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# KINETICS AND MECHANISM OF AROMATIC THALLIATION AND MERCURIATION—AN NMR STUDY

R. M. G. ROBERTS

Department of Chemistry, University of Essex, Colchester, England

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**Abstract**—The rates of reaction of Tl (III) tris(trifluoroacetate) with benzene toluene and t-butylbenzene in solvent trifluoroacetic acid have been measured by an NMR method. The reaction products have been unambiguously determined from the thallium–hydrogen coupling constants. In the case of toluene, *p*-tolylthallium bis(trifluoroacetate) crystallised from reaction mixtures.

Thalliation was shown to be reversible and to be between one and two orders of magnitude slower than mercuriation. The inductive order of the reactivity (tBu > Me ≫ H) was found in contrast to the hyperconjugative order for mercuriation. Hammett plots using $\sigma^+$ values yielded a $\rho$ value of $-7.4$ but the limited data correlated better with $\sigma$ values ($\rho = -12.8$). A primary isotope effect of 5.0 was found for toluene indicating rate-determining proton transfer. The mechanism is discussed in the light of these and other findings. In addition the rates of interconversion of the products of mercuriation of toluene are reported from NMR data.

Aromatic thalliation is now extensively used in the synthesis of a large number of aromatic compounds. Its importance was first recognised and developed by Mckillop *et al.*[1] However, although the products of the reactions have been extensively investigated, evidence concerning the mechanism of the reactions has been rather sparse, being confined to studies of acid catalysed reactions which showed complex kinetics[2-4] and competitive methods.[5,6] In view of the discrepancies revealed in the above work, it was decided to investigate the reactions by a direct kinetic method using NMR spectroscopy. In addition, the same technique was used in product analyses on the corresponding mercuriation reactions.

## DISCUSSION AND RESULTS

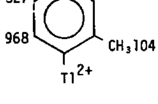
Aromatic thalliation proceeds rapidly and smoothly with TL(III) trifluoroacetate as the electrophilic species. Few direct comparisons of the rates of thalliation and mercuriation have appeared. Henry[2] reported that thalliation was much slower than mercuriation in acid catalysed reactions, a result which parallels the reactivity sequence in the reactions of olefins with heavy metal salts.[7,8] Briody and Moore[3] however state that the reaction of $Tl(OCOCF_3)_3$ with benzene in trifluoroacetic acid was too rapid for conventional kinetic procedures. Since mercuration by $Hg(OCOCF_3)_2$ in this solvent can be very conveniently measured by standard UV[9] and titrimetric methods,[10] an anomaly is apparent. Accordingly, the rates of thalliation have been measured by the direct observation of changes in the NMR spectra of equimolar solutions of Tl(III) trifluoroacetate and the relevant aromatic compounds. The first product of thalliation should be the monoaryl thallium derivative

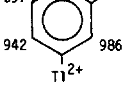
$$ArH + Tl(OCOCF_3)_3 \rightarrow ArTl(OCOCF_3)_2 + HOCOCF_3 \qquad (1)$$

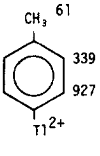
although disproportionation is possible yielding the more thermodynamically stable dialkyl derivative

$$2\,ArTlX_2 \rightarrow Ar_2TlX + TlX_3 \quad [X = OCOCF_3]. \qquad (2)$$

The true nature of the final product can be readily determined from the large Tl–H coupling constants. Thus for the monoalkyl derivatives the thallium-*ortho*, *meta* and *para* hydrogen coupling constants are 948, 365 and 123 (Hz) respectively,[11] whereas those for the corresponding dialkyl species are 451, 139 and 51 (Hz), as measured for the perchlorates in $D_2O$. In addition, the coupling constants for the tolylthallium dications are as follows:







Apart from the extremely large values of the constants, the long range coupling is a striking feature of these derivatives. Thus the methyl group in the original toluene molecule is split by $^{203,205}$Tl–H coupling into two broad peaks. (The $^{203}$Tl and $^{205}$Tl species are not usually separable except under very high resolution.) Values of J Tl–$C\underline{H}_3$ are thus of great value in the structural determination of the products. The coupling constants themselves are dependent on the solvent and on the anion present. In solvents where the aryl thallium salt is undissociated, J Tl–H values are significantly higher for the trifluoroacetates than the corresponding perchlorates or halides.[12] McKillop *et al.*[13] reported ortho and meta coupling constants for *p*-tolylthallium bis(trifluoroacetate) as 1025 and 376 Hz respectively in DMSO-$d_6$ with the corresponding Tl–$CH_3$ constant at 66 Hz.

