The Kinetics and Mechanism of the Reactions of the Halogenotrimethylsilanes with Methylmagnesium Halides.

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[Reprint Order No. 6025.]

The kinetics of reactions of the halogenotrimethylsilanes with methylmagnesium chloride, bromide, and iodide have been followed in ether solution by iodometric titration of the Grignard reagent. With initial concentrations of 0·2—0·4M the reactions obey second-order kinetics until a second magnesium halide-rich layer separates. The effect of a polar substituent in the halogenosilane has been examined using chloro(chloromethyl)dimethylsilane and by comparing the behaviours of chlorodimethylphenyl- and -*p*-tolylsilane.

The results indicate a reaction mechanism involving magnesium–halogen co-ordination of the type $Me_3SiX \rightarrow Mg(Me)X$, associated with transfer of the methyl group and simultaneous rupture of the silicon–halogen bond.

No direct information about the mechanism of the reaction between Grignard reagents and silicon halides is available; we accordingly sought kinetic evidence, especially as few reactions of silicon halides or of Grignard reagents have hitherto been subjected to quantitative kinetic study. However, 90% yields of pure tetra-alkylsilanes have been obtained from triethylfluorosilane or tri*iso*butylfluorosilane and methylmagnesium iodide (Eaborn, *J.*, 1949, 2755) and from chloro(chloromethyl)dimethylsilane and methylmagnesium bromide (Whitmore, Sommer, and Gold, *J. Amer. Chem. Soc.*, 1947, **69**, 1976).

In the systems for which results are given in Tables 1 and 2 the reactions followed second-order kinetics until a relative increase in speed associated with the separation of a second liquid phase. With 0·2—0·4M-solutions in ether this usually did not occur until the reaction was at least half completed. In the reactions of fluorotrimethylsilane with methylmagnesium bromide and iodide, early separation of crystalline magnesium halide did not disturb the kinetics. It was not possible to obtain comparable data on the systems bromotrimethylsilane–methylmagnesium chloride or iodotrimethylsilane–methylmagnesium bromide probably owing to the occurrence of halogen exchange as well as methylation. The reaction between iodotrimethylsilane and methylmagnesium chloride was not examined since a similar complication seemed likely. The system fluorotrimethylsilane–methylmagnesium chloride failed to yield significant results owing to the separation of a second liquid and a solid phase very early in the reaction.

The Nature of Ethereal Solutions of Grignard Reagents.—The reagents are associated (probably dimeric) in ether (Meisenheimer and Schichenmaier, *Ber.*, 1928, **61**, 721), and there is a slight electrolytic dissociation, probably to give the ions RMg^+, $RMgX_2^-$, MgX^+, and R_2MgX^- (Evans and co-workers, *J. Amer. Chem. Soc.*, 1936, **58**, 721; 1942, **64**, 2865; Young and Roberts, *ibid.*, 1946, **68**, 1472). There is no evidence for the existence of an appreciable concentration of carbanions in the solutions, but the possibility that the mechanism requires the methyl ion cannot be excluded.

Recent evidence (Noller and co-workers, *ibid.*, 1937, **59**, 1345; 1940, **62**, 1749; 1942, **64**, 2509; Stewart and Ubbelohde, *J.*, 1949, 2649; Kullmann, *Compt. rend.*, 1950, **231**, 866) does not favour the existence, in solutions of alkylmagnesium bromides and iodides, of the equilibrium: $2RMgX \rightleftharpoons MgR_2 + MgX_2$ leading to the formation of dialkylmagnesium (Schlenk and Schlenk, *Ber.*, 1929, **62**, 920). For several reactions as between methylmagnesium iodide and acetone (Aston and Bernhard, *Nature*, 1950, **165**, 485), and phenylmagnesium bromide and valeronitrile (Gilman and Brown, *J. Amer. Chem. Soc.*, 1930, **52**, 1181) or benzonitrile (Swain, *ibid.*, 1947, **69**, 2306), kinetic or other evidence excludes the reactivity of the Grignard reagent's being due to dialkyl- or diaryl-magnesium. In ether " methylmagnesium chloride," however, differs from the bromide and iodide in being deficient in halogen (Cope, *ibid.*, 1935, **57**, 2238). Hence this solution must contain either free dimethylmagnesium or some complex having a magnesium atom linked to more than one methyl group. The kinetic behaviour of methylmagnesium chloride towards chlorotrimethylsilane does not suggest any peculiarity arising from the halogen deficiency, but comparison with other systems should be treated with reserve.

