# Electrophilic Aromatic Substitution. 13.[1] Kinetics and Spectroscopy of the Chloromethylation of Benzene and Toluene with Methoxyacetyl Chloride or Chloromethyl Methyl Ether and Aluminum Chloride in Nitromethane or Tin Tetrachloride in Dichloromethane. The Methoxymethyl Cation as a Remarkably Selective Common Electrophile

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Vacuum line kinetics studies have been made of the reaction in nitromethane between benzene and/or toluene, methoxyacetyl chloride (MAC), and $AlCl_3$ to produce benzyl or xylyl chlorides, CO, and a $CH_3OH^-AlCl_3$ complex. For both arenes, the rate law appears to be $R = (k_3/[AlCl_3]_0)\,[AlCl_3]^2$-[MAC]. When chloromethyl methyl ether (CMME) is substituted for MAC, a similar rate law is obtained. Both chloromethylation reactions yielded similar, large $k_T/k_B$ ratios (500−600) and similar product isomer distributions with low meta percentages (~0.4) which suggest $CH_3OCH_2^+$ or the $CH_3OCH_2^+Al_2Cl_7^-$ ion pair as a common, remarkably selective, electrophile. The kinetics of MAC decomposition to CMME and CO in the presence of $AlCl_3$ yielded the rate law $R = k_2[AlCl_3]_0[MAC]$. Here $AlCl_3$ is a catalyst (no $CH_3OH$ is formed), and thus the rate law is equivalent to the chloromethylation rate law. All three reactions have comparable reactivities, which is consistent with rate-determining production of the electrophile. Kinetics studies of benzene or toluene with $SnCl_4$ and MAC or CMME in dichloromethane were also completed. With MAC and benzene the rate law is $R = k_3[SnCl_4]_0[MAC][benzene]$ and with toluene $R = k_2[SnCl_4]_0[MAC]$. MAC decomposition, again followed by CO production, was unaffected by the presence of either aromatic and obeyed the rate law $R = k_2'\,[SnCl_4]_0[MAC]$ where $k_2 \approx k_2'$. Chloromethylation with CMME followed the rate law $R = k_3[SnCl_4]_0[CMME][arene]$ for benzene and toluene and produced a $k_T/k_B$ ratio and product isomer distributions very similar to those determined with $AlCl_3$ in nitromethane, further supporting a common electrophile. Low-temperature $^{13}C$ and $^{119}Sn$ FT-NMR and Raman spectroscopic studies suggest the existence of a weak 1:1 adduct between MAC and $SnCl_4$ of the type $RCXO \rightarrow SnCl_4$, with electron donation to the metal through carboxy oxygen. Finally, an explanation is provided for the range of chloromethylation $k_T/k_B$ values and product isomer percentages published in the literature.

## Introduction

The family of reactions known as chloromethylation has been of synthetic importance for many years.[2] Although the literature includes a number of papers which deal with kinetics and/or mechanistic aspects of chloromethylation, it is clear that significant questions remain unresolved. For example, many different values have been published for the competitive rate of chloromethylation of toluene to benzene $k_T/k_B$: 3.0,[3] 3.1,[4] 28.2,[5] 30,[6] 39.1,[7] 40.3,[5] and 112 ± 12,[8] for essentially the same reaction.[9] Of these the last value, 112 ± 12, when combined with toluene product isomer percentages of 34.7 ortho, 1.3 meta, and 64.0 para was found by Brown and Nelson[8] to fit Brown's selectivity relationship. However, Olah, Beal, and Olah[5] obtained $k_T/k_B$ ratios which increased from 21 to 317 when the $SnCl_4$ catalyst concentration was decreased by a factor of 13. Product chloromethylated toluene isomer percentages also changed but to a more modest extent. It should be noted that both Brown and Olah used the competitive method to determine substrate selectivities. We have previously pointed out that this is valid only if the rate order for the arene is invariant. Because of the uncertainty surrounding the mechanism of chloromethylation, we undertook a complete (competitive and noncompetitive) vacuum line kinetics study of this reaction. Given the known carcinogenic character of the more commonly used chloromethylating reagent bis(chloromethyl) ether, we followed McKillip's suggestion[10] and worked initially with methoxyacetyl chloride (MAC).

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[1] For Electrophilic Aromatic Substitution, part 12, see: DeHaan, F. P.; Chan, W. H.; Chang, J.; Cheng, T. B.; Chiriboga, D. A.; Irving, M. M.; Kaufman, C. R.; Kim, G. Y.; Kumar, A.; Na, J.; Nguyen, T. T.; Nguyen, D. T.; Patel, B. R.; Sarin, N. P.; Tidwell, J. H. *J. Am. Chem. Soc.* **1990**, *112*, 356.

[2] Olah, G. A.; Tolgyesi, W. S. *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Interscience: New York, 1964; Vol. 2, p 659.

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[8] Brown, H. C.; Nelson, K. L. *J. Am. Chem. Soc.* **1953**, *75*, 6292.

[9] Professor R. Taylor states "a notable feature of this reaction is that nobody seems to agree on the partial rate factors and hence the $\rho$ factor for the reaction": Taylor, R. *Aromatic and Heteroaromatic Chemistry*; Specialist Periodical Reports; The Chemical Society: London, 1975; Vol. 3, p 240.

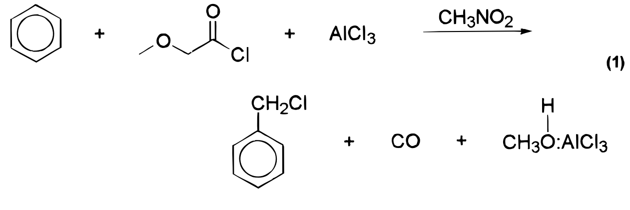
[10] McKillip, A.; Madjdabadi, F. A.; Long, D. A. *Tetrahedron Lett.* **1983**, *24*, 1933.

**Table 1. Product Isomer Distribution (Run 6) for Chloromethylation of Toluene with MAC and $AlCl_3$ in Nitromethane at 0 °C**

| | | product xylyl chlorides | | |
|---|---|---|---|---|
| sample | time (min) | %ortho | % meta | % para |
| 11 | 33.3 | 26.54 | 0.52 | 73.22 |
| 16 | 201.2 | 29.44 | 0.44 | 70.12 |
| 20 | 1072.5 | 29.26 | 0.44 | 70.14 |

## Results and Discussion

**A. Kinetic Results in Solvent Nitromethane. 1. Chloromethylation of Benzene or Toluene with Methoxyacetyl Chloride (MAC) and $AlCl_3$.** The reaction of methoxyacetyl chloride (MAC) and benzene or toluene proceeds homogeneously and at a convenient rate in solvent nitromethane at 0 °C. However, to our surprise, *no* primary products, benzyl chloride or the xylyl chlorides, were found in our GC analysis. We established that they were not lost either through hydrolysis during reaction quenching or through decomposition in the GC injection port. Apparently, in the presence of $AlCl_3$, both benzyl chloride and the xylyl chlorides react immediately with the arene(s) present to form secondary benzylation products. As a consequence one must calculate primary product concentrations from secondary product peak areas and GC response factors. This was straightforward for benzene chloromethylation (since the only product is diphenylmethane), but involved certain assumptions for toluene chloromethylation and competitive chloromethylation (*vide infra*). In the case of toluene, six dimethyldiphenylmethane secondary product isomers are possible: o-o′, m-m′, p-p′, o-m′, o-p′, and p-m′. In practice, m-m′ was never seen, and the p-m′ and o-o′ peaks were superimposed. Our method of inferring the original xylyl primary product distribution was as follows. The p-p′ isomer could only be formed by *p*-xylyl chloride. In a separate study, but under the same conditions, we determined product isomer percentages for the $AlCl_3$-catalyzed *p*-xylylation of toluene; the data indicated 68.9% para isomer, 28.7% ortho isomer, and 2.4% meta isomer. Thus from the area of the p-p′ secondary product we can calculate the expected amount of p-m′ and o-p′ secondary products formed from *p*-xylyl chloride. By assigning the remainder of the o-p′ peak area to toluene attack by *o*-xylyl chloride and by using the known isomer distribution of the $AlCl_3$-catalyzed *o*-xylylation of toluene (74.5% para, 22.7% ortho, 2.8% meta), we can calculate the peak areas for the three primary product xylyl chlorides. Our calculated primary isomer percentages remained relatively constant during each individual run and consistent among a group of runs (Tables 1 and 2).



(1)

It should be noted that $AlCl_3$ is a true reagent in these reactions. In all cases where $AlCl_3$ was present as a limiting reagent, the reaction stopped when all of the $AlCl_3$ was consumed. For example, the last toluene run (Table 3) stopped at 18% reaction on the basis of MAC concentration but at 100% on the basis of that for $AlCl_3$. The most reasonable explanation of the noncatalytic behavior of $AlCl_3$ would appear to be the formation of a stable $CH_3OH{-}AlCl_3$ complex. This is consistent with the fact that in the absence of aromatic hydrocarbons (*vide infra*) no methanol is formed and $AlCl_3$ acts catalytically.

**Table 2. Product Isomer Distribution for Chloromethylation of Toluene with MAC and $AlCl_3$ in Nitromethane at 0 °C**

| | product xylyl chlorides | | |
|---|---|---|---|
| $[AlCl_3]_0$ (M) | % ortho | % meta | % para |
| 0.1128 | 29.34 | 0.43 | 70.23 |
| 0.0728 | 29.31 | 0.46 | 70.22 |
| 0.0648 | 28.86 | 0.44 | 70.70 |
| 0.0558 | 28.46 | 0.40 | 71.15 |
| 0.0440 | 29.26 | 0.44 | 70.14 |
| 0.0327 | 30.99 | 0.55 | 68.45 |
| 0.0186 | 30.68 | 0.47 | 68.85 |
| avg ± SD[a] | 29.6 ± 0.9 | 0.45 ± 0.05 | 70 ± 1 |

[a] Standard deviation.