On treating a 0.6 M solution of toluene in $CF_3CO_2D$ with an equal volume of 0.6 M $Tl(OCOCF_3)_3$ solution, the original sharp aromatic and aliphatic signals at 6.72 and 1.87 ppm respectively decreased in intensity whilst two broad singlets developed at 2.53 and 1.47 ppm. These signals correspond almost exactly to those expected for the coupled methyl protons in *p*-tolyl-thallium bis(trifluoroacetate) (i.e. J Tl–$CH_3$ = 64 Hz). In addition, two pairs of sharp doublets appeared symmetrically on either side of the decreasing aromatic signal with separations of 1076 and 436 Hz respectively, corresponding to the J ($Tl^{203.205}$-*ortho* H) and J ($^{203.205}Tl$-*meta* H) coupling constants respectively. Thus by monitoring the decrease in the aromatic signal, or by measuring the ratio of the integrals of the product Me doublet to the decreasing toluene Me group, the rate of reaction can be measured. As an additional check, use can be made of the developing aromatic signal at 3.33 ppm which represents *one half* of the protons *ortho* to the thallium substituent (i.e. 1 H). The results of such an analysis appear in Table 1 and the agreement is satisfactory. There also appears to be no significant dithalliation. Thalliation results in dominant *para*-substitution (9.7% *ortho*, 3.5% *meta* and 86.8% *para*[6]) and at low temperatures is not susceptible to isomer redistribution as is the case with mercuriation.[5]

The NMR method is not sufficiently sensitive to detect the small amounts of *ortho* and *meta* products but it is likely that the integration of the product Me groups includes the *meta* (J Tl–$CH_3$ ~ 50$H_2$) but not the *ortho* product (J Tl–$CH_3$ ~ 104 Hz). However over 90% of the product is monitored in this way and, as Table 1 shows, the discrepancy is not serious. For t-butylbenzene the complex aromatic multiplet at ~6.9 ppm disappeared slowly whilst the original Me singlet of the substrate at 0.88 ppm was replaced by a singlet at 0.93 ppm'. These signals were too close to make use of independently, and the reaction was monitored by measuring the ratio of the disappearing aromatic signal to the total aliphatic signal. It appears that the additional C–C linkage destroys any coupling between the thallium and Me groups. As with toluene, peaks due to Tl–H coupling in the aromatic ring appear. For benzene the reaction was followed from the decrease in the aromatic proton signals. Like mercuriation, thalliation is a reversible process. For benzene, the reaction came to equilibrium at 76% conversion, an appreciably lower value than that for mercuriation (92%). For toluene at 0.3 M, crystallisation of *p*-tolylthallium bis(trifluoroacetate) occurred (31% yield) and hence the position of equilibrium could not be determined. However using 0.1 M solutions, no crystallisation occurred and a conversion of 90% was found, identical to that obtained for t-butylbenzene. Thus the overall equilibrium constant ($K_{eq}$) followed the order tBu ~ Me > H in marked contrast to that for mercuriation (H > Me). In view of the reversible nature of the reaction modified kinetic equations were employed for benzene to take account of the back reaction. For toluene and t-butylbenzene, the conventional second order plots $\left(\frac{x}{a-x} \text{ vs } t\right)$ were linear up to 45–50% reaction but thereafter deviations occurred. Such behaviour cannot be explained by the incursion of the reverse reaction since the modified approach used for benzene also showed some curvature. The origin of this behaviour is not clear. Possibly some redistribution occurs via eqn (2). This would clearly affect the concentration of the thallium salt, rendering the simple second order equation inapplicable. It must be added that no clear evidence for $Ar_2TlX$ species is apparent from the NMR spectra but it is possible that the methyl resonances (J Tl–$\underline{CH}_3$ = 50 $H_2$) could be masked by those of the $ArTlX_2$ derivatives.