The Reaction Mechanism.—There is no evidence for ionisation of the trialkylhalogenosilanes in ether. Gingold, Rochow, Seyferth, Smith, and West (*ibid.*, 1952, **74**, 6306) report these solutions to have no detectable conductivity and this was confirmed in the present work.

It is probable that the transition state contains halogen from both the Grignard reagent and the silane. Otherwise, if the Grignard reagent (or *mutatis mutandis* the silane) participated through a halogen-free component, then, subject to the restriction of second-order kinetics, the rates of reaction of each silane with methylmagnesium bromide and iodide at a particular temperature should be in a constant ratio; but this was not found to be so.

Mechanisms having the following broad characteristics may be considered.

(I) *Attack on silicon with simultaneous breaking of the* Si–X *bond.*

(II) *Attack on silicon to give a quinquecovalent complex* $(Me)_4SiX^-$ (cf. Price, *ibid.*, 1947, **69**, 2600; Swain, Esteve, and Jones, *ibid.*, 1949, **71**, 965; Gilman and Dunn, *ibid.*, 1951, **73**, 3404). The rate-determining step may be (*a*) formation of the complex; or its decomposition through either (*b*) spontaneous elimination of a halide ion, or (*c*) removal of halogen by a magnesium centre (*e.g.*, MgX^+, following initial attack by Me^-).

(III) *Initial co-ordination of halogen by magnesium.* The slowest step may be (*a*) formation of the complex by attack of a magnesium centre carrying a methyl group, or (*b*) decomposition through intramolecular transfer of the methyl group from magnesium to silicon. Alternatively the slowest process may be (*c*) reaction between Me^- and a complex $(Me)_3SiX{\rightarrow}MgX^+$.

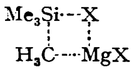
The experimental results enable us to reject several of these possibilities. The absence of any marked influence of the polar chloromethyl group on the activation energies (Table 1) discounts steps II*a*, II*b*, II*c*, and III*a*. Mechanisms of class I (as also II*a* and II*b*) could hardly account either for the small range of activation free energies within the halogenosilane series or for the steric sensitivity of the reaction (Eaborn, *J.*, 1952, 2840) to the sizes not only of the alkyl groups but also of the halogen atoms of both the silane and the Grignard reagent. The remaining mechanisms III*b* and III*c* are free from these objections provided that formation of the silicon–carbon bond and rupture of the silicon–halogen bond are simultaneous. For III*b* the rate-determining step would represent the concerted reorganisation of a cyclic transition state (inset). This mechanism is preferable to III*c* in not requiring the methyl ion for which there is no independent evidence, and moreover it can provide an explanation of trends in activation energies. It is closely similar to the mechanism offered by Swain (*loc. cit.*) on quite different grounds for the reaction between phenylmagnesium bromide and benzonitrile.

TABLE 1. *Activation functions.*

	Activation energies (kcal. ± 0·6)			Activation free energies at 0° c * (kcal. ± 0·05)		
	MeMgCl	MeMgBr	MeMgI	MeMgCl	MeMgBr	MeMgI
Me_3SiF	—	8·8	13·5	—	20·86	21·04
Me_3SiCl	8·0	8·1	10·6	21·20	20·47	20·35
Me_3SiBr	—	10·6	11·3	—	20·21	19·32
Me_3SiI	—	—	9·2	—	—	18·46
$Cl{\cdot}CH_2{\cdot}SiMe_2{\cdot}Cl$	8·3	11·5 ± 2	9·8	19·40	19·72	20·52

