1047. *Proton Magnetic Resonance Spectra of Thallium Trialkyls, Chemical Exchange, and the Formation of a Mixed Tri(methyl,vinyl)-thallium.*

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It is shown from the proton resonance spectra of trimethylthallium that the intermolecular exchange of methyl groups follows second-order kinetics and has an activation energy of 6·3 ± 0·5 kcal. in [α-$^2H_3$]toluene. A mixed tri(methyl,vinyl)thallium has been prepared in which a very rapid exchange of the vinyl groups occurs. At low temperature the mixed species dimethylvinylthallium and methyldivinylthallium were characterised. The effect of trimethylamine and dimethyl ether in slowing these exchanges, and the corresponding exchange of phenyl groups in triphenylthallium, has been studied. This effect is particularly marked with triphenylthallium, and a stable adduct, $TlPh_3,NMe_3$, has been prepared.

WE showed, in a previous note,[1] from the proton resonance spectra, that a rapid intermolecular exchange of alkyl groups occurs in solutions of trimethylthallium and triethylthallium at room temperature. At low temperatures, for a solution containing a mixture of these two species, it was possible to characterise two mixed alkyls, $TlMeEt_2$ and $TlMe_2Et$. In the present work the rate of exchange of methyl groups in solutions of trimethylthallium has been studied in detail. Although trivinylthallium has not been reported in the literature, and our attempts to prepare this compound were unsuccessful, we found that the reaction of methyl-lithium with divinylthallium chloride gave a mixed tri(methyl,-vinyl)thallium. The proton resonance spectra of this species, and that of triphenylthallium, have been measured.

EXPERIMENTAL

Trimethylthallium Solutions.—Trimethylthallium was prepared from methyl-lithium and dimethylthallium chloride,[2] and purified by repeated vacuum sublimation. While preparing the solutions care was taken to exclude traces of oxygen or water which might lead to the formation of catalytic impurities. The solvents were dried over lithium aluminium hydride, or Linde molecular sieves, and thoroughly degassed. The solutions were prepared and sealed *in vacuo* in Pyrex nuclear magnetic resonance tubes (5 m.m., o.d.) which had been previously baked out at *ca.* 300°. The solutions were analysed by opening the tubes under dilute nitric acid, destroying the product with concentrated nitric acid–sulphuric acid, and titrating the thallium (after reduction with sulphur dioxide) with potassium iodate.

Preparation of Tri(methyl,vinyl)thallium.—A solution of methyl-lithium (0·04 mole) in anhydrous diethyl ether (25 ml.) was slowly added, under nitrogen, to a stirred suspension of divinylthallium chloride (5 g., 0·018 mole) in ether (25 ml.) at *ca.* −5°. After stirring for 1 hr., the bulk of the ether was pumped off, and the residue was fractionally sublimed on a vacuum line using as short a distillation path as possible to reduce decomposition. A colourless, needle-like crystalline solid was obtained, and characterised by its proton magnetic resonance spectrum in solution. From the relative peak areas in the spectrum, the molar ratio of methyl to vinyl groups, in the sample on which measurements were made, was found to be 1·75 : 1. It is stable in the absence of air or light, but its solutions at room temperature slowly deposit crystals of thallium.

Attempts to prepare the corresponding phenylvinylthallium and n-octylvinylthallium systems using phenyl-lithium and n-octyl-lithium gave black precipitates of thallium, and styrene and dec-1-ene, respectively, as the only volatile products. These compounds were characterised as styrene dibromide and the 2,4-dinitrobenzenesulphenyl derivative of dec-1-ene. Hence a rather unusual vinylation reaction had occurred. Similarly, an ethereal solution

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[1] Maher and Evans, *Proc. Chem. Soc.*, 1961, 208.
[2] Gilman and Jones, *J. Amer. Chem. Soc.*, 1946, **68**, 517.

containing triphenylthallium and vinyl-lithium,[3] on removal of the ether and vacuum distillation, gave a residue of thallium, and styrene was again the only volatile product. However, no reaction was observed between 9-lithioanthracene [4] and divinylthallium chloride in ether.

Attempts to prepare pure trivinylthallium directly from vinyl-lithium and divinylthallium chloride or bromide were unsuccessful, no reaction taking place even in boiling tetrahydrofuran.