The effect of substituents on rate (Table 2) followed the inductive order t Bu > Me ≫ H in agreement with previous findings[5] and in contrast to the observed hyperconjugative sequence for mercuriation. The rate differences are, however, rather small and could result

Table 1. Analysis of NMR data for the reaction of toluene with Tl(III) trifluoroacetate (0.3 M in each) in $CF_3CO_2H$ at 22.4°

| | integrals* | | | | % product formed | | | |
|---|---|---|---|---|---|---|---|---|
| Time (min) | $I_1^a$ | $I_2^b$ | $I_3^c$ | $I_4^d$ | a | b | c | d |
| 0 | 118 | 80 | 0 | | | | | |
| 3 | 93 | 55.5 | 13.5 | - | 21 | 22 | 19 | - |
| 9 | 71 | 45 | 27 | 7.5 | 40 | 37 | 38 | 32 |
| 14.5 | 62.5 | 39.5 | 32.5 | 11 | 47 | 44 | 46 | 47 |
| 21.5 | 53 | 34 | 35.5 | 12.5 | 55 | 52 | 50 | 53 |
| 31.5 | 48 | 31.5 | 40 | 13 | 59 | 56 | 56 | 55 |
| 41.5 | 43 | 28.5 | 43 | 15.5 | 64 | 60 | 61 | 65 |

* Arbitrary units

a,b From decreasing aromatic and aliphatic signals respectively

d,c From increasing aromatic and aliphatic signals respectively

Table 2. Second order rate constants ($k_2$ l mole$^{-1}$ s$^{-1}$) and % conversions for the thalliation of aromatic compounds with Tl(III) tris(trifluoroacetate) in $CF_3CO_2H$ at 0.3 M concentration in both reagents

| R | T | $10^4$ $k_2$ | % | $k_H/k_D$ |
|---|---|---|---|---|
| $C_6H_6$ | 18 | 1.21 ± 0.05 | 76 | - |
| " | 22.4 | 1.47 ± 0.11 | 76 | - |
| $C_6H_5CH_3$ | 18 | 30 ± 1 | - | - |
| " | 18 | 28 ± 1 | 90[a] | - |
| " | 22.4 | 35 ± 1 | - | - |
| " | 23.2 | 35 ± 1 | - | 5.0 ± 0.4 |
| " | " | 37.6 ± 0.7 | - | |
| " | " | 34.4 ± 1.0 | - | |
| $C_6D_5CH_3$ | " | 7.1 ± 0.5 | - | |
| " | " | 7.1 ± 0.3 | - | |
| $C_6H_5O(CH_3)_3$ | 22.4 | 48 ± 0.3 | 90 | - |

a - using 0.1 M solutions

from quite subtle differences of mechanism (differential solvation for example). On the other hand the differences observed in the $K_{eq}$ sequences for the two reactions lead one to suspect some significant differences in mechanism, though this must await further more detailed investigation.

The toluene/benzene rate ratio ($k_T/k_B$ = 24) was found to be smaller than those recently reported (33–Ref. 5, 44–Ref. 6). Both the latter values were obtained by the more indirect quenching technique using aqueous KI. Organomercury compounds undergo anion (particularly halide ion) acid catalysed solvolysis[14] and it is likely that similar processes occur for thallium derivatives.† The apparent relative reactivities would be affected by the rates of these catalysed reactions

$$ArTl(OCOCF_3)_2 \xrightarrow{KI} ArTlI_2 \qquad (3)$$

$$ArTlI_2 + H_3\overset{+}{O} + I^- \longrightarrow ArH + TlI_3 + H_2O \qquad (4)$$

$$ArTlI_2 \longrightarrow ArI + TlI \qquad (5)$$

if the solvolysis rates were comparable with the rates of decomposition of the aryl thallium di-iodides.[5]

Briody and Moore[4] reported $^kT/k_B$ values in the range 2–11, the higher figures pertaining to higher catalytic acid concentrations. This is at first sight a curious result, since, as the authors themselves suggest, an increase in the acid concentration would produce more of the stronger electrophilic reagent $TlX_3$ (X = $ClO_4$, $HSO_4$). If this is so, then the selectivity of the reagent would be lower, and hence the $k_T/k_B$ values should decrease. However the results can be rationalised in terms of a weak formal Tl–C bond in the transition state. The highly positive thallic ion interacts at a greater internuclear distance and hence the localised charge distributions are relatively less important.