For both benzene and toluene, the initial rates data (Table 3) clearly support a rate law which is first order in $AlCl_3$ and in MAC. However, second-order plots exhibited more curvature, and as shown in Table 3, second-order rate constants showed more scatter from run to run than third-order rate constants—calculated for second-order dependence upon $AlCl_3$ and first order in MAC. However, the calculated third-order rate constants vary with inital $AlCl_3$ concentration, but the product of the third-order constant and $[AlCl_3]_0$ is relatively constant, particularly for benzene reactions. These results suggest a rate law

$$\text{rate} = (k_3[\text{AlCl}_3]^2[\text{MAC}])/[\text{AlCl}_3]_0 \tag{2}$$

which simplifies under initial rates conditions to

$$\text{rate} = k_2[\text{AlCl}_3]_0[\text{MAC}]_0 \tag{3}$$

and reflects the inverse relationships observed between $k_3$ and initial $AlCl_3$ concentrations, $[AlCl_3]_0$ (Figure 1). The calculated constants $k_3[AlCl_3]_0$ are consistent for benzene runs but vary with initial $AlCl_3$ concentration for toluene reactions.

From benzene chloromethylation at −15°, 0°, and 15 °C (Table 3), Arrhenius/Eyring values were calculated from a regression analysis of an initial rates $k_2$ vs $1/T$ plot: $E_a = 130 \pm 30$ kJ/mol, $\Delta H^\ddagger = 130 \pm 30$ kJ/mol, $\Delta G^\ddagger = 81 \pm 1$ kJ/mol, and $\Delta S^\ddagger = 160 \pm 120$ J/(mol °C) (± standard deviation).

Since both reactions are independent of arene, the toluene/benzene rate constant ratio $k_T/k_B$ was determined competitively. This is given in Table 4 along with competitively determined product isomer percentages.

In competitive runs there are at least[11] three groups of secondary products: diphenylmethane, dimethyldiphenylmethanes, and methyldiphenylmethanes. The first two are easily apportioned into benzene and toluene products. However, the third results from both benzyl chloride−toluene and xylyl chloride−benzene reactions, and apportionment requires an additional assumption. From earlier work the competitive benzylation of benzene

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[11] Both tertiary products and benzyl or xylyl chloride polymerization were minimized by maintaining high arene:chloromethylating agent ratios.

**Table 3. Initial Rates and Rate Constants for the Chloromethylation of Benzene and Toluene with Methoxyacetyl Chloride and AlCl$_3$ in Nitromethane**

| temp (°C) | [C$_6$H$_5$CH$_3$] (M) | [C$_6$H$_6$] (M) | [MAC] (M) | [AlCl$_3$] (M) | initial rates ($\times10^5$ M s$^{-1}$) | inital rates/-[AlCl$_3$]$_0$[MAC]$_0$ ($\times10^2$ M$^{-1}$ s$^{-1}$) | inital rates/-[AlCl$_3$]$_0$$^2$[MAC]$_0$ ($\times10^2$ M$^{-2}$ s$^{-1}$) | $k_2$[a] ($\times10^3$ M$^{-1}$ s$^{-1}$) | $k_3$[b] ($\times10$ M$^{-2}$ s$^{-1}$) | $k_3$[AlCl$_3$]$_0$ ($\times10^2$ M$^{-1}$ s$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0.3504 | | 0.0329 | 0.1128 | | | | 2.7 ± 0.2 | 1.03 ± 0.09[c] | 1.2 ± 0.1[c] |
| | 0.3689 | | 0.0228 | 0.0798 | 5.6 ± 0.3[c] | 3.1 ± 0.2[c] | 38 ± 2[c] | 3.1 ± 0.2 | 1.03 ± 0.02 | 0.82 ± 0.01 |
| | 0.2273 | | 0.0242 | 0.0648 | 3.7 ± 0.1 | 2.36 ± 0.06 | 36 ± 1 | 7.8 ± 0.6 | 3.88 ± 0.06 | 2.51 ± 0.04 |
| | 0.3499 | | 0.0406 | 0.0558 | 6.0 ± 0.5 | 2.6 ± 0.2 | 47 ± 4 | 19.6 ± 0.3 | 5.4 ± 0.2 | 3.0 ± 0.1 |
| | 0.718 | | 0.1010 | 0.0440 | 11.2 ± 0.4 | 2.5 ± 0.1 | 57 ± 2 | 70 ± 6 | 6.4 ± 0.5 | 2.8 ± 0.2 |
| | 0.6486 | | 0.0335 | 0.0327 | 2.94 ± 0.05 | 2.68 ± 0.04 | 82 ± 1 | 32.7 ± 0.1 | 9.2 ± 0.6 | 3.0 ± 0.2 |
| | 0.633 | | 0.1112 | 0.0186 | 6.0 ± 0.4 | 2.9 ± 0.2 | 156 ± 10 | 370 ± 40 | 25 ± 5 | 4.6 ± 0.9 |
| | | | | | avg ± SD[d] | 2.7 ± 0.3 | | | | 2.6 ± 1.2 |
| | | 0.3754 | 0.0356 | 0.0952 | 0.73 ± 0.08 | 0.21 ± 0.02 | 2.2 ± 0.2 | 0.90 ± 0.05 | 0.154 ± 0.008 | 0.145 ± 0.008 |
| | | 0.6097 | 0.0415 | 0.0635 | 0.57 ± 0.03 | 0.22 ± 0.01 | 3.5 ± 0.2 | 2.9 ± 0.4 | 0.325 ± 0.007 | 0.206 ± 0.004 |
| | | 0.5634 | 0.0911 | 0.0435 | 0.81 ± 0.03 | 0.20 ± 0.02 | 4.7 ± 0.5 | 9.0 ± 0.8 | 0.44 ± 0.04 | 0.19 ± 0.02 |
| | | 0.7230 | 0.0410 | 0.0369 | 0.31 ± 0.06 | 0.20 ± 0.06 | 5.4 ± 1.6 | 15 ± 2 | 0.50 ± 0.02 | 0.183 ± 0.007 |
| | | | | | avg ± SD[d] | 0.21 ± 0.01 | | | | 0.18 ± 0.03 |
| −15 | | 0.4706 | 0.0396 | 0.0510 | | 0.0067 ± 0.0009 | | | 0.021 ± 0.003 | 0.011 ± 0.002 |
| 15 | | 0.5240 | 0.0360 | 0.0538 | | 3.0 ± 0.2 | | | 15 ± 1 | 8.1 ± 0.5 |

[a] Rate = $k_2$[AlCl$_3$] [MAC]. [b] Rate = $k_3$[AlCl$_3$]$^2$[MAC]. [c] 95% confidence limits. [d] Standard deviation.

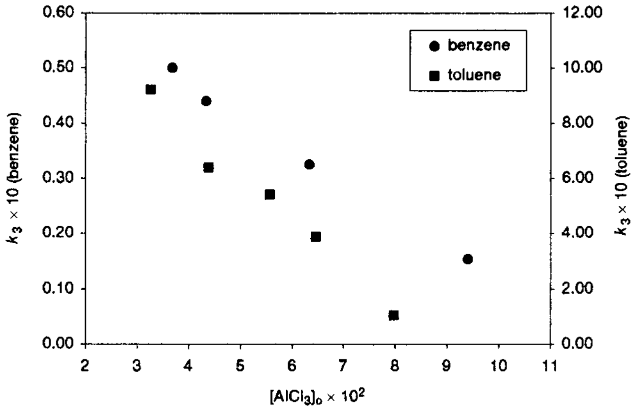

**Figure 1.** Inverse dependence of third-order rate constants upon initial AlCl$_3$ concentration.

**Table 4. Competitively Determined Rate Constant Ratios and Product Isomer Percentages for the Chloromethylation of Toluene and Benzene with MAC or CMME and AlCl$_3$ in Nitromethane at 0 °C**

| substrate | $k_T/k_B$ | % ortho | % meta | % para | $b$[a] |
|---|---|---|---|---|---|
| MAC[b] | 585[c] ± 44[d] | 30 ± 1[d] | 0.46 ± 0.06[d] | 70 ± 1[d] | 1.4 |
| CMME[e] | 516 ± 86 | 31 ± 2 | 0.37 ± 0.07 | 68 ± 2 | 1.3 |

[a] Brown selectivity relationship slope. [b] Methoxyacetyl chloride. [c] Average of three competitive runs. [d] Standard deviation. [e] Chloromethyl methyl ether.

and toluene yielded $k_T/k_B = 2.3 \pm 0.4$.[12] This value and the amount of diphenylmethane formed were used to estimate the amount of intermixed products resulting from benzyl chloride reacting with toluene. The remainder is then assigned to xylyl chloride–benzene reactions.

Also worthy of note is the fact that, during all competitive runs, $k_T/k_B$ would remain relatively constant early on and then drop sharply as the reaction progressed (Table 5). We found this to be an artifact of the huge substrate selectivity exhibited by the electrophile, which necessitated large initial benzene:toluene concentration ratios, typically 20:1, to produce a measurable amount of benzene product. When GC analysis included comparison of both products to an internal standard, it was clear that the precipitous drop in $k_T/k_B$ coincided with the end of the toluene reaction, i.e., when the small initial concentration of toluene was essentially used up, continued benzene reaction would, of course, lower $k_T/k_B$. Consequently only $k_T/k_B$ ratios calculated before that point were reported (Table 4).

