The Reactions of Organometallic Compounds containing Silicon. Part V.[1] The Spectra of Triphenylsilyl-Lithium, -Sodium, -Potassium, -Rubidium, and -Caesium and the Reactions of these Compounds with 1,1-Diphenylethylene in Tetrahydrofuran

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We have studied the reaction of Ph_3SiM, where M is Li, Na, K, Rb, or Cs, with $CH_2{=}CPh_2$ in tetrahydrofuran. We have also examined the spectra of the reactants and reaction products. It is found that when M is Li, exceptional results are obtained both in the kinetic and in the spectroscopic experiments, and we have discussed the relationship between these two sets of data.

We have previously reported our results for the reaction of triphenylsilyl-lithium with 1,1-diphenylethylene,[2a] tetrahydrofuran,[2b] and fluorenes.[2c] Here we give results for the effect of changing the gegenion on the spectra of triphenylsilyl alkali-metal and on the thermodynamic constants of activation for the reaction of triphenylsilyl alkali-metal with 1,1-diphenylethylene.

Triphenylsilyl alkali-metal compounds were prepared and estimated as previously described.[2c] Yields were *ca.* 80% and only slightly lower than in the case of triphenylsilyl-lithium. 1,1-Diphenylethylene, distilled under reduced pressure of dry nitrogen, was further purified by adding butyl-lithium until the red colour of the $BuCH_2CPh_2Li$ appeared. Pure olefin was obtained from this by three successive distillations under high vacuum, by discarding first and final fractions. (Found: C, 93·3; H, 6·8. Calc. for $C_{14}H_{12}$: C, 93·3; H, 6·7%). Its i.r. spectrum was identical with a reference spectrum.

Kinetics.—The reaction of Ph_3SiM with 1,1-diphenylethylene showed first-order kinetics in both reagents, and an overall second-order kinetics up to at least 80% of total reaction (Figure 1). This confirms that the reaction we are studying is:

$$Ph_3\overset{-}{Si}\overset{+}{M} + CH_2{=}CPh_2 \longrightarrow Ph_3Si{\cdot}CH_2{-}\overset{-}{C}Ph_2\overset{+}{M}$$

The second-order rate constants and the thermodynamic constants of activation are shown in Table 1.

Spectra.—The solutions of the triphenylsilyl alkali-metal compound in tetrahydrofuran (THF) were deep

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[1] Part IV, A. G. Evans, M. A. Hamid, and N. H. Rees, *J. Chem. Soc.* (*B*), 1971, 2164.

[2] (*a*) A. G. Evans, M. Ll. Jones, and N. H. Rees, *J. Chem. Soc.* (*B*), 1967, 961; (*b*) A. G. Evans, M. Ll. Jones, and N. H. Rees, *J. Chem. Soc.* (*B*), 1969, 894; (*c*) A. G. Evans, M. A. Hamid, and N. H. Rees, *J. Chem. Soc.* (*B*), 1971, 1110.

TABLE 1

Thermodynamic constants of activation for the reaction between Ph_3SiM and $CH_2{=}CPh_2$ in THF at −40 °C

$Ph_3\overset{-}{Si}\overset{+}{M}$	Ph_3SiLi	Ph_3SiNa	Ph_3SiK	Ph_3SiRb	Ph_3SiCs
k (l mol^{-1} s^{-1})	4·8	45·8	139	169	250
$\Delta G^‡$ (kcal mol^{-1})	12·8	11·8	11·2	11·2	11·0
$\Delta H^‡$ (kcal mol^{-1})	3·4	0·97	3·16	4·76	5·62
$\Delta S^‡$ (cal deg^{-1} mol^{-1})	−40·3	−46·3	−34·7	−27·4	−23·0

yellow for sodium, dark amber for potassium, orange for rubidium, and reddish brown for caesium. The u.v./visible spectra of these compounds are shown in Figure 2, and the values of $\lambda_{max.}$ and $\varepsilon_{max.}$ are given in Table 2.

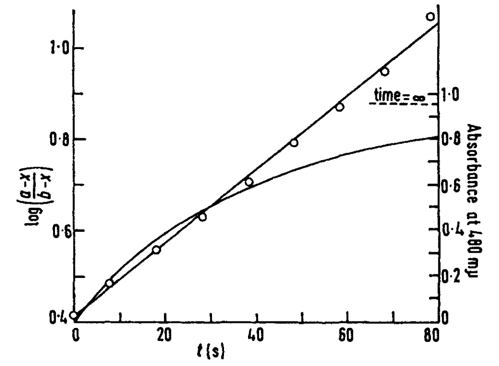

FIGURE 1 Rate curve and second-order analysis for reaction of Ph_3SiNa with $CH_2{=}CPh_2$ in THF at −62·5 °C: $[Ph_3SiNa]_i$ = 1·03 × 10^{-3}M, $[CH_2{=}CPh_2]_i$ = 3·96 × 10^{-4}M. The rate curve is the direct trace from the recording spectrophotometer