A striking feature of the acid catalysed work are the large values of ΔH‡ and the large *positive* values of ΔS‡ found at low acid concentrations and the observation that the ΔS‡ values become negative at higher acidities. The species $TlX_3$ and $ArTlX_2$ are both at least partially ionic (probably completely so for X = $ClO_4$, $HSO_4$) and it seems unreasonable to attribute the large apparent positive ΔS‡ values to the "freeing" of solvent molecules in the transition state. It was noted that the Arrhenius parameters were obtained at only *two* temperatures, which can lead to considerable errors. Until further substantiative work is done, the origin of these remarkable effects must remain obscure.

Hammett correlations using $\sigma^+$ values for thalliation give a $\rho$ value of about $-7$,[5,6] being somewhat higher than that of mercuriation. A rather better correlation was obtained using the Yukawa-Tsumo equation which gave $\rho = -8.3$ and r = 0.44.

Using the isomer ratios quoted by Stock[6] and Olah[5] and the $k_{ArH}/k_{C_6H_6}$ ratios reported here, partial rate factors were calculated and plotted in the usual manner against both $\sigma^+$ and $\sigma$ values. The former gave a $\rho$ value of $-7.4$ (correlation coefficient = 0.970) whilst the latter gave $-12.4$ (correlation coefficient = 0.991). The $\sigma^+$ correlation for mercuriation gave $\rho = -6.3$. The data, albeit very limited, correlate better with $\sigma$ than with $\sigma^+$ values. This could be due to the effect of some charge transfer in an initially rapidly formed $\pi$ complex resulting in a compensation effect. Such complexes have been recently characterised spectrophotometrically in these laboratories and similar work on thalliation is in hand. The question of the existence of discrete intermediates in thalliation remains open at present. The observation that in the corresponding mercuriation reactions, added $CF_3CO_2Na$ (a strong base in solvent $CF_3CO_2H$) had no effect on the reaction rate,[9] strongly suggests a concerted mechanism involving proton transfer to the

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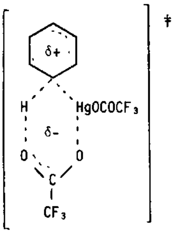
†Preliminary experiments show that *p*-tolylthallium bis(trifluoroacetate) liberates small quantities of toluene (*ca* 4%) on treatment with acidified KI solution.

incipient $CF_3CO_2^-$ group as shown in the transition state depicted below.



Primary kinetic isotope effects ($^kH/k_D$) have been reported for acid catalysed thalliation of benzene using $Tl(OAc)_3$ as 2.4[4] and 3.7 and 3.6 for benzene and toluene respectively for reactions in acetic acid-trifluoroacetic acid mixtures. In the present work a value of $k_H/k_D$ of 5.0 ± 0.4 has been found for thalliation of toluene (Table 2). This is lower than that for mercuriation[9] (7.0) but still implies pronounced proton transfer in the rate determining step.

Finally the relative rates of mercuriation and thalliation can be calculated as ~30 for benzene and ~140 for toluene using the data in this work and that obtained in Ref. 9.

A corollary of the Hammond postulate† is that an increase in reaction rate makes the transition state structurally more reactant-like. Applying this concept to mercuriation and thalliation, the former reaction will be more reactant-like than the latter. This in turn means that the carbon–metal interaction should be weaker in the case of mercuriation compared with thalliation resulting in the former process being less selective. This is supported by selectivity factors, $\log p_f^{Me}/m_f^{Me}$ of 1.3 and 1.8 respectively and the corresponding $\rho$ values of $-6.4$[5] and $-7.4$ (this work). Thus the charge built up on the aromatic ring seems to be greater for thalliation than for mercuriation. This is in keeping with the lower value observed for $k_H/k_D$ for the former reaction, since pronounced C–H cleavage in the transition state would effectively reduce the charge on the ring. The lower isotope effect can be rationalised, therefore, in terms of stronger carbon–metal and carbon H- bonding of C4 in the transition state for thalliation compared with mercuriation.