**Table 5. Competitively Determined Rate Constant Ratios (Run 27[a]) for Chloromethylation of Toluene and Benzene with MAC and AlCl$_3$ in Nitromethane at 0 °C**

| time (s) | $k_T/k_B$ | time (s) | $k_T/k_B$ |
|---|---|---|---|
| 56 | 1062 | 291 | 275 |
| 77 | 568 | 561 | 115 |
| 99 | 442 | 996 | 35 |
| 163 | 595 | | |

[a] [Toluene]$_0$ = 0.0428; [benzene]$_0$ = 0.7521.

**2. Decomposition of Methoxyacetyl Chloride.** Since chloromethylation of benzene and toluene was independent of arene, it seemed appropriate to study the reaction between MAC and AlCl$_3$, which was readily followed by collecting and measuring the CO(g) produced (eq 1).

Here AlCl$_3$ is acting as a catalyst. This is readily seen from the fifth run (Table 6), when the reaction went to 90% completion based on the concentration of MAC, even though the AlCl$_3$ concentration was limiting.

The data suggest a rate law which is first order in MAC and first order in AlCl$_3$ as catalyst (Table 6).

$$\text{rate} = k_2[\text{AlCl}_3]_0[\text{MAC}] \qquad (4)$$

However, it is noteworthy that again (see Table 3) there appears to be an inverse effect with respect to initial AlCl$_3$ concentrations, with the highest values for the $k_1$/[AlCl$_3$]$_0$ being found at the lowest AlCl$_3$ concentrations. Also, the gas evolution data were unaffected by the speed with which the solutions were stirred.

**3. Chloromethylation of Benzene or Toluene with Chloromethyl Methyl Ether (CMME) and AlCl$_3$.** Since Stadlwieser[13] reported that the two main products of the reaction of MAC with AlCl$_3$ were CO and chloro-

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[12] DeHaan, F. P.; Delker, G. L.; Covey, W. D.; Ahn, J.; Anisman, M. S.; Brehm, E. C.; Chang, J.; Chicz, R. M.; Cowan, R. L.; Ferrara, D. M.; Fong, C. H.; Harper, J. D.; Irani, C. D.; Kim, J. Y.; Meinhold, R. W.; Miller, K. D.; Roberts, M. P.; Stoler, E. M.; Suh, Y. J.; Tang, M.; Williams, E. L. *J. Am. Chem. Soc.* **1984**, *106*, 7038. Although this $k_T/k_B$ value was determined with TiCl$_4$, values with other catalysts or with AlCl$_3$ and *p*-chlorobenzyl chloride all clustered in the 1.9–2.6 range in nitromethane.

[13] Stadlwieser, J. *Synthesis* **1984**, 490.

**Table 6. Initial Rates and Rate Constants for the $AlCl_3$-Catalyzed Decomposition of Methoxyacetyl Chloride (MAC) in Nitromethane at 0 °C**

| [MAC] (M) | $[AlCl_3]$ (M) | initial rates ($\times 10^5$ M $s^{-1}$) | inital rate/$[AlCl_3]_0[MAC]_0$ ($\times 10^2$ $M^{-1}$ $s^{-1}$) | $k_1$ ($\times 10^3$ $s^{-1}$) | $k_1/[AlCl_3]_0$ ($\times 10^2$ $M^{-1}$ $s^{-1}$) |
|---|---|---|---|---|---|
| 0.0372 | 0.1126 | $4.4 \pm 0.4^a$ | $1.0 \pm 0.1^a$ | $1.83 \pm 0.03^a$ | $1.62 \pm 0.03^a$ |
| 0.0346 | 0.0750 | $5.81 \pm 0.03$ | $2.24 \pm 0.01$ | $1.88 \pm 0.04$ | $2.51 \pm 0.05$ |
| 0.0740 | 0.0608 | $16 \pm 1$ | $3.7 \pm 0.2$ | $2.86 \pm 0.08$ | $4.7 \pm 0.1$ |
| 0.0252 | 0.0456 | $3.84 \pm 0.07$ | $3.34 \pm 0.06$ | $1.53 \pm 0.02$ | $3.36 \pm 0.04$ |
| 0.0737 | 0.0218 | $8.3 \pm 0.4$ | $5.2 \pm 0.2$ | $1.18 \pm 0.05$ | $5.4 \pm 0.2$ |
| | | avg ± SD | $3.1 \pm 1.6$ | $1.9 \pm 0.6$ | $3.5 \pm 1.5$ |

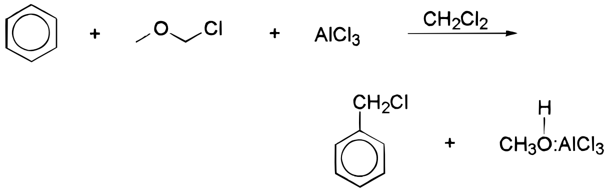
[a] 95% confidence limits. [b] Standard deviation.

**Table 7. Initial Rates and Rate Constants for the Chloromethylation of Benzene with Chloromethyl Methyl Ether (CMME) and $AlCl_3$ in Nitromethane**

| temp °C | $[C_6H_6]$ (M) | [CMME] (M) | $[AlCl_3]$ (M) | initial rates ($\times 10^5$ M $s^{-1}$) | inital rates/$[AlCl_3]_0[MAC]_0$ ($\times 10^2$ $M^{-1}$ $s^{-1}$) | $k_2$ ($\times 10^2$ $M^{-1}$ $s^{-1}$) | $k_3$ ($\times 10$ $M^{-2}$ $s^{-1}$) | $k_3[AlCl_3]_0$ ($\times 10^2$ $M^{-1}$ $s^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 0 | 0.8507 | 0.0521 | 0.0741 | | | $2.1 \pm 0.1^b$ | $4.8 \pm 0.7^b$ | $3.6 \pm 0.5^b$ |
| | 0.3345 | 0.0417 | 0.0448 | $3.44 \pm 0.09^b$ | $1.84 \pm 0.05^b$ | $2.5 \pm 0.1$ | $5.4 \pm 0.3$ | $2.4 \pm 0.1$ |
| | 0.8902 | 0.0430 | 0.0358 | $3.3 \pm 0.4$ | $2.1 \pm 0.3$ | $2.2 \pm 0.2$ | $5.1 \pm 0.3$ | $1.8 \pm 0.1$ |
| | 0.4572 | 0.1192 | 0.0206 | $2.5 \pm 0.3$ | $1.0 \pm 0.1$ | $8.5 \pm 1.0$ | $6.2 \pm 0.6$ | $1.3 \pm 0.1$ |
| | 0.3546 | 0.0660 | 0.0172 | $1.46 \pm 0.08$ | $1.29 \pm 0.07$ | $6.4 \pm 0.3$ | $9.5 \pm 0.4$ | $1.63 \pm 0.07$ |
| | | | | avg ± SD[c] | $1.6 \pm 0.5$ | | | $2.1 \pm 0.9$ |
| −15 | 0.3635 | 0.0499 | 0.0412 | | $0.11 \pm 0.01$ | | $0.32 \pm 0.02^b$ | $0.131 \pm 008^b$ |
| 15 | 0.4132 | 0.0448 | 0.0249 | | $26 \pm 17$ | | $220 \pm 20$ | $53 \pm 4$ |

[a] Rate = $k_3[AlCl_3]^2[CMME]$. [b] 95% confidence limits. [c] Standard deviation.

methyl methyl ether (CMME), it seemed appropriate to see if CMME played a role as an intermediate in chloromethylation with MAC. To that end we undertook a kinetics study of the reaction of CMME with benzene or toluene under the influence of $AlCl_3$.



(5)

The results are very similar to that obtained with chloromethylation involving MAC. Here also $AlCl_3$ is acting as a reagent, not as a catalyst. In those cases where $AlCl_3$ concentration was limiting (Table 7), the reaction stopped when it was consumed. Again primary products were rapidly converted to secondary products and were not seen on chromatograms. Even though chloromethylation with CMME is somewhat faster than that with MAC, the rate laws are essentially the same. The reaction appears to be second order in $AlCl_3$ and first order in CMME, but the third-order rate constant exhibits an inverse behavior with $[AlCl_3]_0$.

$$\text{rate} = (k_3[AlCl_3]^2[CMME])/[AlCl_3]_0 \qquad (6)$$

This again simplifies to

$$\text{rate} = k_2[AlCl_3]_0[CMME]_0 \qquad (7)$$

under initial rates conditions.

Additional benzene chloromethylation runs with CMME at −15 and 15 °C were used with the average results at 0 °C (Table 7) to determine Arrhenius/Eyring values: $E_a = 110 \pm 30$ kJ/mol, $\Delta H^{\ddagger} = 110 \pm 30$ kJ/mol, $\Delta G^{\ddagger} = 76 \pm 1$ kJ/mol, and $\Delta S^{\ddagger} = 130 \pm 100$ J/(mol °C)

Finally, a competitive run with concentrations $[C_6H_5CH_3]_0 = 0.0424$ M, $[C_6H_6]_0 = 0.8931$ M, $[CMME]_0 = 0.0842$ M, and $[AlCl_3]_0 = 0.0317$ M yielded a $k_T/k_B$ value and product xylyl chloride product isomer percentages within experimental error to those for analogous competitive reactions with MAC (Table 4). As before, only early $k_T/k_B$ values were averaged.