	−$T\Delta S$ at 0° c (kcal. ± 0·7) ($\log_{10} A$ in parentheses)		
	MeMgCl	MeMgBr	MeMgI
Me_3SiF	—	12·0(3·1)	7·5(6·7)
Me_3SiCl	13·1(2·2)	12·3(2·9)	9·2(5·0)
Me_3SiBr	—	9·6(5·0)	7·9(6·4)
Me_3SiI	—	—	9·2(5·3)
$Cl{\cdot}CH_2{\cdot}SiMe_2{\cdot}Cl$	11·1(3·9)	8·1±2(5·9)	10·6(4·2)

* Calc. from the expression $-\Delta F = 2{\cdot}303\boldsymbol{RT}\,[\log(\boldsymbol{RT/Nh}) - \log k]$



The decreasing activation energies from the fluoro- to the iodo-silane in the methylmagnesium iodide series reflect the contribution from the breaking of the silicon–halogen bond. For the methylmagnesium bromide reactions activation energies are lower and the decreasing trend is lost. Breaking of the silicon–halogen bond must therefore be less important in this series, as would be expected for a cyclic transition state since increasing electronegativity of the halogen atom of the Grignard reagent would assist rupture of this bond but hinder release of the methyl group from the magnesium atom.

The accumulation of magnesium halide in the solution during the reaction does not produce any detectable kinetic effect arising from its polarity or from interaction with remaining methylmagnesium halide (Stewart and Ubbelohde, *loc. cit.*) but mutual cancellation of such effects is possible. However, the reaction is probably insensitive to solvent polarity since in several systems : Me_3SiF–MeMgBr, Me_3SiF–MeMgI, and Me_3SiCl–MeMgCl an increase in the concentration of halogenosilane from 0·2—0·3M to 0·7—1·0M did not alter the rate constants. Hence, within the limits of available evidence, the rate-determining step does not involve a net change in the formal charge on any atom. This again favours mechanism III*b*.

Trends in entropies of activation receive plausible interpretation on the basis of halogen interactions associated with a magnesium co-ordination process as in mechanisms III*b* or III*c*. The more negative value for the activation entropy of the reaction of each silane with methylmagnesium bromide than with methylmagnesium iodide may be related to the higher polarities induced in the silicon–halogen bonds through co-ordination with the former, which in turn produces a greater orientation of solvent molecules. Chloro(chloromethyl)dimethylsilane shows a higher entropy of activation than chlorotrimethylsilane in the reactions with methylmagnesium chloride and bromide. This may likewise be attributed in part to a reduction in the polarity of the silicon–halogen bond by the chloromethyl substituent, in so far as this reduces repulsions between the halogen attached to silicon and the groups on magnesium. It is suggested that the reverse trend for the corresponding reactions with methylmagnesium iodide is due to steric interference between the chloromethyl group and the iodine atom which more than offsets the polar effect.

Variants of mechanism III*b* require mention. Co-ordination by magnesium centres of the anions Me_2MgX^- or $MeMgX_2^-$ is unlikely, but there seems no reason to exclude direct participation of the dimer in the reaction. Certain conditions could reduce kinetic complications arising therefrom. Thus any shift in the equilibrium between monomer and dimer as the reaction proceeds could be reduced by co-ordination of accumulating magnesium dihalide with the remaining unreacted monomer. Also, as apart from the possible effects of co-ordination, similarity in the reactivities of the carbon–magnesium bonds of the monomer and dimer would lessen deviation from second-order kinetics.

*The Reactions of Chlorodimethylphenylsilane and Chlorodimethyl-*p*-tolylsilane with Methylmagnesium Iodide.*—Activation functions are summarised in Table 2 which includes data on the reaction of chlorotrimethylsilane with the same Grignard reagent.

TABLE 2.

Silane	ΔH (kcal. ± 0·6)	ΔF (kcal. ± 0·05)	$-T\Delta S$ (kcal. ± 0·7)	$\log_{10} A$
Me_3SiCl	10·6	20·35	9·6	5·0
$PhSiMe_2Cl$	11·2	20·12	8·9	5·6
$C_7H_7{\cdot}SiMe_2Cl$	10·1	20·19	10·1	4·7

The figures for chlorodimethylphenylsilane and chlorotrimethylsilane are sufficiently similar to warrant the assumption that the introduction of an aromatic substituent does not alter the reaction mechanism. Values for the phenyl and *p*-tolyl compounds are also rather similar and the differences are hardly outside experimental error. Nevertheless, the entropy of activation is almost certainly raised by the presence of the electron-releasing *p*-methyl group, as would be expected on the basis of the mechanism proposed.