*Mercuriation.* It was recently shown that the products of aromatic mercuriation undergo rearrangement[5] with time, based on measurement of isomer ratios of quenched reaction mixtures. Such rearrangements can be followed directly by NMR measurements. Immediately on mixing equal volumes of 0.6 M toluene and Hg(II)bis(trifluoroacetate) three new peaks appear in the aliphatic region ($\delta = 1.87$–$2.00$ ppm) at +7.2 (I) (sharp), +3.0 (II) (sharp) and −2.0 Hz (III) (broad) from the original Me signal of toluene (1.88 ppm), a positive sign indicating a downfield shift. II predominated and can be readily assigned to the *para* isomer. For t-butylbenzene, immediately on reaction a quartet appeared in the aromatic region ($\delta = 6.92$, J = 8.5 Hz) with a sharp singlet at 0.85 ppm (t-Bu protons). On standing for 24 hr a new peak developed 1.8 H *upfield* from the original t-Bu proton signal. Since no *ortho* substitution has been observed in mercuriation of t-butylbenzene, the new signal must be due to the thermodynamically more stable *meta* isomer formed by isomerisation from the initially formed *para* isomer. Referring back to mercuriation of toluene, it would seem probable that III is in fact due to the *meta* isomer and hence I is assigned *ortho*. Further support comes from the fact that the initial I/II ratio of 0.38 is quite close to that reported for the *o*/*p*-ratio of 0.30 or short reaction times[5] that for the *m*/*p*-ratio being 0.1.

It was possible by scanning over short sweep widths (0.5 ppm) to calculate the *o*- and *p*-concentrations. Unfortunately the *m*-absorption was rather broad and overlapped to some extent with unreacted toluene (84% conversion at equilibrium at 0.3 M in each reagent). However Olah's data show that for the initial stages of the reaction the *o*/*m*-ratio is sensibly constant at 3.10 ± 0.12, thus enabling the concentration of the *meta* isomer to be determined. The results appear in Table 3 and show reasonably good agreement with Olah's values. (Using the 84% conversion figure it was possible to calculate the final equilibrium composition after 3 days as *o* 31%, *p* 31%, *m* 38%.) At suitable times during the reaction the ratio of aromatic to aliphatic protons was determined and was found not to vary significantly from that predicted for mono-substitution. The results indicate that the *para* isomer is converted to both *ortho* and *meta* derivatives and that eventually a slow conversion of ortho to meta occurs. The results seem to parallel those for the catalysed isomerisation of the xylenes where no *meta* to *ortho* conversion occurred.[15,16] Plots of log {[*para*] − [*para*]$_\infty$} *vs* time (Table 4) showed good linearity, giving an observed first order rate constant ($k_1^{obs}$) of $6.7 \pm 0.4 \times 10^{-5}\ sec^{-1}$ at 18° (0.3 M) which represents the sum of the true rate constants for *p*- to o- and *p*- to *m*-isomerisations. The value of $k_1^{obs}$ did not change appreciably when lower reactant concentrations were used ($k_1^{obs} = 6.7 \pm 0.7 \times 10^{-5}\ sec^{-1}$ at 0.1 M) confirming the unimolecular nature of the rearrangement. Isotope effects for the isomerisation would be illuminating and are currently being investigated.

## EXPERIMENTAL

*Starting materials.* Trifluoroacetic acid was redistilled prior to use. The deuteriated acid was prepared by careful addition of $D_2O$ to a 10% excess of the anhydride at 40° with vigorous stirring.

Mercuric(II)bis(trifluoroacetate) was prepared by adding yellow HgO to a warm soln of 10% trifluoroacetic anhydride in $CF_3CO_2H$ followed by cooling to yield a crystalline product (mp 165° 85%). Thallium(III) tris(trifluoroacetate) was obtained from Aldrich Chemicals Ltd. Aromatic substrates were redistilled prior to use. Toluene-$d_5$ was

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†As Farcasiu[19] has pointed out, care must be exercised in applying the Hammond postulate. In particular, the relative energies of the products should be known since in some cases the process with the higher activation energy leads to the most thermodynamically stable product which results in the *less* reactive compound having an "early" transition case. This however is not the case for thalliation and mercuriation of benzene since the slower reaction gives lower yields (75% for thalliation, 92% for mercuriation).

The situation is almost reversed for toluene (90% for thalliation, 77% for mercuriation). However these differences in factor-product stability amount to less than 1 kcal mol$^{-1}$, and thus the Hammond postulate can be used as a broad guide.