A peculiar aspect of our mathematical model is the second-order rate dependence upon $AlCl_3$, which was suggested for chloromethylation of arenes with either MAC or CMME and may be inferred for MAC → CO(g) decomposition. In the latter instance, rate law (4) could have been written as

$$\text{rate} = (k_3[AlCl_3]_0^{\,2}[MAC])/[AlCl_3]_0 \qquad (4')$$

which is consistent with the appearance again of an inverse dependence on initial $AlCl_3$ (Table 6). Typically second-order dependence upon metal halides in electrophilic aromatic substitution reactions is more common for the less active catalysts. However, the requirement of a second molecule of a strong Lewis acid to effect reaction is not unknown. Jensen and Brown[14] found this to be the case with benzoylation catalyzed by $SbCl_5$, $FeCl_3$, and $GaCl_3$.

Another peculiar aspect of these results is that $k_T/k_B$, determined noncompetitively, should be essentially one, since both toluene and benzene reactions are zero order in arene (Table 3). However, the average value of $k_T = 2.6(\pm 1.2) \times 10^{-2}$ $M^{-1}$ $s^{-1}$ and $k_B = 0.18(\pm 0.03) \times 10^{-2}$ $M^{-1}$ $s^{-1}$ (Table 3) yields a $k_T/k_B$ value of 14 ± 9 (or 13 ± 2 if initial rates data are used). Since the formation of the electrophile and not its attack on the arene is rate determining, this nonunity value[15] cannot reflect substrate selectivity but might be an artifact of the ability of $AlCl_3$, particularly in nitromethane,[16] to produce an electron donor−acceptor or charge transfer (CT) complex

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(14) Jensen, F. R.; Brown, H. C. *J. Am. Chem. Soc.* **1958**, *80*, 3039.

(15) We have observed $k_T/k_B$ ratios in the range of 1.5−2.2 in other kinetics studies in nitromethane which are zero order in the arene. See refs 1, 12, and Covey, W. D.; DeHaan, F. P.; Delker, G. L.; Dawson, S. F.; Kilpatrick, P. K.; Rattinger, G. B.; Read, W. G. *J. Org. Chem.* **1984**, *49*, 3967.

(16) Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 155.

with toluene, as suggested by the appearance of a yellow color[17] when toluene is added to a colorless solution of $AlCl_3$ in nitromethane. We observed no color change with benzene, which is consistent with its lower ionization potential. Although our chromatograms showed none of the typical photochemical products[17] of the CT structure—benzyl chloride, chlorotoluenes, bibenzyl, methyldiphenylmethanes—this does not prelude its existence.[18] However, how either complex [$ArCH_3$, $CH_3NO_2$, $AlCl_3$] or [$ArCH_3^{\bullet +}$, $CH_3NO_2^{\bullet -}$, $AlCl_3$] would accelerate toluene chloromethylation is unclear.

Although the zero-order arene dependence in the case of both chloromethylation with MAC and with CMME prevents meaningful $k_T/k_B$ determination from absolute rate constants, the competitive method measures $k_T/k_B$ for the electrophile−arene reactions from benzene and toluene reaction products. The results of our competitive studies are presented in Table 4, and point to a common, remarkably selective electrophile. While either a chloromethyl methyl ether−aluminum chloride polarized adduct or ion pair $CH_3OCH_2^+Al_2Cl_7^-$ or the methoxymethyl cation $CH_3OCH_2^+$ would appear to be possibilities, we think the evidence favors $CH_3OCH_2^+$ as the electrophile.

First, since a polarized addition compound between CMME and $AlCl_3$ should readily form, one would expect chloromethylation with CMME to involve arene dependence in the rate-determining step. Second, if either a polarized complex or ion pair were the electrophile, one would expect different substrate and positional selectivity with $SnCl_4$, which was not observed (*vide infra*). Third, as we will argue shortly, inverse rate order dependence on $[AlCl_3]_0$ implies solvent-separated ions.

The exceedingly high selectivity exhibited in these chloromethylation reactions requires a diffusionally equilibrated electrophile of low reactivity. This is consistent with a methoxymethyl cation in which the resonance contribution of the methoxy group is important (Taft *et al.*[19] calculate a $CH_3OCH_2^+(g)$ stabilization energy, relative to $CH_3^+(g)$, of 66 ± 3 kcal/mol) but which maintains its carbonium ion character, as is suggested by $^{13}C$ NMR of $CH_3OCH_3$[20] ($CH_3$, 59.4 ppm) and $CH_3OCH_2^+$ [20] ($CH_3$, 82.3 ppm; $CH_2$, 219.8 ppm). This also fits with Olah's finding[21] that the very weak electrophilicity of $MeSCH_2^+$ could be enhanced by lowering the electron-donating tendency of S through complexation with $AlCl_3$. Although $k_T/k_B$ ratios were not determined, there was "no detectable amount of meta [product] isomer", suggesting similar very high selectivity of the $CH_3SCH_2^+$ electrophile.

$$CH_3OCH_2^+ \leftrightarrow CH_3^+O{=}CH_2$$

Although alkoxymethyl cations have been postulated as intermediates in solvolysis reactions,[22] most of the work on these ions has involved the gas phase[22,23] or low-temperature NMR studies in Magic acid.[20,24] Of particular interest is the ICR study[25] of the same reaction, ArH + $CH_3OCH_2^+$, where the electrophile exhibits low substrate selectivity ($k_T/k_B$ = 1.8 ± 0.1) and statistical positional selectivity, a marked contrast to our solution phase results. However, it is important to note that intramolecular isomerization of the intermediate arenium ion was also suggested as a possible reason for the seemingly nonexistent positional selectivity.

Finally, the inverse rate order dependence on metal halides has been reported elsewhere for reactions involving acyl chlorides: for benzoylation reactions involving $AlCl_3$ in nitrobenzene,[26] with $SbCl_5$, $FeCl_3$ and $GaCl_3$ in excess benzoyl chloride,[14] and with 2,4-dichlorobenzoyl chloride and $AlCl_3$ in nitromethane.[27] It appears that the explanation offered by Jensen and Brown[14] might apply to our reaction, i.e., the production of an ionic aluminum species—$AlCl_4^-$, $Al_2Cl_7^-$—through other processes could decrease the $CH_3OCH_2^+$ concentration and thus inhibit the reaction. Evidence for the production of such species comes from an $^{27}Al$ NMR study of solutions of $AlCl_3$ or $AlBr_3$ in nitromethane, nitroethane, and nitrobenzene.[28] Tarasov *et al.* observed narrow (≤10 Hz) $^{27}Al$ signals characteristic of $AlCl_4^-$ (−101.9 ppm) and $AlBr_4^-$ (−79.9 ppm) for all solutions in the 0 to −30 °C range, which increased with increasing $AlX_3$ concentration.

We hoped NMR studies of $AlCl_3$−MAC and $AlCl_3$−CMME complexation would help elucidate the mechanisms of these reactions. However, even at temperatures around the freezing point of $CD_3NO_2$, the $^1H$ and $^{13}C$ spectra of the reagents were essentially unchanged by the presence of $AlCl_3$. This is consistent with the heat of solution of $AlBr_3$ in nitrobenzene,[29] being some 23 kcal/mol more exothermic than that of $AlBr_3$ in ethyl bromide,[30] and that $AlCl_3$ preferentially coordinates with nitrobenzene over benzoyl chloride.[31] Given our inability to perform complexometric studies as well as the kinetics complexities of this system, we switched our efforts to $SnCl_4$-catalyzed chloromethylation in dichloromethane.

**B. Kinetic and Spectroscopic Results in Solvent Dichloromethane. 1. Chloromethylation of Benzene or Toluene with Methoxyacetyl Chloride (MAC) and $SnCl_4$.** For the reasons just enumerated, a series of kinetics studies were begun using dichloromethane, a solvent of weaker donating ability.[1] Because $AlCl_3$ has very limited solubility in this solvent and because $SnCl_4$ is soluble in $CH_2Cl_2$, has been used successfully in other chloromethylation studies and has a fairly abundant isotope, $^{119}Sn$, that has proven useful in NMR studies of complexes of Sn compounds with

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**Table 8. Rate Constants for the Chloromethylation of Benzene and Toluene with Methoxyacetyl Chloride (MAC) and $SnCl_4$ in Dichloromethane at 25 °C**