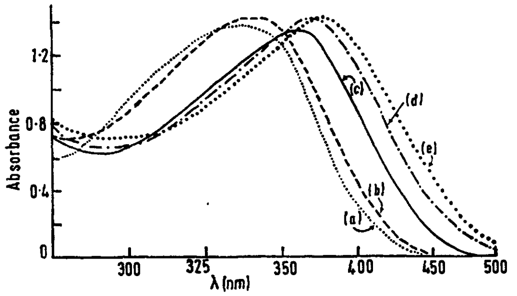

FIGURE 2 Absorption spectra of Ph_3SiM in THF at 20 °C; cell path length = 1 mm: (a), Ph_3SiLi (1·30 × 10^{-3}M); (b), Ph_3SiNa (1·02 × 10^{-3}M); (c), Ph_3SiK (1·09 × 10^{-3}M); (d), Ph_3SiRb (1·13 × 10^{-3}M); and (e), Ph_3SiCs (1·14 × 10^{-3}M)

TABLE 2

Spectra of Ph_3SiM in THF at 20°

$Ph_3\overset{-}{Si}\overset{+}{M}$	$\lambda_{max.}$/nm	$10^4 \times \varepsilon_{max}$
Ph_3SiLi	335	1·03
Ph_3SiNa	346	1·3
Ph_3SiK	363	1·2
Ph_3SiRb	368	1·3
Ph_3SiCs	376	1·3

The Warhurst-type[3] plot of $1/(r_c + 2)$ against $\tilde{\nu}_{max.}$ (see Figure 3), where r_c is the ionic radius of the cation and $\tilde{\nu}_{max.}$ is the wavenumber of the absorption maximum, is a good straight line for the gegenions Na, K, Rb, and Cs; Li lies off the line. The bathochromic shift of $\lambda_{max.}$ with increase in gegenion radius has been found for other substrates and explanations for this shift have been proposed by Warhurst *et al.*[3] and Smid *et al.*[4] We interpret our plot in Figure 3 as meaning that the ion pairs are contact in the case of sodium, potassium, rubidium, and caesium, but that for lithium, contact-ion pairs and solvent separated ion pairs exist in equilibrium.

The spectra of the products of reaction, $Ph_3Si{\cdot}CH_2{\cdot}\overset{-}{C}{\cdot}Ph_2\overset{+}{M}$, show a single absorption maximum at 480, 482, 483, and 482 nm for Na, K, Rb, and Cs as gegenions respectively; extinction coefficients for these gegenions are constant at 2·4 × 10^4. In the case of lithium, the absorption maximum is at 506 nm and the extinction coefficient is 2·7 × 10^4. On cooling from 20° to −80° there is no change in the absorption maximum for lithium, potassium, rubidium and caesium, and only a small increase in $\lambda_{max.}$ of *ca.* 5 nm in the case of sodium. We believe these results to show that we are dealing here with solvent-separated ion-pairs in all cases, the extent of solvation increasing from Cs to Li.

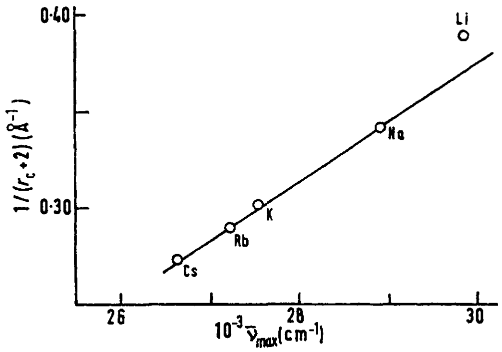

FIGURE 3 Plot of $1/(r_c + 2)$ against $\tilde{\nu}$ for $Ph_3\overset{-}{Si}\overset{+}{M}$

DISCUSSION

In Figure 4, we have plotted log k against $1/(r_c + 2)$ and it is seen that the results for sodium, potassium, rubidium, and caesium lie on an excellent straight line, but that lithium lies off this line. In addition, the plots of $\Delta S^‡$ and $\Delta H^‡$ against $1/(r_c + 2)$, and of $\Delta S^‡$ against $\Delta H^‡$, Figures 5 and 6 also show Li to be abnormal.

Systems involving Na^+, K^+, Rb^+, *and* Cs^+.—The spectral results of the reactants show that all these

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[3] H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, 1960, **56**, 455.