If any conclusion can be drawn from the comparative figures (Table 2) for chlorotrimethylsilane and chlorodimethylphenylsilane it is that the phenyl group attached to silicon is more electronegative than a methyl group (cf. Roberts, McElhill, and Armstrong, *J. Amer. Chem. Soc.*, 1949, **71**, 2923).

EXPERIMENTAL

The apparatus, based on a 300-ml. three-necked flask, is shown in Fig. 1. The funnel and burette carried two-way taps connected to a nitrogen supply as shown.

After the assembly had been flushed with nitrogen the Grignard reagent was introduced from a 240-ml. transfer bulb (*D*, Fig. 2), attached at *A*, by opening the lower tap *E*. For withdrawal of samples for analysis a suitable extra pressure of nitrogen was maintained in the apparatus and the burette filled by opening the tap *B* to the atmosphere. The tap was then reversed to the nitrogen supply, thus allowing the solution to level off to the side-arm. This known volume was run into the reagent solution for analysis. A suitable quantity of halogenosilane diluted to a known volume with ether was introduced into the funnel and brought to bath temperature by circulating thermostat liquid through the jacket. The reaction was started by opening tap *C*.

FIG. 1. *Apparatus for following reaction kinetics.*

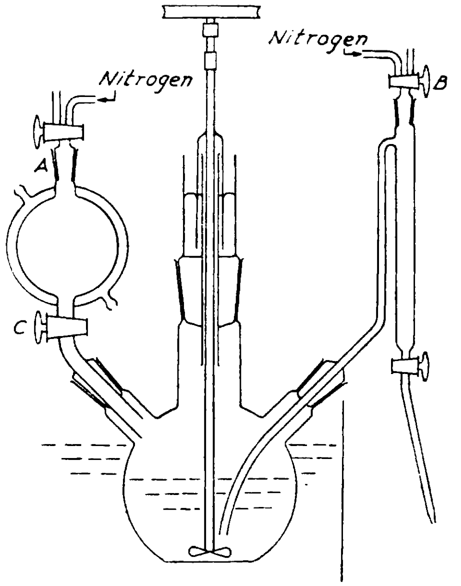
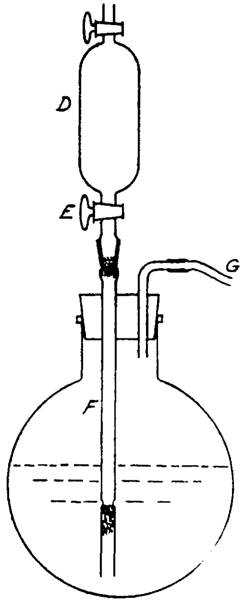


FIG. 2. *Method of transferring Grignard reagent.*



The thermostat bath could be operated from −10° to +30° (±0·03°). Measurements on each system were made over ranges of 20—30°.

Preparation, Storage, and Transfer of Solutions of the Grignard Reagents.—These solutions (0·2—0·4M) were prepared under nitrogen in quantities of 3—4 litres. Redistilled methyl halides were used, care being taken to avoid excess. The solutions were stored in the flasks used for their preparation. A mercury bubbler released undue pressure of ether vapour.