| $[C_6H_5CH_3]$ (M) | $[C_6H_5]$ (M) | [MAC] (M) | $[SnCl_4]$ (M) | $10^5k_1$ ($s^{-1}$) | $10^5k_1/[SnCl_4]_0$ ($M^{-1}\ s^{-1}$) | $10^5k_2/[SnCl_4]_0$ ($M^{-2}\ s^{-1}$) |
|---|---|---|---|---|---|---|
| 0.5728 | | 0.1253 | 0.0856 | 1.37 ± 0.07 | 16.0 ± 0.8 | 29.9 ± 0.7 |
| 0.5700 | | 0.1120 | 0.1426 | 2.6 ± 0.6 | 18 ± 4 | 34.4 ± 0.1 |
| 0.5621 | | 0.0934 | 0.0420 | 0.76 ± 0.02 | 18.1 ± 0.4 | 32.4 ± 0.5 |
| 0.8305 | | 0.2528 | 0.0183 | 0.47 ± 0.01 | 25.6 ± 0.5 | 31.1 ± 0.5 |
| 1.093 | | 0.1179 | 0.0559 | 0.95 ± 0.04 | 17.0 ± 0.7 | 15.6 ± 0.5 |
| 0.5670 | | 0.2610 | 0.0961 | 2.4 ± 0.2 | 24 ± 2 | 44.7 ± 0.1 |
| 0.2056 | | 0.1419 | 0.1182 | 1.4 ± 0.2 | 12 ± 2 | 61 ± 15 |
| 0.5273 | | 0.1748 | 0.2158 | 3.1 ± 0.1 | 14.6 ± 0.5 | 28 ± 2 |
| 0.5139 | | 0.1220 | 0.1769 | 2.4 ± 0.05 | 13.6 ± 0.3 | 27 ± 1 |
| | | | | avg ± SD[a] | 18 ± 4 (24%) | 34 ± 12 (36%) |
| | 0.7399 | 0.2057 | 0.0822 | | 0.85 ± 0.1 | 1.2 ± 0.2 |
| | 0.8119 | 0.4032 | 0.0828 | | 1.67 ± 0.07 | 2.1 ± 0.1 |
| | 0.7045 | 0.2292 | 0.1755 | | 1.65 ± 0.06 | 1.6 ± 0.1 |
| | 0.6878 | 0.3904 | 0.1381 | | 1.69 ± 0.08 | 1.5 ± 0.2 |
| | 0.3623 | 0.2185 | 0.1145 | | 0.35 ± 0.08 | 2.8 ± 0.3 |
| | 0.1401 | 0.2019 | 0.0299 | | 0.04 ± 0.01 | 1.5 ± 0.3 |
| | 0.6647 | 0.2200 | 0.0379 | | 0.99 ± 0.04 | 1.4 ± 0.1 |
| | 0.3098 | 0.1922 | 0.0267 | | 0.38 ± 0.04 | 1.1 ± 0.1 |
| | 0.3524 | 0.2235 | 0.0334 | | 0.65 ± 0.02 | 1.7 ± 0.1 |
| | | | | avg ± SD[a] | 0.9 ± 0.6 (67%) | 1.7 ± 0.5 (29%) |

[a] Standard deviation.

**Table 9. Initial Rates Data for the Chloromethylation of Benzene and Toluene with Methoxyacetyl Chloride (MAC) and $SnCl_4$ in Dichloromethane at 25 °C**

| $[C_6H_5CH_3]$ (M) | $[C_6H_6]$ (M) | [MAC] (M) | $[SnCl_4]$ (M) | initial rates ($\times 10^6\ s^{-1}$) | initial rate/$[SnCl_4]_0[MAC]_0$ ($\times 10^5\ M^{-1}\ s^{-1}$) | initial rate/$[SnCl_4]_0[MAC]_0[arene]_0$ ($\times 10^5\ M^{-2}\ s^{-1}$) |
|---|---|---|---|---|---|---|
| 0.5728 | | 0.1253 | 0.0856 | 1.61 ± 0.04 | 15.0 ± 0.4 | 26.2 ± 0.6 |
| 0.5700 | | 0.1120 | 0.1426 | 3.3 ± 0.1 | 20.7 ± 0.6 | 36 ± 1 |
| 0.5621 | | 0.0934 | 0.0420 | 0.67 ± 0.02 | 17.1 ± 0.5 | 30.4 ± 0.9 |
| 0.8305 | | 0.2528 | 0.0183 | 1.15 ± 0.03 | 24.8 ± 0.2 | 29.9 ± 0.8 |
| 1.093 | | 0.1179 | 0.0559 | 0.97 ± 0.01 | 14.7 ± 0.2 | 13.5 ± 0.1 |
| 0.5670 | | 0.2610 | 0.0961 | 5.9 ± 0.2 | 23.5 ± 0.8 | 42 ± 1 |
| 0.2056 | | 0.1419 | 0.1182 | 1.9 ± 0.2 | 11 ± 1 | 55 ± 5 |
| 0.5273 | | 0.1748 | 0.2158 | 5.2 ± 0.4 | 14 ± 1 | 26 ± 2 |
| 0.5139 | | 0.1220 | 0.1769 | 2.87 ± 0.06 | 13.3 ± 0.3 | 25.9 ± 0.5 |
| | | | | avg ± SD[a] | 17 ± 5 (29%) | 32 ± 12 (38%) |
| | 0.7399 | 0.2057 | 0.0822 | 0.15 ± 0.01 | 0.881 ± 0.006 | 1.19 ± 0.01 |
| | 0.8119 | 0.4032 | 0.0828 | 0.532 ± 0.008 | 1.59 ± 0.02 | 1.96 ± 0.03 |
| | 0.7045 | 0.2292 | 0.1755 | 0.50 ± 0.01 | 1.25 ± 0.02 | 1.78 ± 0.04 |
| | 0.6878 | 0.3904 | 0.1381 | 0.64 ± 0.04 | 1.18 ± 0.07 | 1.7 ± 0.1 |
| | 0.3623 | 0.2185 | 0.1145 | 0.231 ± 0.004 | 0.94 ± 0.02 | 2.58 ± 0.04 |
| | 0.1401 | 0.2019 | 0.0299 | 0.012 ± 0.002 | 0.20 ± 0.03 | 1.5 ± 0.2 |
| | 0.6647 | 0.2200 | 0.0379 | 0.080 ± 0.002 | 0.96 ± 0.02 | 1.44 ± 0.04 |
| | 0.3098 | 0.1922 | 0.0267 | 0.0166 ± 0.0002 | 0.323 ± 0.004 | 1.04 ± 0.01 |
| | 0.3524 | 0.2235 | 0.0334 | 0.0389 ± 0.0006 | 0.521 ± 0.008 | 1.47 ± 0.02 |
| | | | | avg ± SD[a] | 0.9 ± 0.4 (44%) | 1.6 ± 0.4 (25%) |

[a] Standard deviation.

various ligands,[32] it was chosen as the metal halide. To make sure the dichloromethane would not itself undergo reaction, a solution of toluene and $SnCl_4$ in $CH_2Cl_2$ was stirred at room temperature for over 6 h and then analyzed by GC. No reaction was observed.

In all runs (MAC and CMME, below), $SnCl_4$ acted catalytically, i.e., reactions proceeded well past 100% when $SnCl_4$ was the limiting reagent. Apparently $SnCl_4$–$CH_3OH$ complexation at 25 °C in $CH_2Cl_2$ is not extensive. Another noteworthy difference was the observation of primary products—benzyl chloride and the xylyl chlorides—in measurable (GC) amounts, as well as secondary products. This required the use of two GC correction factors, since the GC responses for primary and secondary products were quite different. Chloromethylation with $SnCl_4$ in dichloromethane also proceeded homogeneously but at a slower rate; therefore 25 °C was chosen as the reaction temperature.

Both regular data (Table 8) and initial rates data (Table 9) for the $SnCl_4$-catalyzed reaction of MAC with benzene and with toluene support *different* rate laws for the two arenes. For benzene, the data suggest the rate law

$$\text{rate} = k_3[\text{SnCl}_4]_0[\text{MAC}][\text{C}_6\text{H}_6] \qquad (8)$$

whereas for toluene

$$\text{rate} = k_2[\text{SnCl}_4]_0[\text{MAC}] \qquad (9)$$

**2. Decomposition of Methoxyacetyl Chloride.** Table 10 lists the reaction rates and rate constants of the $SnCl_4$-catalyzed decomposition of MAC as determined

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(32) For example, see: Merbach, A. E.; Knight, C. T. G. *J. Am. Chem. Soc.* **1984**, *106*, 804. Keck, G. E.; Castellino, S. *J. Am. Chem. Soc.* **1986**, *108*, 3847. Coltar, R.; Dakternieks, D. *Inorg. Chim. Acta* **1988**, *143*, 151. Mao, X. A.; You, X. Z.; Dai, A. B. *Inorg. Chim. Acta* **1989**, *156*, 177.

**Table 10. Initial Rates and Rate Constants for the $SnCl_4$-Catalyzed Decomposition of Methoxyacetyl Chloride (MAC) in Dichloromethane at 25 °C**

| $[C_6H_5CH_3]$ (M) | [MAC] (M) | $[SnCl_4]$ (M) | initial rates ($\times 10^5$ M $s^{-1}$) | inital rates/$[SnCl_4]_0[MAC]_0$ ($\times 10^4$ $M^{-1}$ $s^{-1}$) | $k_1$ ($\times 10^5$ $s^{-1}$) | $k_1/[SnCl_4]_0$ ($\times 10^4$ $M^{-1}$ $s^{-1}$) |
|---|---|---|---|---|---|---|
| 0.5989 | 0.5659 | 0.1167 | 3.31 ± 0.08 | 5.0 ± 0.1 | 5.8 ± 0.2 | 5.0 ± 0.2 |
| 0.6652 | 0.0959 | 0.1958 | 0.61 ± 0.02 | 3.2 ± 0.1 | 6.2 ± 0.3 | 3.1 ± 0.2 |
| 0.5475 | 0.5054 | 0.1853 | 4.05 ± 0.02 | 4.32 ± 0.02 | 8.2 ± 0.1 | 4.40 ± 0.05 |
| 0.5195 | 0.4457 | 0.2647 | 5.71 ± 0.03 | 4.84 ± 0.03 | 13.6 ± 0.1 | 5.14 ± 0.04 |
| 0.2368 | 0.1524 | 0.1723 | 0.93 ± 0.02 | 3.54 ± 0.08 | 6.5 ± 0.1 | 3.79 ± 0.06 |
| 0.5268 | 0.4824 | 0.1229 | 2.77 ± 0.01 | 4.67 ± 0.02 | 6.03 ± 0.04 | 4.91 ± 0.03 |
| 0.1094 | 0.4368 | 0.1956 | 2.85 ± 0.01 | 3.34 ± 0.01 | 6.95 ± 0.04 | 3.55 ± 0.02 |
| 0.0 | 0.4942 | 0.1826 | 2.71 ± 0.01 | 3.00 ± 0.01 | 5.71 ± 0.02 | 3.13 ± 0.01 |
| 0.0 | 0.4314 | 0.0838 | 1.90 ± 0.02 | 5.26 ± 0.06 | 4.32 ± 0.05 | 5.16 ± 0.06 |
| $[C_6H_6]$ | | | | | | |
| 0.1233 | 0.3962 | 0.2406 | 2.90 ± 0.03 | 3.04 ± 0.03 | 7.9 ± 0.1 | 3.28 ± 0.04 |
| | | | avg ± SD[a] | 4.0 ± 0.9 | 7 ± 3 (43%) | 4.1 ± 0.9 (22%) |

[a] Standard deviation.