Triphenylthallium was prepared from diphenylthallium chloride and phenyl-lithium,[5] and purified by recrystallisation from benzene–light petroleum in an atmosphere of nitrogen.

Triphenylthallium–Trimethylamine Adduct.—Triphenylthallium (1 g.) was dissolved in trimethylamine (*ca.* 5 ml.), and the excess of trimethylamine was evaporated at room temperature in a stream of oxygen-free nitrogen, giving a white crystalline product (Found: C, 51·5; H, 5·45; N, 2·95. $C_{21}H_{24}NTl$ requires C, 51·0; H, 4·9; N, 2·85%). The formulation as a 1 : 1 complex was confirmed from the relative peak areas in the proton resonance spectrum of a carbon disulphide solution. The crystals had a negligible vapour pressure of trimethylamine at room temperature, indicating that the complex is reasonably stable.

Proton magnetic resonance spectra were measured on a Varian V4311 spectrometer at 56·45 Mc./sec., or at 40 Mc./sec. using a Varian V4340 variable-temperature probe. Tetramethylsilane was normally used as an internal reference. The chemical shifts are accurate to *ca.* ±0·01 p.p.m.

RESULTS AND DISCUSSION

Trimethylthallium Exchange.—At low temperatures in [α-$^2H_3$]toluene, where the methyl exchange rate is slow, solutions of trimethylthallium show two proton resonance peaks separated by 250·4 c./sec., due to spin–spin coupling between the two thallium isotopes and the methyl protons (the separate ^{203}Tl and ^{205}Tl splittings are not resolved). As the temperature is raised the two peaks broaden and eventually coalesce. The separations of the two broad peaks were measured over a range of temperatures (20° to —50°) and the exchange rates calculated from eqn. (1):[6]

$$\frac{\text{Separation of peaks}}{\text{Separation of peaks for large } \tau} = \left[1 - \frac{1}{2\pi^2\tau^2(\nu_A - \nu_B)^2}\right]^{\frac{1}{2}}, \quad . \quad . \quad (1)$$

where τ is the mean lifetime of a methyl group on a thallium nucleus in a given spin state, and $(\nu_A - \nu_B)$ refers to the separation of the doublet in the absence of exchange.

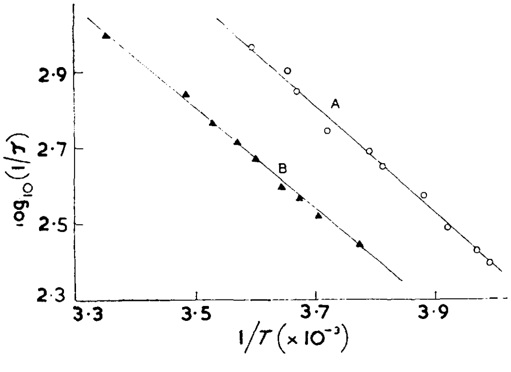

FIG. 1. Temperature-dependence of the exchange rates for solutions of trimethylthallium in toluene α-d_3.

A (3·46M); $\log_{10} 1/\tau = 8{\cdot}079 - 1{\cdot}42_4 \times 10^3 T^{-1}$.

B (1·80M); $\log_{10} (1/\tau) = 7{\cdot}470 - 1{\cdot}33_4 \times 10^3 T^{-1}$.

Fig. 1 shows a plot of $\log_{10} 1/\tau$ against $1/T$ for two concentrations of trimethyl thallium in [α-$^2H_3$]toluene. Good straight almost parallel lines, are obtained, giving an activation energy of 6·3 ± 0·5 kcal. for the intermolecular methyl exchange. This value agrees with that (6 ± 1 kcal.) obtained previously for solutions of trimethylthallium in dichloromethane.[1] Since only exchanges between thallium in different spin states will

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[3] Seyferth and Weiner, *Chem. and Ind.*, 1959, 402.

[4] Mikhailov and Chemova, *Doklady Akad. Nauk, S.S.S.R.*, 1951, **78**, 489.

[5] Birch, *J.*, 1934, 1132.