Table 3. Changes in composition of the reaction mixture of toluene and Hg(II) bis(trifluoroacetate) (0.3 M in each reagent) in $CF_3CO_2H$ with time at 18°. ($I_x$ = NMR integral of methyl groups in arbitrary units)

| | | | | % products | | |
|---|---|---|---|---|---|---|
| Time (min) | $I_{ortho}$ | $I_{para}$ | $I^a_{meta}$ | ortho | para | meta[b] |
| 0 | | | | | | |
| 13 | 42 | 93 | 24 | 28 | 63 | 9 |
| 55 | 42 | 81 | 28 | 31 | 59 | 10 |
| 99 | 48 | 71 | 31 | 36 | 53 | 11.5 |
| 134 | 47 | 63 | 33 | 37.5 | 50 | 13.5 |
| 184 | 52 | 62 | 38 | 40 | 47 | 13 |
| 221 | 52 | 55 | 39 | 42 | 44 | 13 |
| 291 | 50 | 50 | 43 | 43 | 43 | 14 |
| 362 | 53 | 46 | 45 | 45.5 | 39.5 | 14.5 |
| 1575 | 41 | 31 | 57 | 38 | 29 | 33[c] |
| 1745 | 43 | 31 | 61 | 38 | 28 | 34[c] |
| 5000 | 32 | 31 | 58 | 31 | 31 | 38[c] |

a contains some unreacted toluene

b calculated from o/m ratios in ref. 5 (see text)

c calculated from known yields of product (see text)

Table 4. Isomerisation of products of mercuriation of toluene (0.3 M) in $CF_3CO_2H$ with Hg(II) bis(trifluoroacetate) (0.3 M) at 18°

| Time (min) | integral para isomer $(Ip)^a$ | $Ip-Ip^{\infty}$ | $\ln(Ip-Ip^{\infty})$ |
|---|---|---|---|
| 0 | | | |
| 13½ | 93 | 62 | 4.127 |
| 55 | 81 | 50 | 3.912 |
| 99 | 71 | 40 | 3.689 |
| 134 | 63 | 32 | 3.466 |
| 184 | 62 | 31 | 3.434 |
| 221 | 55 | 24 | 3.178 |
| 291 | 50 | 19 | 3.944 |
| 362 | 46 | 15 | 2.708 |
| 5000 | 31 | | |

a - arbitrary units

b - correlation coefficient 0.992, $k_1^{obs} = 6.7 \pm 0.4 \times 10^{-5}\ s^{-1}$

prepared by equilibration of toluene in $CF_3CO_2D$ in the presence of $CF_3SO_3D$ as catalyst.[17]

*Products*. Thallium(III) trifluoroacetate (5.1 g, 9.4 mmole) in $CF_3CO_2H$ (18 ml) was added dropwise to toluene (1.0 ml, 0.867 g, 9.4 mmole) in $CF_3CO_2H$ (18 ml) and allowed to stand overnight at room temp. The white crystals of tolylthallium bis(trifluoroacetate) were filtered off, washed with a little cold $CCl_4$ and sucked dry to give 1.5 g (31%) product, mp 185°. (Found: C 25.3, H 1.3, F 21.8. Calc. for $C_{11}H_7O_4F_6Tl$: C, 25.3; H, 13.5; F, 21.8%). The IR spectrum showed the following absorptions:- 1680 s, 1600 s, 1495 w, 1480 w, 1415 m, 1395 vw, 1170 vs, broad, 1007 m, 872 s, (795 785 s), (735 725 s). The sharp doublets (in parentheses) are typical of arylthallium bistrifluoroacetates,[13] being assigned to the C–$CO_2$ in plane bending and $CF_3$ stretching modes respectively.

