphenyldisilane [5] were purified and dried as described in the previous papers. 1,1',2,2'-tetraphenyl-1,2-dimethyldisilane and 1,2-diphenyl-1,1',2,2'-tetramethyldisilane were prepared by the reaction of sodium with the respective chlorosilane as described by Gilman *et al.* [6] and purified as described earlier [5].  $\text{Ph}_3\text{SiK}$ ,  $\text{Ph}_2\text{MeSiK}$  and  $\text{PhMe}_2\text{SiK}$  were prepared by the cleavage of the corresponding symmetrical disilanes with potassium in THF using a method similar to that described for the organosilyllithium compounds [7].

**Spectral Measurement.** The electronic spectra of  $\text{R}_3\text{SiK}$  and 9-fluorenyl potassium were determined at temperatures varying from  $20$  to  $-80^\circ$  using the same technique as described for 9-phenylfluorene-9-yl-lithium in the previous papers [5].

**Kinetic Measurements.** The reactions of  $\text{R}_3\text{SiK}$  with fluorene in THF were studied using the stop-flow technique, by following the changes in optical density with time at  $470\text{ nm}$  which is one of the absorption peaks of the product, 9-fluorenyl potassium. The order of reaction in  $\text{R}_3\text{SiK}$  and fluorene was

determined using a procedure similar to that described for the reactions of organosilyllithiums with 9-phenylfluorene [5].

#### RESULTS

**Spectra.** The spectra of  $\text{R}_3\text{SiK}$  determined at  $20^\circ$  are shown in Fig. 1. The position of maximum absorption is  $363\text{ nm}$  for both  $\text{Ph}_3\text{SiK}$  ( $\epsilon_{\lambda\text{ max}} 1.28 \times 10^4$ ) and  $\text{Ph}_2\text{MeSiK}$  ( $\epsilon_{\lambda\text{ max}} 1.06 \times 10^4$ ) with shoulders at  $262$  and  $255\text{ nm}$  respectively. The spectrum of  $\text{PhMe}_2\text{SiK}$  is very broad and it is difficult to locate the absorption maximum in this case, the principal absorption maximum is, however, designated at  $340\text{ nm}$  ( $\epsilon_{\lambda\text{ max}} 7.6 \times 10^3$ ) with a shoulder at  $275\text{ nm}$ . The positions of absorption maxima and the values of extinction coefficients for these spectra do not change as the temperature is reduced to  $-80^\circ$ .

The product of the reaction between  $\text{R}_3\text{SiK}$  and fluorene in THF, 9-fluorenyl potassium gave a spectrum with absorption maxima at  $470$  ( $\epsilon_{\lambda\text{ max}} 1.5 \times 10^3$ ) and  $500\text{ nm}$  ( $\epsilon_{\lambda\text{ max}} 1.08 \times 10^3$ ) and a shoulder at  $520\text{ nm}$ . The spectrum of 9-fluorenyl potassium also remained unaltered at reduced temperatures.

**Kinetics** The rates of reaction of  $\text{R}_3\text{SiK}$  with fluorene in THF were measured at  $-50^\circ\text{C}$  to investigate the order of reaction. The order of reaction found from the dependence of initial rate on initial reactant concentration was  $1.01 \pm 0.02$  for  $\text{R}_3\text{SiK}$ , and  $1.01 \pm 0.03$  for fluorene (Tables 1 and 2). The overall order of reaction found on the analysis of the optical density vs. time curve was 2 for at least 90% of the reaction (Fig. 2). The  $\text{R}_3\text{SiK}$  reactions with fluorene in THF may be considered as irreversible under the experimental conditions used.