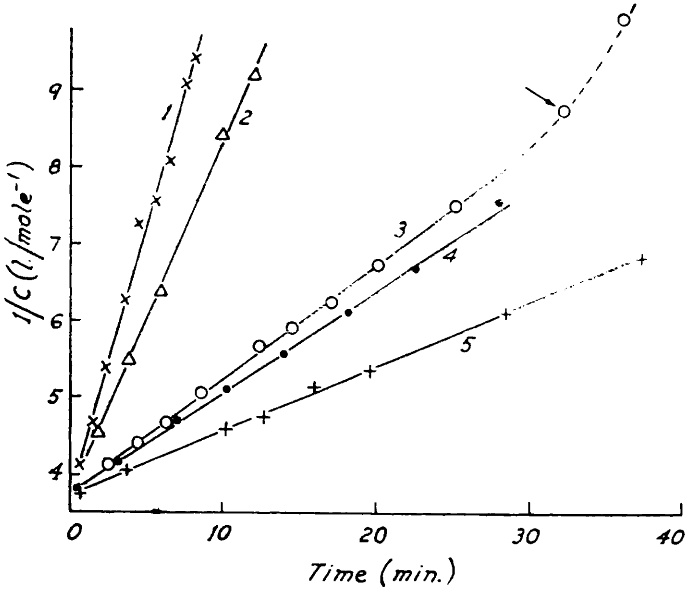
To transfer the solution to the reaction vessel the tube *F* containing a glass-wool filter was inserted through the rubber stopper until its lower end was just above the surface of the liquid. The transfer bulb was fitted to the ground joint at the top of the tube as shown and nitrogen passed into the apparatus at *G* to flush air from the bulb. The lower end of the tube was then pushed beneath the surface of the liquid so that the clear solution was forced into the bulb by the nitrogen pressure. When the bulb was full both taps were closed and this known volume of solution was transferred to the reaction vessel without contact with air.

Analysis of Methylmagnesium Halide Solutions.—The iodometric method alone was used for analysis during a reaction but was supplemented by gasometric and acidimetric procedures for the initial analysis of the Grignard reagent. The gasometric method is in theory the most accurate since only magnesium-carbon bonds are estimated, but as each determination is lengthy the method was used primarily for analysis of each new preparation of methylmagnesium halide. The iodometric method gives results lower (by 5—6% in the present experiments) than those obtained gasometrically (Gilman and Meyers, *Rec. Trav. chim.*, 1926, **45**, 314; Mackle and Ubbelohde, *J.*, 1948, 1161) and a correction factor was used to obtain the true molarity of the solution.

The acidimetric method on the other hand, while affording the most precise experimental procedure, gives results somewhat higher than the gasometric, probably because it also estimates any oxy-compounds present. An acidimetric analysis was always made before a run since any variation in the ratio $\text{M}_{\text{acid}} : \text{M}_{\text{iodine}}$ would give warning of the solution's having deteriorated. In fact no such difficulty was encountered and this analytical ratio changed very little during several weeks.

With 12 ml. of methylmagnesium halide solution (about 0·25M), acidimetric titrations were reproducible to ±0·4%, and iodometric to ±0·7%. In the latter procedure methylmagnesium halide was delivered beneath 25 ml. of a solution (0·45N) of iodine in benzene (see Champetier and Kullmann, *Bull. Soc. chim. France*, 1949, **53**, 693).

FIG. 3. *Plots of* 1/c *against time for the system* $(CH_3)_3SiBr–CH_3MgI$ (*the reactants being in equimolar proportions*).



The scale refers directly to plots 1 and 4. For convenience the remaining curves have been drawn from the same origin, 2 and 5 having been lowered by 0·50 unit and 3 by 1·40 units. Temperatures and rate constants are: (1) 24·8°, 0·670; (2) 20·0°, 0·452; (3) 4·7°, 0·150; (4) 0·2°, 0·127; (5) −3·3°, 0·086. The broken extension to curve 3 shows the typical kinetic effect associated with separation of the second liquid phase which was observed at the point indicated by the arrow.

The apparatus for gasometric analysis was as used by Gilman, Wilkinson, Fishel, and Meyers, (*J. Amer. Chem. Soc.*, 1923, **45**, 150) but having provision for recirculation of the methane through the sulphuric acid bubbler to ensure complete removal of ether vapour.

Results.—Experimental results for runs on the reaction between (equivalent quantities of) bromotrimethylsilane and methylmagnesium iodide, which may be taken as typical, are plotted as $1/c$ against time in Fig. 3. The parameters of the Arrhenius equation $k = A \exp(-E/\boldsymbol{R}T)$ expressing the bimolecular rate constant (l. mole^{-1} sec.$^{-1}$) for each system are included in Tables 1 and 2.