[4] T. E. Hogan-Esch and J. Smid, *J. Amer. Chem. Soc.*, 1966, **88**, 307.

gegenions give contact ion-pairs. Since the reaction product exists to some extent as solvent-separated ion-pairs in all cases, the change from initial to transition state will involve an increase in solvation of the gegenion. As the gegenion changes along the sequence Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ the increase in ionic size should cause the $\Delta S^‡$ values to become more positive, and this is found experimentally Figure 5. The $\Delta H^‡$ values, too, give a good straight line when plotted against $1/(r_c + 2)$, Figure 5. The value of $\Delta H^‡$ increases as $\Delta S^‡$ becomes more positive, as one would expect if the main factor causing a change in $\Delta H^‡$ was a change in the heat of solvation; this is supported by the good plot of $\Delta S^‡$ against $\Delta H^‡$ for these gegenions, Figure 6.

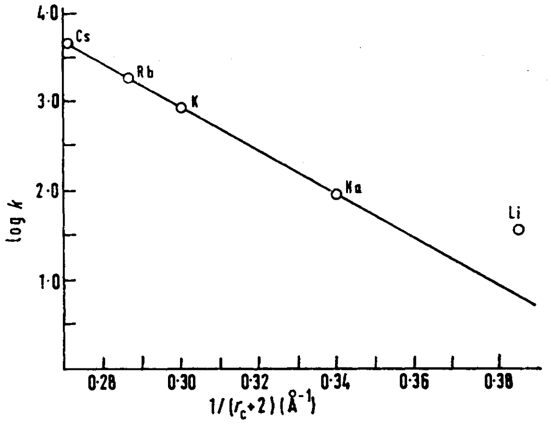

FIGURE 4 Plot of $\log_{10}k$ against $1/(r_c + 2)$

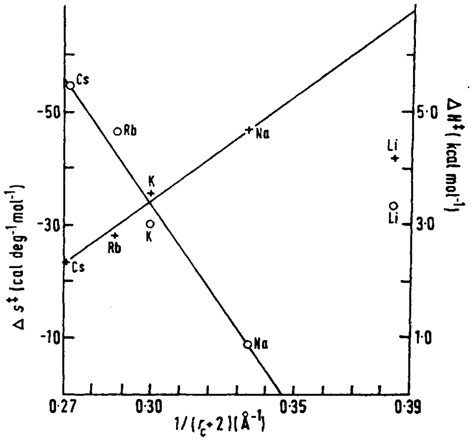

FIGURE 5 + Plot of $\Delta S^‡$ against $1/(r_c + 2)$; ○ Plot of $\Delta H^‡$ against $1/(r_c + 2)$

System involving Li$^+$.—In the case of Li$^+$, on the other hand, the reactant exists as a contact/solvent-separated ion-pair equilibrium, and, since the solvent-separated ion-pair will react faster than the contact ion-pair, the reaction will have a larger velocity constant than expected from the log *k* against $1/(r_c + 2)$ plot. It will proceed fully through the solvent-separated ion-pair species of the reactant (unless the contact/solvent-separated ion-pair equilibrium lies very heavily over to the side of the contact ion-pair). In the case of Li$^+$ both the initial state and the final state are solvated to a greater extent than for the other systems, and so the change of solvation in proceeding from initial to transition state will depend on the relative degree of solvation of these two states. The fact that $\Delta S^‡$ for Ph$_3$SiLi is displaced from the plot in Figure 5 in the positive direction, indicates that this increased solvation is more important in the initial state than in the transition state. The fact that $\Delta H^‡$ for Ph$_3$SiLi is displaced from the plot in Figure 5 in the positive direction and that Ph$_3$SiLi is out of sequence for the $\Delta S^‡$ against $\Delta H^‡$ plot, Figure 6, is also in accord with the suggestion that the increase in solvation of the initial state is more important than that of the transition state.

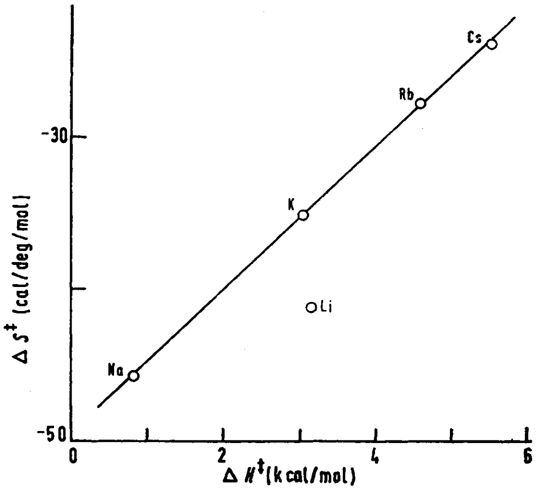

FIGURE 6 Plot of $\Delta H^‡$ against $\Delta S^‡$

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