The activation energy and the  $A$  factor were determined from the change in rate constant of reaction over the temperature range of  $-8$  to  $-57^\circ\text{C}$ . (Table 3.) The values found for the activation energy

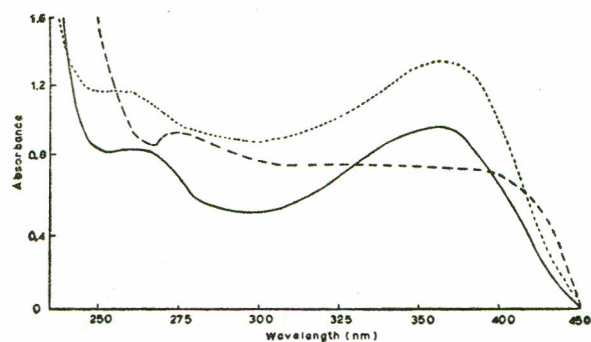


Fig. 1. Spectra of organosilylpotassium compounds in THF at 20° ————  $\text{Ph}_3\text{SiK}$  ( $7.81 \times 10^{-4} M$ ), .....  $\text{Ph}_2\text{MeSiK}$  ( $1.28 \times 10^{-3} M$ ) and - - - -  $\text{PhMe}_2\text{SiK}$  ( $1.05 \times 10^{-3} M$ ). (Path length 1 mm).

Table 1. Reaction data in THF at  $-50^\circ$

	$10^3[\text{Fluorene}]_i$ mole $l^{-1}$	$10^3[\text{R}_3\text{SiK}]_i$ mole $l^{-1}$	$k$ mole $^{-1}$ sec $^{-1}$
$\text{Ph}_3\text{SiK}$	4.21	3.82	10.8
	4.21	6.53	11.0
	4.21	9.75	11.1
	4.21	12.91	11.0
$\text{Ph}_2\text{MeSiK}$	3.12	1.82	35.5
	3.12	2.76	36.4
	3.12	4.16	36.0
$\text{PhMe}_2\text{SiK}$	3.06	2.15	32.5
	3.06	3.65	32.1
	3.06	4.78	33.0
	3.06	6.22	32.5

$$k = \frac{\text{Initial rate}}{[\text{R}_3\text{SiK}]_i [\text{Fluorene}]_i}$$

from the Arrhenius plot were 4.6, 4.3, and 4.5 kcal mole $^{-1}$  for  $\text{Ph}_3\text{SiK}$ ,  $\text{Ph}_2\text{MeSiK}$  and  $\text{PhMe}_2\text{SiK}$  reactions with fluorene in THF, respectively. For this sequence of  $\text{R}_3\text{SiK}$  the value of A factor calculated for  $-50^\circ$  were  $3.7 \times 10^5$ ,  $5.9 \times 10^5$  and  $8.2 \times 10^5$  mole $^{-1}$  sec $^{-1}$ . The thermodynamic constants of activation calculated for  $-50^\circ\text{C}$  are given in Table 4. The values quoted have the following estimated systematic errors:  $k$  and A factor  $\pm 7\%$ ,  $\Delta H^\ddagger$  and  $\Delta G^\ddagger \pm 5\%$  and  $\Delta S^\ddagger \pm 9\%$ .

**Products of Reactions.** The product analysis of the reaction between  $\text{R}_3\text{SiK}$  and fluorene was carried using the procedure similar to that described for the corresponding reactions of  $\text{R}_3\text{SiLi}$  with fluorene [1] in THF. The results were in full agreement with the previous findings [1] that only one of the 9-hydrogen atom of fluorene was replaced by the potassium atom of  $\text{R}_3\text{SiK}$ .