For most of the individual systems the same preparation of Grignard reagent was used throughout. The variation in the individual experimental values of log k from the values defined by the best straight lines of the Arrhenius plots, expressed as a standard deviation over all such systems, was 5½%. This may be compared with the predicted maximum random deviation of 6½%, based on an assessment of the various errors arising from analysis and transfer of the reactants. The maximum deviation was slightly greater for systems where different preparations of methylmagnesium halide were used since systematic errors would thereby have been introduced, but was always within the predicted deviation of 10%. Experimental errors in the thermodynamic functions for each system are shown in Tables 1 and 2.

There was no evidence that variations in the degree of oxidation of a Grignard reagent, within the range $\mathrm{M}_{\text{iodine}} : \mathrm{M}_{\text{acid}} = 0{\cdot}91$—$0{\cdot}87$, influenced the kinetics. The kinetics were unaltered by using sodium-dried ether either directly or immediately after efficient fractional distillation. Redistillation of each of the silanes was also without effect. It must be mentioned however, that for some reason there was initial difficulty in obtaining reproducible results on the system chlorotrimethylsilane–methylmagnesium bromide, and that the results for the system chloro(chloromethyl)dimethylsilane–methylmagnesium bromide showed a wider scatter than usual.

Preparation of Halogenosilanes.—Most of these compounds were obtained by published methods and were purified to distillation ranges of less than 0·2° unless otherwise stated.

Fluorotrimethylsilane (Booth and Suttle, *ibid.*, 1946, **68**, 2658) had d_4^0 0·793.

Pure chlorotrimethylsilane (Pray, Sommer, Goldberg, Kerr, DiGiorgio, and Whitmore, *ibid.*, 1948, **70**, 433) could be obtained in 73% yield from antimany trichloride and the bromo-silane (Pray *et al.*, *loc. cit.*), and material from this source was also used.

Photo-chemical decomposition of the iodo-compound (Eaborn, *J.*, 1950, 3084) during preparation was avoided, and the kinetic experiments were made in a darkened room.

Chloro(chloromethyl)dimethylsilane was obtained by refluxing chlorotrimethylsilane (108 g.), sulphuryl chloride (135 g.), and benzoyl peroxide (0·5 g.) for 12 hr. (Contrary to McBride and Beachell, *J. Amer. Chem. Soc.*, 1948, **70**, 2532, a high-boiling diluent was not found necessary.) Fractionation gave 47 g. of material boiling between 113° and 120°. On re-distillation a small fraction, possibly from decomposition, passed over at 80—90°. After removal of this fraction no further accumulation of low-boiling material occurred on refluxing so that no progressive decomposition of the desired product occurs. The fraction (37 g.) distilling at 115—116° was collected.

Chlorodimethyl-p-*tolylsilane* (Lewis and Gainer, *ibid.*, 1952, **74**, 2931) had to be repeatedly fractionated to obtain the product (b. p. 216·5—218°) free from a volatile bromine compound (Found, by Mohr's titration : Cl, 19·3. Calc. for $C_9H_{13}SiCl$: Cl, 19·2%).

Halogen Exchange between Halogenotrimethylsilanes and Methylmagnesium Halides.—In kinetic experiments on the system iodotrimethylsilane–methylmagnesium bromide a fast initial disappearance of Grignard reagent, not obeying the second-order rate law, but giving place to a slower second-order process when the reaction was about one-third completed, was observed. This latter reaction was closely similar kinetically ($E = 10{\cdot}9 \pm 0{\cdot}8$ kcal.; $\Delta F = 19{\cdot}3$ kcal.) to the reaction between bromotrimethylsilane and methylmagnesium iodide. It would thus appear that halogen exchange in addition to methylation occurred during the first rapid stage of the reaction. Halogen exchange between the initial reactants was not independently confirmed, but was found to occur between magnesium bromide–diether complex and iodotrimethylsilane in ether, though probably considerably more slowly than in the system iodotrimethylsilane–methylmagnesium bromide itself. The kinetic behaviour of the system bromotrimethylsilane–methylmagnesium chloride was qualitatively similar.

We acknowledge the assistance of Miss M. K. Morris with the initial development of the work, and of Mr. G. H. McLellan with the experiments using chlorodimethyl-phenyl- and -*p*-tolyl-silane. We also acknowledge a grant from the research fund of the University of New Zealand.

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[*Received, January 10th,* 1955.]