*Kinetic measurements*. The reactions were followed by observing the changes in the NMR spectra of reaction solns (usually 0.3 M in each reagent) using a Varian EM 360 spectrometer housed in a constant temp room (18° ± 1). The probe temp was measured as 23.2 ± 0.1 over a period of several hr. Reactions quoted at other temps were performed

Table 5. Data for the evaluation of the second order rate constant ($k_2$, $l\,mol^{-1}\,s^{-1}$) for the thalliation of benzene (0.3 M) by $Tl(OCOCF_3)_3$ (0.3 M) at 18 in $CF_3CO_2H$

| T (min) | integral of aromatic signal[a] | a-x | x | $x_e$-x | $x_e$x | $a^2-x_ex$ | $\ln \frac{a^2-x_ex}{x_e-x}$ [b,c,d] |
|---|---|---|---|---|---|---|---|
| 0 | 113 | 0.300 | 0.000 | 0.228 | 0.0000 | 0.0900 | -0.930 |
| 41 | 102 | 0.271 | 0.029 | 0.199 | 0.0066 | 0.0834 | -0.870 |
| 73 | 96 | 0.255 | 0.045 | 0.183 | 0.0103 | 0.0797 | -0.831 |
| 105 | 91 | 0.241 | 0.059 | 0.169 | 0.0135 | 0.0765 | -0.793 |
| 138 | 85 | 0.226 | 0.074 | 0.154 | 0.0169 | 0.0731 | -0.745 |
| 188 | 80 | 0.212 | 0.088 | 0.140 | 0.0201 | 0.0699 | -0.694 |
| 4320 | 27 | 0.072 | 0.228[e] |  | 0.0520 | 0.0380 | - |

a measured at $\delta$ = 7.00 in arbitrary units

b see Ref. 18

c correlation coefficient 0.999

d $k_2 = 1.21 \pm 0.01 \times 10^{-4}\ l\ mol^{-1}\ s^{-1}$

e 76% conversion

either at room temp (18°) or in a thermostat bath, the samples being rapidly analysed (30 sec) and returned to their reaction environment.

In view of the pronounced reversibility of thalliation of benzene, the usual modified equation was used for equimolar reactant concentrations a

$$\ln\frac{a^2 - xxe}{xe - x} = k_2\frac{a^2 - xe^2}{xe}t \qquad (6)$$

where xe is the final equilibrium concentration of the product. $k_2$ was evaluated graphically. Table 5 shows the relevant data for benzene, the reaction being monitored by measuring the decrease in the aromatic signal. For toluene, the ratio of the methyl groups of starting material and product (Me appears as doublet $J(Tl\text{–}CH_3) = 64$ Hz) was measured (Table 6). For t-butylbenzene the reaction was followed by measuring the ratio of aromatic to the total aliphatic proton signal (= R) and the amount of reaction x was calculated from eqn (7).

$$x = (1 - \tfrac{9}{5}R)a. \qquad (7)$$

The rates for toluene-$d_5$ were measured as for toluene itself. It was found unnecessary to use deuteriated solvent since little or no isotopic exchange occurred during reaction. This was shown by the non-appearance of the usual Tl-*ortho* H signal at $\delta$ = 3.33 ppm'.

*Mercuriation.* The isomerisation of the products of mercuriation was followed by the NMR method already outlined (*vide supra*). Tables 3 and 4 show the relevant data.

Table 6. Second order rate constants ($k_2\,l\,mol^{-1}\,s^{-1}$) for the thalliation of toluene (0.3 M) by $Tl(OCOCF_3)_3$ (0.3 M) at 23.2° in $CF_3CO_2H$

| Time (sec) | $I_1^a$ | $I_2$ | $I_3$ | $\frac{x}{a-x}$ [b] | $10^3 \frac{x}{a-x} \cdot \frac{1}{at}(=k_2)$ [c] |
|---|---|---|---|---|---|
| 0 |  |  |  |  |  |
| 150 | 10 | 107 | 10 | 0.187 | 4.1 |
| 255 | 13 | 95 | 14 | 0.284 | 3.7 |
| 330 | 16 | 84 | 16 | 0.381 | 3.8 |
| 465 | 20.5 | 73.5 | 21 | 0.565 | 4.1 |
| 555 | 21 | 71 | 22.5 | 0.613 | 3.7 |
| 645 | 23.5 | 68 | 26 | 0.728 | 3.8 |
| 750 | 26 | 65.5 | 30 | 0.855 | 3.8[d] |
| 960 | 28 | 60 | 28 | 0.933 | 3.2 |

a $I_1$,$I_3$ are the integrals of the methyl group (doublet) in the product, $I_2$ is the integral of the toluene $CH_3$, all in arbitrary units.

b from $\frac{I_2}{I_1+I_2}$

c correlation coefficient for data excluding final point = 0.998

d 46% conversion

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