[6] Pople, Schneider, and Bernstein, " High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959; Arnold, *Phys. Rev.*, 1956, **102**, 136.

affect the proton resonance spectrum, the mean lifetime of a methyl group between exchanges is $\tau/2$. In relating τ to the second-order rate constant k_2, since any of the three equivalent methyl groups can be involved in exchange, a further statistical factor of $\frac{1}{3}$ enters. Thus $k_2 \sim 6/\tau$. The order of the exchange is calculated to be 2·0, and the second-order rate constants, k_2, can be calculated from the equation: [7,8,8a]

$$k_2 = 6/\tau[\mathrm{Me_3Tl}] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

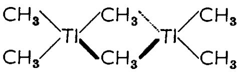
At 26°, $k_2 = 3{\cdot}43 \pm 0{\cdot}15 \times 10^3$ l. mole^{-1} sec.$^{-1}$ for the [α-$^2H_3$]toluene solutions of trimethylthallium.

For solutions of trimethylthallium in deuterobenzene the observed line shapes were compared with the theoretical shapes calculated from the shape function g(ν): [6]

$$g(\nu) = K[(\nu_A - \nu_B)^2]/\{[\tfrac{1}{2}(\nu_A + \nu_B) - \nu]^2 + 4\pi^2\tau^2(\nu_A - \nu)^2(\nu_B - \nu)^2\}, \quad . \quad (3)$$

where K is a normalising constant. The results are given in Table 1.

From the plot of $\log^{10}\tau$ against $\log_{10}[\mathrm{TlMe_3}]$, a value of $1{\cdot}8_4$ is derived for the order of reaction. Thus within the (fairly large) limits of experimental error, the exchange is second order in both solvents. It seems likely that a dimeric transition state is involved, which can be represented as (I), analogous to the stable trimethylaluminium dimer. (Trimethylthallium is monomeric in solution.[9])



(I)

Table 2 shows results for trimethylthallium in dimethyl ether and trimethylamine. In both cases, the exchange rates are slower than in deuterobenzene. This can be attributed to weak complex formation between the two components (a rather unstable solid complex $\mathrm{Me_3Tl,NMe_3}$ is known [10]). The exchange of methyl groups between dimethylzinc and dimethylcadmium in various solvents has recently been studied by McCoy and Allred.[8] No comparable effect of donor solvents was observed, which is consistent with the even lower tendency of these alkyls to form complexes.

TABLE 1.

Second-order rate constants, k_2, and τ values, for solutions of trimethylthallium in deuterobenzene at 26°.

[TlMe$_3$] (moles/l.)	0·31	0·46	0·96	1·22
$\tau \times 10^{-3}$ (sec.)	1·85	1·30	0·78	0·54
$10^{-3}k_2$ (l. mole^{-1} sec.$^{-1}$)	10·2	10·1	8·0	9·1

TABLE 2.

Trimethylthallium exchange in dimethyl ether and trimethylamine.

Solvent	$\tau \times 10^{-3}$ (sec.) *	[TlMe$_3$] (moles/l.)	J(^{205}Tl–H) (c./sec.) †
Trimethylamine.....................	3·86	0·74	270·3
Dimethyl ether	3·25	1·65	269·6

* Calculated using eqn. (1); at 26°. † At −60°.

Triphenylthallium Exchange.—The spectrum of triphenylthallium in dichloromethane is given in Fig. 2b. No thallium splitting is observed, and the spectrum resembles that of a phenyl group in compounds such as nitrobenzene,[6] indicating that a rapid intermolecular exchange of phenyl groups is occurring. In trimethylamine solution (Fig. 2a) the exchange has been very considerably slowed down, and the ortho-, meta-, and para-thallium–proton coupling constants can be determined (Table 3). Because of the overlap of groups B′ and C′, only approximate values for the meta- and para-thallium proton

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[7] Meiboom, *Z. Elektrochem.*, 1960, **64**, 50.
[8] McCoy and Allred, *J. Amer. Chem. Soc.*, 1962, **84**, 912.
[8a] Loewenstein and Connor, *Ber.*, 1963, **67**, 280.
[9] Coates, " Organo-metallic Compounds," Methuen, London, 1960.
[10] Coates and Whitcombe, *J.*, 1956, 3351.