**Table 11. Initial Rates and Rate Constants for the Chlormethylation of Benzene and Toluene with Chloromethyl Methyl Ether (CMME) and $SnCl_4$ in Dichloromethane at 25 °C**

| $[C_6H_6]$ (M) | [CMME] (M) | $[SnCl_4]$ (M) | inital rate ($\times 10^7$ M $s^{-1}$) | initial rate/$[SnCl_4]_0$ $[CMME]_0$ ($\times 10^5$ $M^{-1}$ $s^{-1}$) | inital rate/$[SnCl_4]_0[CMME]_0[C_6H_6]_0$ ($\times 10^5$ $M^{-2}$ $s^{-1}$) | $k_2/[SnCl_4]_0$ ($\times 10^5$ $M^{-2}$ $s^{-1}$) |
|---|---|---|---|---|---|---|
| 0.4312 | 0.2949 | 0.1249 | 11.7 ± 0.2[a] | 3.18 ± 0.05[a] | 7.47 ± 0.1[a] | 7.2 ± 0.9[a] |
| 0.3438 | 0.2404 | 0.1042 | 6.40 ± 0.08 | 2.55 ± 0.03 | 7.43 ± 0.09 | 8.2 ± 0.1 |
| 0.4525 | 0.2623 | 0.0651 | 5.3 ± 0.2 | 3.1 ± 0.1 | 6.9 ± 0.3 | 8.1 ± 0.3 |
| 0.3661 | 0.2771 | 0.186 | 13.0 ± 0.3 | 2.52 ± 0.06 | 6.9 ± 0.2 | 8.3 ± 0.5 |
| 0.1064 | 0.3131 | 0.0952 | 2.30 ± 0.02 | 0.772 ± 0.007 | 7.25 ± 0.06 | 8.3 ± 0.6 |
| | | | avg ± SD[b] | 2 ± 1 (50%) | 7.2 ± 0.3 (4%) | 8.0 ± 0.5 |
| $[C_6H_5CH_3]$ | | | | | | |
| 0.2624 | 0.0246 | 0.1809 | 300 ± 90[b] | 700 ± 200[b] | 3000 ± 800[b] | 3000 ± 1500 |

[a] 95% confidence limits. [b] Standard deviation.

**Table 12. Noncompetitively Determined Rate Constant Ratio and Product Isomer Percentages for the Chloromethylation of Toluene and Benzene with Chloromethyl Methyl Ether and $SnCl_4$ in Dichloromethane at 25 °C**

| substrate | $k_T/k_B$ | % ortho | % meta | % para | *b* |
|---|---|---|---|---|---|
| CMME | 400 ± 200[a] | 31 ± 3[a] | 0.5 ± 0.2[a] | 69 ± 3[a] | 1.3 ± 0.2[b] |

[a] Standard deviation. [b] 95% confidence limits.

by CO evolution. The reaction rate is clearly unaffected by the presence or absence of arene and follows the rate law

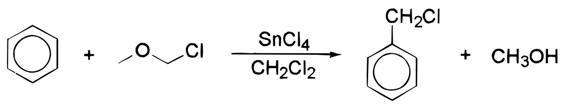
$$\text{rate} = k_2'[SnCl_4]_0[MAC] \qquad (10)$$

with $k_2' = 2.3k_2$.

**3. Chloromethylation of Benzene or Toluene with Chloromethyl Methyl Ether (CMME) and $SnCl_4$.** It again seemed appropriate to examine the kinetics of this reaction with CMME as the chloromethylating reagent. With benzene the reaction is catalyzed by $SnCl_4$ and is clearly first order in $SnCl_4$, in CMME, and in benzene

$$\text{rate} = k_3'[SnCl_4]_0[CMME][C_6H_6] \qquad (11)$$

with $k_3' = 4.7k_3$ for the reaction



(12)

The analogous reaction with toluene was much faster and much more difficult to analyze. In the early part of the run no *m*-xylyl chloride peak was seen but the *o*-xylyl- and *p*-xylyl chloride peak areas remained constant at 31(±3)% and 69(±3)%, respectively (Table 12). For these reaction aliquots, a percent of *m*-xylyl chloride product could be crudely estimated by a method somewhat similar to that used for the $AlCl_3$ reactions, but through the use of new data for the $SnCl_4$-catalyzed *p*-xylylation of toluene (33.3 ± 0.5% ortho, 2.0 ± 0.2% meta, and 64.5 ± 0.4% para product) and *o*-xylylation of toluene (24.6 ± 0.3% ortho, 2.6 ± 0.2% meta, and 72.7 ± 0.4% para product). However, as reaction time progressed the relative amounts of *o*- to *p*-xylyl chloride product increased[33] as did the amount of secondary ($[CH_3Ph]_2CH_2$) to primary xylyl chloride products. Tertiary products also appeared on the chromatograms, but with extensive overlapping. Assignment of peak areas to primary product isomers became impossible at this point as did total product estimates for meaningful rate constant calculations. Meaningful calculations of $k_T/k_B$ ratios and product isomer percentages were thus limited to a few early reaction aliquots, and the uncertainties inherent in limited data sets are reflected in the results for the toluene reaction (Tables 11 and 12).

**4. Spectroscopic (FT-NMR and Raman) Studies of Complexation between $SnCl_4$ and Methoxyacetyl Chloride or Chloromethyl Methyl Ether.** $^{13}C$ and $^{119}Sn$ FT-NMR spectra were determined for solutions of $SnCl_4$ with MAC, CMME, $Et_2O$, or 1-chlorobutane in $CD_2Cl_2$. In the case of MAC the broad single $^{119}Sn$ signal (relative to external $Me_4Sn$) shifted to higher fields (increased shielding) as the temperature was dropped and as the concentrations of reagents were increased (Figure 2), suggesting the existence of fast equilibria.

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[33] Our competitive studies of the $SnCl_4$-catalyzed reactions of *p*-xylyl chloride and *o*-xylyl chloride with benzene and toluene yielded $k_T/k_B$ values of 48 ± 2 and 32.7 ± 0.5 for the two xylyl chlorides. Since *p*-xylyl chloride is the more reactive electrophile, the decrease in its concentration relative to *o*-xylyl chloride is expected.

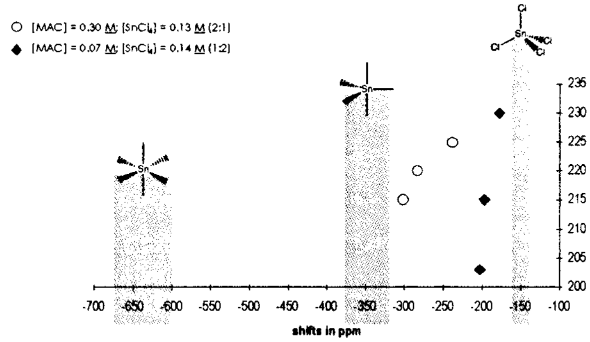


**Figure 2.** Plot of $^{119}$Sn FT-NMR signal shifts as a function of temperature.

**Table 13. Representative $^{119}$Sn NMR Data for Various Reagents and $SnCl_4$ in $CD_2Cl_2$**

| reagent (M) | [$SnCl_4$] (M) | temp (K) | chemical shift (ppm) (external $SnMe_4$) |
|---|---|---|---|
| | 0.33 | 255 | −156 |
| | 0.33 | 200 | −158 |
| 1-chlorobutane | 0.31 | 308 | −154 |
| (0.29 M) | | 200 | −158 |
| CMME | 0.14 | 298 | −172 |
| (0.30 M) | | 277−220 | −178 ± 1 |
| diethyl ether | 0.415 | 298 | −247 |
| (0.57 M) | | 270−255 | −265 ± 1 |

With CMME and $Et_2O$ the broad single $^{119}$Sn signal stayed at −178 and −265 ppm, respectively, below 270 K. Finally, the $^{119}$Sn spectra of solutions containing 1-chlorobutane were indistinguishable from those containing just $SnCl_4$ (Table 13).

Although all MAC−$SnCl_4$ solutions showed $^{119}$Sn shifts dependent on concentration and temperature, the averaging effect of uncomplexed and complexed MAC masked $^{13}$C shifts until MAC was present as a limiting reagent. In this case, with $SnCl_4$:MAC at 2:1, the $^{13}$C spectra showed a ~6 ppm downfield shift for the carbonyl carbon while the methyl and methylene carbon shifts were both <1 ppm (Table 14).

Reproducible Raman spectra were more difficult to obtain. Even after prolonged irradiation, samples in the concentration range suitable for NMR produced little more than background Raman scattering. Furthermore, at the low temperatures necessary to avoid MAC decomposition (−70 °C and lower), a white MAC−$SnCl_4$ complex precipitated out of solution at higher concentrations. However, we were able to obtain reproducible spectra from light scattered from the solid and observed a definitive shift of the carboxy stretch from 1802 to 1675 $cm^{-1}$ in the complex.