#### DISCUSSION

The spectra of  $\text{R}_3\text{SiK}$  reagents in THF do not give

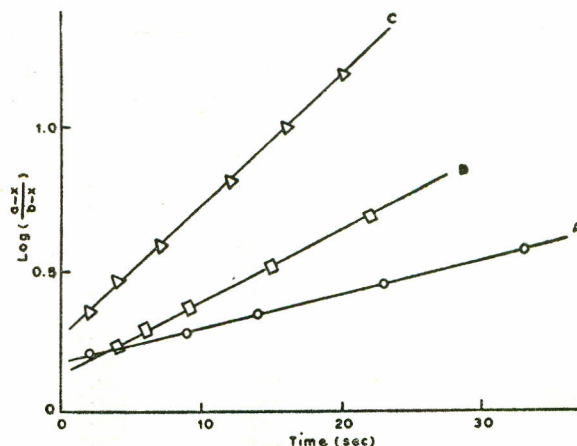


Fig. 2. The second order plots of the reactions between organosilylpotassiums and fluorene in THF at  $-50^\circ$ . A =  $\text{Ph}_3\text{SiK}$ -fluorene system:  $[\text{Ph}_3\text{SiK}]_i = 7.28 \times 10^{-3} M$ ,  $[\text{Fluorene}]_i = 4.63 \times 10^{-3} M$ ,  $k = 10.3$  l mole $^{-1}$  sec $^{-1}$ ; B =  $\text{Ph}_2\text{MeSiK}$ -fluorene system:  $[\text{Ph}_2\text{MeSiK}]_i = 5.12 \times 10^{-3} M$ ,  $[\text{Fluorene}]_i = 3.54 \times 10^{-3} M$ ,  $k = 36.4$  l mole $^{-1}$  sec $^{-1}$ , and C =  $\text{PhMe}_2\text{SiK}$ -fluorene system:  $[\text{PhMe}_2\text{SiK}]_i = 6.57 \times 10^{-3} M$ ,  $[\text{Fluorene}]_i = 3.42 \times 10^{-3} M$ ,  $k = 33.2$  l mole $^{-1}$  sec $^{-1}$ .

Table 2. Reaction data in THF at  $-50^\circ$

	$10^3[\text{R}_3\text{SiK}]_i$ mole $^{-1}$	$10^3[\text{Fluorene}]_i$ mole $^{-1}$	$k$ mole $^{-1}$ sec $^{-1}$
$\text{Ph}_3\text{SiK}$	4.93	4.08	11.0
	4.93	7.09	10.9
	4.93	9.57	11.2
	4.93	11.10	11.0
$\text{Ph}_2\text{MeSiK}$	4.79	2.13	36.3
	4.79	3.46	35.9
	4.79	5.33	36.5
	4.79	6.52	36.0
$\text{PhMe}_2\text{SiK}$	3.26	2.06	32.5
	3.26	3.52	32.7
	3.26	4.83	32.9
	3.26	6.15	32.7

any significant absorption in the wavelength region above 450 nm even for the highest concentration used in the kinetics experiments (path length 1 mm). Therefore, the rates of reactions between  $\text{R}_3\text{SiK}$  and fluorene in THF could be most conveniently measured at 470 nm wavelength, one of the 9-fluorenylpotassiums (product of reaction) highest absorption peak in the visible region.

Comparison of  $\lambda_{\text{max}}$  values of  $\text{R}_3\text{SiK}$  ( $\lambda_{\text{max}}$  363 nm) with the corresponding values of  $\text{R}_3\text{SiKNa}$  ( $\lambda_{\text{max}}$   $338.5 \pm 1.5$  nm) and  $\text{R}_3\text{SiLi}$  ( $\lambda_{\text{max}}$  335 nm) reveals that a red shift occurs in absorption maximum with the increase in radius of cation. These results are consistent with the results reported for various organometallic compounds [8-14].

Table 3. Temperature dependence of rate constants.

	Temp.	$k$ 1 mole <sup>-1</sup> sec <sup>-1</sup>
Ph <sub>3</sub> SiK	-10	55.0
	-22	33.9
	-30	26.7
	-38	18.7
	-45	13.9
	-50	11.0
Ph <sub>2</sub> MeSiK	-8	165.5
	-18	127.4
	-30	79.3
	-40	56.5
	-50	36.1
	-54	30.3
PhMe <sub>2</sub> SiK	-12	141.2
	-22	101.2
	-30	76.2
	-40	51.3
	-50	32.6
	-57	23.5

Table 4. Thermodynamic constants of activation for the reactions of R<sub>3</sub>SiK with fluorene in THF at -50°C.