coupling constants could be obtained. The appearance of the spectrum suggests that these two coupling constants have the same sign, and a double irradiation experiment [1] showed conclusively that the ortho- and meta-coupling constants have the same sign. Intermediate rates of exchange, giving broad featureless spectra, were observed in dimethyl ether and deuterobenzene solutions of triphenylthallium. From the values of the coupling constants given above it can be deduced that the average lifetime, τ, of the phenyl groups is more than 0·05 sec. for the trimethylamine solution and less than 3×10^{-4} sec. for the other solutions. The rates of phenyl exchange in these solutions may have been affected by catalytic impurities. Nevertheless, the very large effect of trimethylamine as a solvent suggests that the triphenylthallium forms complexes more strongly with trimethylamine than does trimethylthallium. In agreement with this a stable complex Ph_3Tl^-–NMe_3^+ was readily obtained on evaporation of a solution of triphenylthallium in trimethylamine (Experimental section).

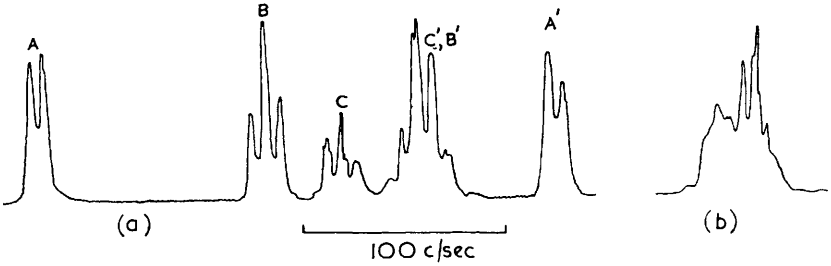


FIG. 2. Proton magnetic resonance spectra of solutions of triphenylthallium in: (a) NMe_3 [AA′, J(Tl–H,ortho); BB′, J(Tl–H,meta); CC′, J(Tl–H,para)]; (b) CH_2Cl_2.

Tri(methyl,vinyl)thallium.—The proton resonance spectra of solutions of this species are shown in Fig. 3. In the deuterobenzene solution, at 26°, the methyl peak is broad,

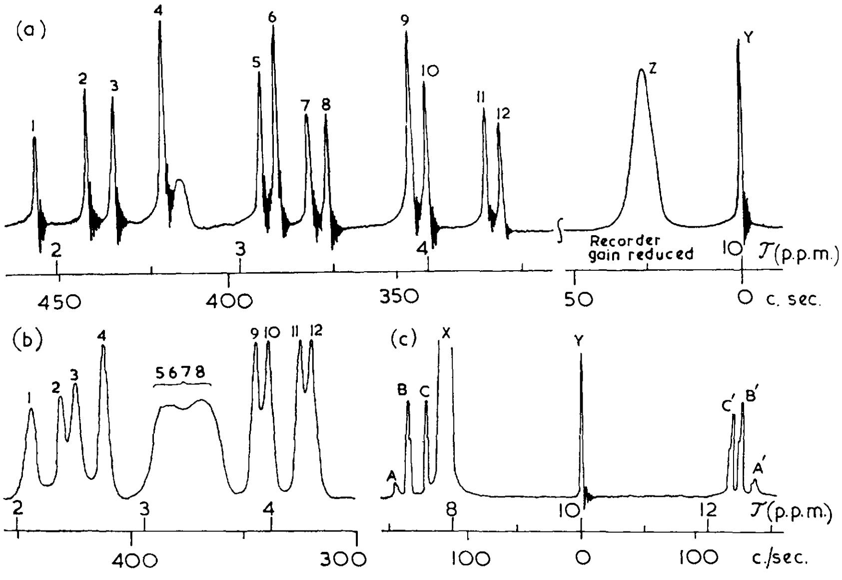


FIG. 3. Proton magnetic resonance spectra of a solution of tri(methyl,vinyl)thallium in: (a) C_6D_6 at 26° (1—12, vinyl group; Z, $TlMe_3$); (b) NMe_3 at 26° (1—12 vinyl group); (c) NMe_3 at $-64°$ [AA′, $TlMe(vinyl)_2$; BB′, $TlMe_2(vinyl)$; CC′, $TlMe_3$). $X = NMe_3$, $Y = SiMe$.

TABLE 3.

Thallium–proton coupling constants for triphenylthallium in trimethylamine.