Solutions of CMME and $SnCl_4$ in $CH_2Cl_2$ were homogeneous at 1 M reagent concentrations, but no shifts in either $SnCl_4$ or CMME bands were observed at room temperature or at −70 °C.

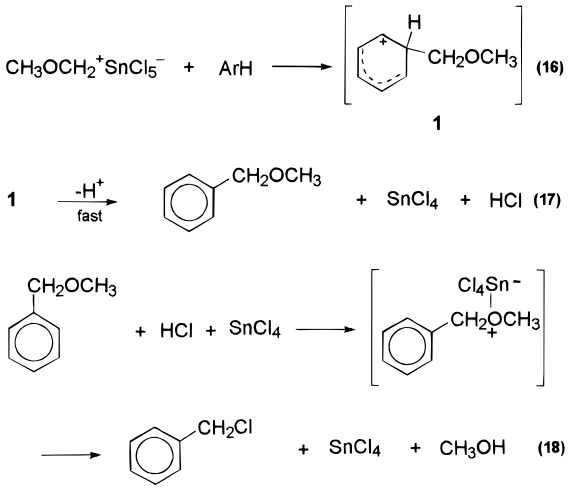
**5. A Suggested Mechanism for $SnCl_4$-Catalyzed Chloromethylation of Arenes in $CH_2Cl_2$.** Although less complicated than the analagous reactions with $AlCl_3$ in nitromethane, chloromethylation with $SnCl_4$ would appear to involve a number of steps. The following mechanisms seem to be consistent with the kinetics and spectroscopic data.

A. With MAC:

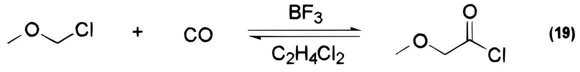
$$\text{MAC} + SnCl_4 \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \text{MAC:}SnCl_4 \qquad (13)$$

$$\text{MAC:}SnCl_4 \overset{\text{slow}}{\rightleftharpoons} \text{CMME:}SnCl_4 + CO_{(g)} \qquad (14)$$

$$\text{CMME:}SnCl_4 \overset{\text{fast}}{\rightleftharpoons} CH_3OCH_2^{+}SnCl_5^{-} \qquad (15)$$

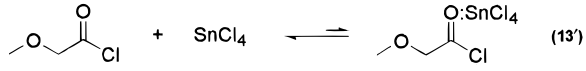


Step 14 is written as a rapid, reversible reaction which lies to the left, suggesting inhibitionary rate effects by CO(g). We have not tested this; however, Mori, Kudo, and Sugita[34] report carbonylation of CMME by CO in the presence of $BF_3$ in 1,2-dichloroethane at 10 °C and calculate an equilibrium constant $K = 2.77\ M^{-1}$ for the reaction at this temperature. Support for proposed intermediate complex **1** comes from our GC analysis. A small peak corresponding to benzyl methyl ether was seen in the early part of a number of reactions.



Our NMR results of solutions of MAC and $SnCl_4$ in $CH_2Cl_2$ show temperature dependent $^{119}$Sn shifts down to −70 °C, the limit of our study. Thus step 13 must be seen as a rapid, reversible equilibrium which lies to the left. Also note that toluene chloromethylation with MAC is zero order in arene and proceeds at a rate within experimental error of MAC decomposition: the two rate constants are 18(±8) × $10^{-5}$ and 41(±18) × $10^{-5}$ $M^{-1}$ $s^{-1}$, respectively (95% confidence limits). Therefore it is reasonable to assume step 14 is rate determining for both toluene chloromethylation and MAC decomposition, while step 16 is slow for benzene chloromethylation, which was first order in arene.

NMR and Raman evidence suggest a 1:1 MAC:$SnCl_4$ complex in which $SnCl_4$ is bound to carbonyl oxygen but not to methoxy oxygen or chlorine.



First, the $^{13}$C NMR shows a carboxyl carbon shift downfield by 6 ppm, but less than 1 ppm shifts for the methylene and methyl carbons. Second, Figure 2 suggests maximum $^{119}$Sn shifts in the −350 ppm range,

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[34] Mori, S.; Kudo, K.; Sugita, N. *Bull. Inst. Chem. Res. Kyoto Univ.* **1986**, *64*, 312. See also: Sugita, N.; *et al. Tetrahedron* **1995**, *51*, 11,119. The promotion of carbonyl insertion reactions of transitional-metal complexes by Lewis acids is well-known. For example, see: Nolan, S. P.; de la Vega, R. L.; Hoff, C. D. *J. Am. Chem. Soc.* **1986**, *108*, 7852. Perhaps the role of the Lewis acid is more involved than simply complexation with the metal acyl complex product.

which is characteristic of pentacoordinate coordination of four Cl and one O about Sn,[35] but far from the −600 to −670 ppm shifts typical of 2:1 (ligand)$_2$:SnCl$_4$ complexes where the ligands bond to Sn through O.[36] Third, Keck, Andrus, and Castellino[37] have shown that even when dealing with $\beta$-alkoxy aldehyde moieties in which chelation through both oxygens to Sn is expected, complexation only through carbonyl oxygen may compete. Fourth, if we assume the amount of 1:1 complexation produces the increased shielding at Sn, the ratio of the $^{119}$Sn shift divided by [MAC][SnCl$_4$] should remain constant for different concentrations of MAC and SnCl$_4$ at a given temperature. It does; we calculated values in the range of $3.9(\pm 0.4) \times 10^3$ for different mixtures at 215 K. Fifth, Raman data support a structure bound through carboxy oxygen; no shifts in the C−O−C stretching region (1136−1156 cm$^{-1}$) or C−Cl stretching region (550−760 cm$^{-1}$)[38] were observed whereas the C═O stretch was shifted from 1802 cm$^{-1}$ in MAC to 1675 cm$^{-1}$ in the MAC−SnCl$_4$ complex. Small shifts to lower wavenumbers are also expected in the COCl in-plane deformation region (420−486 cm$^{-1}$)[38] but were not observed probably because of inherent limitations of our study. Sixth, the existence of donor−acceptor complexes of the type RCXO → MX$_n$, with electron donation to the metal through carboxy oxygen, typically show a decrease in carbonyl stretching to 1550−1600 cm$^{-1}$ whereas oxocarbenium ions increase the frequency to the 2200−2300 cm$^{-1}$ range.[39]

B. With CMME:

$$\text{CMME} + \text{SnCl}_4 \rightleftharpoons \text{CMME:SnCl}_4 \qquad (20)$$

$$\text{CMME:SnCl}_4 \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \text{CH}_3\text{OCH}_2^{+}\text{SnCl}_5^{-} \qquad (21)$$

$$\text{CH}_3\text{OCH}_2^{+}\text{SnCl}_5^{-} + \text{ArH} \xrightarrow{\text{slow}} \text{products} \qquad (22)$$

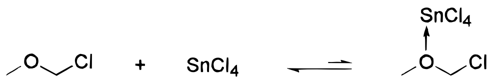
This mechanism accounts for the different kinetics results which were found with CMME. The production of CMME:SnCl$_4$ is now fast compared to decarbonylation of MAC (step 14). Chloromethylation with CMME is first order in arene, involving rate-determining attack by the electrophile on the aromatic species. The similarity in $k_T/k_B$ ratios and product isomer distributions (Table 12) to those for chloromethylation with AlCl$_3$ in CH$_3$NO$_2$ (Table 4) strongly suggests a common electrophile, which would be either CH$_3$OCH$_2^+$ or the CH$_3$OCH$_2^+$SnCl$_5^-$ intimate ion pair. On the basis of our earlier arguments, the methoxymethyl cation would seem to be the better choice. However, CH$_2$Cl$_2$ is a solvent of considerably lower polarity than CH$_3$NO$_2$, and therefore ion association should be more widespread. Also, inverse rate order dependence upon metal halides seems to appear only in more polar solvents, like CH$_3$NO$_2$, where solvent-separated ion pairs are plausible.

**Table 14. $^{13}$C NMR Data for the Solutions of SnCl$_4$ and MAC, CMME, and Et$_2$O in CD$_2$Cl$_2$ as Solvent and Internal Standard**

| | concn | [SnCl$_4$] | $\delta$ ($^{13}$C) (ppm) | | |
|---|---|---|---|---|---|
| compound | (M) | (M) | C$_a$ | C$_b$ | C$_c$ |
| $C_cH_3OC_bH_2C_aOCl$ | *a* | 0 | 172.4 | 77.86 | 59.77 |
| | 0.07[b] | 0.14 | 178.1 | 77.97 | 60.28 |
| $C_bH_3OC_aH_2Cl$ | *a* | 0 | 84.5 | 57.6 | |
| | 0.30[a] | 0.14 | 85.3 | 57.9 | |
| $C_bH_3C_aH_2OC_aH_2C_bH_3$ | *a* | 0 | 65.4 | 14.1 | |
| | 0.57[a] | 0.415 | 66.5 | 14.4 | |

[a] Room temperature. [b] 230 K.