	Ph <sub>3</sub> SiK	Ph <sub>3</sub> SiNa	Ph <sub>3</sub> SiLi	Ph <sub>2</sub> MeSiK
$k$ (1 mole <sup>-1</sup> sec <sup>-1</sup> )	11.0	5.7	0.3	36.1
$A$ (1 mole <sup>-1</sup> sec <sup>-1</sup> )	$3.7 \times 10^5$	$5.7 \times 10^2$	$9.2 \times 10^5$	$5.9 \times 10^5$
$\Delta H^\ddagger$ (kcal mole <sup>-1</sup> )	4.2	1.6	6.2	3.8
$\Delta G^\ddagger$ (kcal mole <sup>-1</sup> )	11.8	12.1	13.5	11.3
$\Delta S^\ddagger$ (cal mole <sup>-1</sup> deg <sup>-1</sup> )	-34.1	-47.2	-32.7	-33.4

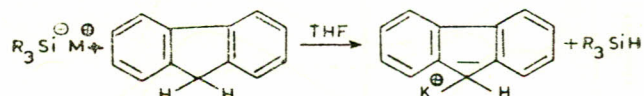
Ph <sub>2</sub> MeSiNa	Ph <sub>2</sub> MeSiLi	PhMe <sub>2</sub> SiK	PhMe <sub>2</sub> SiNa	PhMe <sub>2</sub> SiLi
13.2	0.8	32.6	..	0.8
$1.2 \times 10^5$	$6.4 \times 10^6$	$8.2 \times 10^5$	..	$3.1 \times 10^6$
1.6	6.6	4.0	..	6.3
11.7	13.0	11.3	..	13.0
-45.3	-28.7	-32.7	..	-30.0

Note. The values quoted for the corresponding reactions of organosilylsodium and organosilyllithium compounds with fluorene in THF, are also calculated for -50°.

In case of 9-fluorenyllithium [1] and 9-fluorenylsodium [2] and  $\epsilon\lambda_{\max}$  was found to increase with the decrease in temperature, which has been attributed to the transformation of contact ion-pairs into the solvent separated ion-pairs at reduced temperatures. On the other hand the position of maximum absorptions and the values of  $\epsilon\lambda_{\max}$  obtained for the spectra of 9-fluorenylpotassium at reduced temperatures were unaltered. This suggests that 9-fluorenylpotassium continues to exist in the form of contact ion-pairs in THF even at temperature as low as -80°. Similar results have been reported by Smid *et al.* [13] in their studies of contact and solvent separated ion-pairs of carbanions.

The first order kinetics found for both the reactants and overall second order kinetics for at least 90% of the reaction, together with the results, of product

analysis; indicate that the reaction under investigation is as follows.



It is seen from Table 4 that the rate constants for R<sub>3</sub>SiK are greater than those for the corresponding R<sub>3</sub>SiLi [1] and R<sub>3</sub>SiNa [2] reactions with fluorene in THF. This relative increase in the reactivity of R<sub>3</sub>SiM compounds is consistent with the fact that the increase in radius of cation enhances the reactivity of R<sub>3</sub>SiM compounds. A similar pattern of reactivity has also been reported for the reactions of triphenylsilyl-alkali metal compounds with 1,1'-diphenylethylene [8] in THF and for the anionic polymerization of styrene in dioxane [15-17], while a reverse trend was observed in THF [18-20].

The values of thermodynamic constants of activation for the reactions of R<sub>3</sub>SiK are given in Table 4, together with the corresponding values for the reactions of R<sub>3</sub>SiLi [1] and R<sub>3</sub>SiNa [2] with fluorene in THF, also calculated for -50°. The sequence for  $A$  factor,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values turns out to be, R<sub>3</sub>SiNa < R<sub>3</sub>SiK < R<sub>3</sub>SiLi. The position of R<sub>3</sub>SiLi does not fall in the right sequence. It is known, however, that R<sub>3</sub>SiLi compounds [8] exist as partially solvent separated ion-pairs, whereas the corresponding R<sub>3</sub>SiNa and R<sub>3</sub>SiK exist as contact-ion pairs in THF. These different kind of species could be responsible for the complex behaviour of R<sub>3</sub>SiM compounds.

Comparison of the values of  $\Delta H^\ddagger$  for the system involving Na<sup>+</sup> and K<sup>+</sup> cations shows that there is a marked difference in these values. It could be suggested that in R<sub>3</sub>SiNa-fluorene system, the reaction involves better solvation of the transition state rather than the initial state (9-fluorenylsodium exists as solvent separated ion-pairs in THF at reduced temperatures), resulting in lower activation enthalpy for this system. On the other hand the R<sub>3</sub>SiK-fluorene system involves equal solvation of both the initial and transition states, and results in relatively higher activation enthalpy.

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