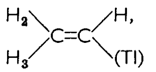
H′ position	$J(^{205}Tl–H)$	J(H–H)	Chemical shift (p.p.m.)
ortho	259·4	7·2	$7{\cdot}87_0$
meta	80 ± 5	1·5	7·4 ± 0·1
para	35 ± 5	–	7·3 ± 0·1

TABLE 4.

^{205}Tl–(methyl)′H coupling constants

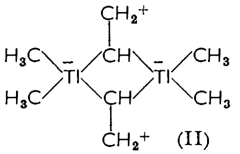
Solvent	$TlMe_3$	$TlMe_2$(vinyl)	TlMe(vinyl)$_2$
Dimethyl ether	269·6	294·6	316·8
Trimethylamine	270·3	295·5	317·4

but the characteristic vinyl spectrum is extremely sharp and shows no evidence of spin–spin splitting by the thallium isotopes (Fig. 3a), presumably owing to a very rapid exchange of the vinyl groups. However, in trimethylamine at 26° the vinyl spectrum has started to broaden (Fig. 3b) and the methyl peak splits into a doublet, the low-field component being obscured by the trimethylamine resonance, showing that the exchange of both the methyl and the vinyl groups has been slowed. At −64° in trimethylamine, the vinyl spectrum cannot be detected, presumably because the peaks have become too broad, but the methyl part of the spectrum (Fig. 3c) shows three well defined pairs of doublets, corresponding to the species $TlMe_3$, $TlMe_2$(vinyl), and TlMe(vinyl)$_2$. Similar effects were observed for dimethyl ether solutions of tri(methyl,vinyl)thallium. The proton–proton coupling constants for the (exchanging) vinyl groups (making the usual assumption that in vinyl derivatives $J_{trans} > J_{cis} > J_{gem}$) are: $J_{trans} = 20{\cdot}0$; $J_{cis} = 12{\cdot}8$; $J_{gem} = 4{\cdot}3$ c./sec. [±0·2 c./sec.]. The chemical shifts of the vinyl protons are concentration- and solvent-dependent, but for a 1·0M-solution in [$^2H_6$]benzene (with respect to thallium) at 26° they are: $H_1 = 7{\cdot}53$; $H_2 = 6{\cdot}63$; $H_3 = 4{\cdot}13$ p.p.m., relative to tetramethylsilane. The thallium–methyl proton coupling constants at −64° are shown in Table 4.



Schaefer,[11] and Banwell and Sheppard,[12] have correlated the sum of the ethylenic proton coupling constants ($J_{gem} + J_{cis} + J_{trans}$), in a series of vinyl compounds, with the electronegativity of the substituent. Using these data we obtain an electronegativity for thallium of 1·95, compared with a value of 2·05 for thallium in triethylthallium calculated using the Dailey–Schoolery equation.[13]

It was estimated that the rate of methyl-group exchange for the 1·0M-solution of tri(methyl,vinyl)thallium in deuterobenzene at 26° was approximately thirty times faster than for a solution of trimethylthallium of the same concentration. The thallium–proton coupling constants for the vinyl protons could not be determined, but from the coupling constants for the divinylthallium cation, and a wide variety of organothallium compounds, it can be estimated that the largest coupling constant (J^{205}Tl–′H,trans) is *ca.* 1000 c./sec. Hence the vinyl exchange rate must be much more rapid than even the methyl exchange rate. This very rapid exchange of vinyl groups is, at first sight, rather surprising, since pπ–pπ bonding (as postulated in the vinylboranes [14]) would tend to slow down the rate of exchange. The transition state may be stabilised by the contribution of structures such as (II). to the resonance hybrid. Alternatively, donation of the π-electrons of the double bond into the



(II)

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[11] Schaefer, *Canad. J. Chem.*, 1962, **40**, 1.

[12] Banwell and Sheppard, *Mol. Phys.*, 1960, **3**, 351.

[13] Dailey and Shoolery, *J. Amer. Chem. Soc.*, 1955, **77**, 3977.

[14] Letsinger and Skoog, *J. Org. Chem.*, 1953, **18**, 895.

vacant *p* orbital of the thallium may occur (cf. ref. 15). It is significant that very recently Oliver and Stevens [15] have shown that trivinylgallium is dimeric in solution and thus more associated than triethylgallium.

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[15] Oliver and Stevens, *J. Inorg. Nuclear Chem.*, 1962, **24**, 953.