Because the structure of the CMME:SnCl$_4$ complex was of interest, we have also examined solutions of CMME and SnCl$_4$ in CH$_2$Cl$_2$ by NMR and Raman spectroscopy. The observed $^{119}$Sn shifts (Table 13) to −178 ppm are larger than those for the SnCl$_4$−CH$_2$Cl$_2$ system, −154 to −158 ppm, but are well below those expected for five- or six-coordinate complexes. Castellino[40] reported a $^{119}$Sn NMR signal for "free" SnCl$_4$ at −175 ppm and ascribed it to a "weak association" between excess SnCl$_4$ and possibly the ring oxygen or "other Lewis base sites" in oxazolidinone, which also chelated SnCl$_4$ on a 1:1 basis through its two carbonyl oxygens. Although the two systems are different, a weak complex between oxygen in CMME and SnCl$_4$ would appear to fit our data as well. First, since 1-chlorobutane showed no interaction with SnCl$_4$ over the temperature range covered (Table 13), interaction of CMME−Cl with SnCl$_4$ is even less likely, given the inductive effect of the methoxy group. Second, the similarity in $^{13}$C and $^{119}$Sn shifts for solutions of Et$_2$O and CMME (Tables 13 and 14) would be consistent with weakly bound five-coordinate complexes[41] with SnCl$_4$ in both cases, with electron donation through oxygen to tin:



(20')

Although we saw no Raman band shifts for CMME or SnCl$_4$ in the presence of the other component, this does not eliminate the possibility of small amounts of a weak adduct which would be difficult to detect via Raman scattering.

Finally, some general comments regarding the mechanism of chloromethylation in CH$_2$Cl$_2$ are in order. It is noteworthy that the kinetics results for arene chloromethylation with CMME and SnCl$_4$ in CH$_2$Cl$_2$ also fit Brown's selectivity relationship (Table 12). Because of the difficulty in assigning secondary product peak areas to the xylyl chloride primary product isomers, good data were limited to a few early points in the toluene reaction. This led to large uncertainities in $k_2$/[SnCl$_4$]$_0$, but given the log−log nature of Brown's relationship, $b$ is still known with enough accuracy, ±0.2, to be valid.

Our $k_T/k_B$ value of 400 ± 200 is far higher than most others reported in the literature. The data agree best[42] with Olah's results[5] for very low SnCl$_4$ concentrations, which produced a $k_T/k_B$ of 317 and product chloromethyltoluene percentages of 32.5 ortho, 1.5 meta, and 66 para, but not with their results at high [SnCl$_4$], which

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(35) The pentacoordinate di-*tert*-butyl ketone: SnCl$_4$ adduct produces a $^{119}$Sn signal at −329.5 ppm. Reetz, M. T.; Harms, K.; Reif, W. *Tetrahedron Lett.* **1988**, *29*, 5881.

(36) Mao, X.; Guangzhi, X. *Wuji Huaxue Xuebao* **1990**, *6*, 95; Chem. Abstr. 1991, *115*, 100512. list 13 solvents which complex SnCl$_4$ through oxygen, all having $\delta$($^{119}$Sn) shifts in the range of −595−−669 ppm. See also: Taylor, M. J.; Coddington, J. M. *Tetrahedron* **1992**, *11*, 1531.

(37) Keck, G. E.; Andrus, M. B.; Castellino, S. *J. Am. Chem. Soc.* **1989**, *111*, 8136.

(38) Katon, J. E.; Feairheller, W. R. *J. Chem. Phys.* **1966**, *44*, 144.

(39) For a review article, see: Chevrier, B.; Weiss, R. *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 1.

(40) Castellino, S. *J. Org. Chem.* **1990**, *55*, 5197.

(41) 1:1 as well as 2:1 ether:SnCl$_4$ complexes are known to exist in CH$_2$Cl$_2$. Blunden, S. J.; Searle, D.; Smith, P. J. *Inorg. Chim. Acta* **1985**, *98*, 185. Myher, J. J.; Russell, K. E. *Can. J. Chem.* **1964**, *42*, 1555. See also: Rafikov, S. R.; Ergozhin, E. E.; Artyukhin, V. I.; Kartseva, I. I.; Emir-Useinova, L. V. *Dokl. Akad. Nauk SSSR* **1974**, *219*, 1379.

were $k_T/k_B = 21$, ortho 45%, meta 4%, and para 55%. Although their method of product analysis, GC, was more accurate and direct than that of Brown,[8] they probably erred by assuming $SnCl_4$ was not capable of causing secondary reactions. Since we have shown that extensive secondary reactions do occur, it is not surprising to find their $k_T/k_B$ values decreased with increasing $[SnCl_4]$ since the xylyl chlorides are considerably more reactive than benzyl chloride or that their ortho/para product ratio increased, since the para isomer is the more reactive xylyl chloride.[33]

## Conclusions

Through the use of vacuum line kinetics techniques, which help minimize the effects of water, we have obtained reproducible chloromethylation kinetics results, both competitive and noncompetitive, which clarify a number of unusual mechanistic aspects of this important reaction: (1) the reaction exhibits *very* high substrate and positional selectivity yet is often zero order in arene; (2) high similar selectivities are maintained with different substrates, metal halides, and solvents, suggesting $CH_3OCH_2^+$ as a common, remarkably selective electrophile; (3) the kinetics results for $AlCl_3$ appear to be complex, those for $SnCl_4$ more straight forward, and mechanisms for the latter reaction are proposed; (4) low-temperature NMR and Raman studies have clarified the structures of complexes formed between MAC and CMME substrates and catalyst $SnCl_4$.

## Experimental Section

**Materials.** Methods of purification, drying, vacuum line apportionment, and storage of solvent nitromethane,[27] solvent $CH_2Cl_2$,[1] $AlCl_3$,[27] benzene,[43] toluene,[43] and internal standard *o*-dichlorobenzene[1] appear in earlier papers. $SnCl_4$ (99.995%, Aldrich) was injected through a standard rubber septum, glass diaphragm, and constriction into a glass chamber which had been flamed out previously under high vacuum and then pressurized to 1 atm with dry $N_2$. The $SnCl_4$ was frozen with liquid $N_2$, the constriction sealed off under partial vacuum, and the $SnCl_4$ sublimed through a glass wool plug into a trap, degassed, and then apportioned into break tip ampoules for further use. Benzyl methyl ether was synthesized by the metathetical reaction of benzyl chloride and $NaOCH_3$ in $CH_3OH$. Reagent grade methoxyacetyl chloride (>99% pure, GC) and chloromethyl methyl ether (purity checked *via* GC and NMR) were used without further purification. [WARNING! Chloromethyl methyl ether is an OSHA-regulated carcinogen. Special precautions (fume hood, gloves, and disposal) must be taken.]

**Kinetics Procedures.** General kinetics procedures have been given earlier.[12,43] Gas evolution studies involved a needle connecting the septum of the reaction vessel and an inverted buret filled with petroleum ether. Verification of the gaseous product as CO was accomplished by attaching an evacuated IR gas cell to the gas buret.

**Gas Chromatographic Analysis.** GC settings: column, 25 m crosslinked methyl silicone; oven temperature program, 117 °C for 7 min, 30°/min to final 170 °C; injection port, 300 °C; detector, 250 °C; typical retention times (min), *o*-dichlorobenzene (7.4), diphenylmethane (15.2), methyldiphenylmethane secondary mixed products (competitive runs) 3- (18.8), 2- (19.1), 4- (19.4); dimethyldiphenylmethane secondary (toluene) products, 2,3′- (23.2), 3,4′- (24.0), 2,2′- (24.1), 2,4′- (24.3), 4,4′- (24.8). For $SnCl_4$-catalyzed reactions, benzyl and the xylyl chlorides are observable. The preferable GC program was as follows: oven temperature, 85 °C for 18 min, 30°/min to final 170 °C; retention times, benzyl chloride (10.3), *o*-dichlorobenzene (11.6), xylyl chlorides 3- (17.3), 2- (17.6), 4- (17.8), diphenylmethane (27.0), dimethyldiphenylmethanes 2,3′- (32.1), 3,4′- and 2,2′- (32.8), 2,4′- (33.0), 4,4′- (33.5). GC retention times were determined through authentic sample matching or by the process of elimination. For example, the retention times of all the possible isomeric dimethyldiphenylmethanes were determined from benzylating toluene with *o*-, *m*-, and *p*-xylyl chloride. Known mixtures of internal standard and authentic products were used to determine GC response factors.

**NMR Analysis.** All NMR spectra were recorded on an IBM/Bruker AF 200 spectrometer with a 10 mm broad band probe. Chemical shifts for $^{119}Sn$ (74.6 MHz) are measured from external $Me_4Sn$, $^{13}C$ (50.3 MHz) from internal $CD_2Cl_2$, and $^1H$ from internal $CH_2Cl_2$. Vacuum line methods analogous to those for kinetics studies were used to transfer reagents to attached, flamed out 10 mm NMR tubes.

**Raman Analysis.** Raman spectra of solutions of MAC or CMME in $CH_2Cl_2$ and in the presence of $SnCl_4$ (in 5 mm sealed tubes prepared by our usual vacuum line techniques) were obtained with a SPEX Ramalog-9I system, Harney-Miller type variable temperature cells,[44] and the 514.5 nm line of a Coherent Innova 70-4 argon ion laser. Spectra were analyzed and smoothed using a moving-average function.

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[42] The similarity in $k_T/k_B$ values may be fortuitous. Some of the earlier chloromethylation studies involved the competitive method and some did not, but in all cases[3−7] the arene rate order was not established. As the differing benzene and toluene rate orders for chlorination with MAC and $SnCl_4$ in $CH_2Cl_2$ show, these may never be assumed to be equal. See footnote 31 of ref 12.

[43] DeHaan, F. P.; Covey, W. D.; Ezelle, R. L.; Margetan, J. E.; Pace, S. A.; Sollenberger, M. J.; Wolf, D. S. *J. Org. Chem.* **1984**, *49*, 3954.

[44] Miller, F. A.; Harney, B. M. *Appl. Spectrosc.* **1970**, *2*, 291.