Reactivity in Methyl Transfer Reactions. 5. Relation between Rates and Equilibria

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Abstract: The methyl transfer reactions of two dimethylarylsulfonium ions with methyl phenyl sulfide are equilibrated in sulfolane solution, as is the methyl transfer from methyldiphenylsulfonium ion to methyl 3,4-dichlorophenyl sulfide, and from dimethyl sulfate to diphenyl sulfide. These equilibria, together with their temperature dependencies, rates, and a few related calorimetric measurements, can be combined with a valuable series of equilibria from the literature to allow a detailed description of these methyl transfers. Correlations, analogous to the Brønsted relation, of rates and equilibria require a considerable variation of the barriers depending on attacking nucleophile and leaving group, but no evidence of unsymmetrical transition states is seen.

Methyl transfer reactions of the form

$$\mathrm{Me^+Nu}_i + \mathrm{Nu}_j \underset{k_{ji}}{\overset{k_{ij}}{\rightleftharpoons}} \mathrm{Nu}_i + \mathrm{Me^+Nu}_j,\ K_{ij} = k_{ij}/k_{ji} \qquad (1)$$

may be considered as the simplest organic analogy to the much-studied proton transfer reactions. In eq 1 and throughout, the first subscript refers to the methylating agent, the second to the nucleophile. In earlier papers in this series[2-5] we have studied reactivities initially aimed at observing the variable transition state or the reactivity–selectivity principle.[6] There were no striking examples of loss of selectivity with increasing reactivity up to some very fast reactions, yet the reactivity–selectivity principle is a qualitative consequence of the Hammond postulate[7] relating the barrier in a series of related reactions to the changes in the overall thermodynamics. In particular, the loss of selectivity with reactivity in a series is a consequence of a concave downward plot of log k^+ (k is the rate constant for the reaction in the forward direction) vs. log K_{eq}, the equilibrium constant for the same process. Such plots, equivalent to Brønsted plots for proton transfers, would clearly be valuable in understanding structure–reactivity relations in many reactions, including the methyl transfers. The necessary combination of rate and equilibrium data for some methyl transfers in water solution have been assembled by Albery and Kreevoy[8] based largely on the indirect, but nevertheless valuable, thermodynamic data of Abraham and McLennan.[9] We shall return to this treatment later. Except for these, very few data are in fact available, and the variety of nucleophiles, leaving groups, solvents, and temperatures make the likelihood very small of any systematic results being available from the literature. We have decided to settle on sulfolane as a solvent because of its resistance to electrophiles, although our first results on equilibrated system were in ethanol solution.[4] This choice has been made especially valuable because of our belated discovery of the methyl transfer equilibrium studies by Jackman and coworkers[10] in the same solvent by NMR methods which are exceedingly useful. The temperature 35 °C is assumed for these results.

The equilibrium constants we report here have also been measured by NMR. They are therefore done in rather concentrated solutions, and we can not yet extrapolate to very dilute solutions. Some of the rates are also measured by NMR in concentrated solutions, and some are measured by UV in quite dilute solutions. The calorimetric measurements are at an intermediate concentration level, and also have not been reduced to very dilute solution values. The calorimetric results are not as precise as our calorimeter ought in principle to achieve. They appear reproducible to better than 1 kcal/mol, but not to 0.1 kcal/mol, which should be attainable with modifications now being undertaken. Thus we claim no high precision of the present results, but believe the rate and equilibrium constants to be reliable enough to be quite interesting.

The results of a number of different reactions are presented in Table I, which shows up to four entries for each combination of methylating agent and nucleophile. It is convenient to use the terms "methylating agent" and "conjugate nucleophile" for $\mathrm{Me^+Nu}_i$ and Nu_i (of any charge type), respectively. Similarly, we may refer to the "conjugate methylating agent" of a nucleophile. In the table the different methylating agents are identified by a number and their conjugate nucleophiles by the same number. The numbers are identified in footnote *b* in Table I.

Under each pair of methylating agent and nucleophile in the table are listed four numbers when available: k ($\mathrm{M^{-1}\,s^{-1}}$), K, E_a, and ΔH, in kcal/mol. Rate constants and equilibrium constants are reported at 35 °C, the temperature assumed for Jackman's results,[8] and either measured or calculated from results at other temperatures, except where noted. It should be noted that all the results are not independent. Thus $k_{ji} = k_{ij}/K_{ij}$, and $E_{aji} = E_{aij} - \Delta H_{ij}$. Similarly, only one equilibrium constant for each methylating agent and for each nucleophile suffices; the rest are simply calculated.

It would clearly be valuable to confirm the equilibrium constants by a different measurement, and an attempt was made to measure k_{82} by assuming that the reaction

$$\mathrm{PhS^+Me_2\ OTf^-} \xrightarrow[k_{82}]{} \mathrm{PhSMe + MeOTf} \qquad (2)$$

would be the rate-determining step in the overall exchange reaction

$$\mathrm{PhS^+Me_2\ OTf^- + CD_3OTf} \rightarrow \mathrm{PhS^+MeCD_3\ OTf^- + CH_3OTf} \qquad (3)$$

which we could follow by the appearance of the $\mathrm{CH_3OTf}$ NMR peak. On treating a sulfolane solution of dimethylsulfonium triflate with methyl-d_3 triflate at about 170 °C for 20 min, no methyl triflate was detected by NMR. The calculated rate constant from Table I using the activation energy given is 0.5 $\mathrm{M^{-1}\,s^{-1}}$; thus equilibrium exchange should have been seen. However, a new singlet ($\delta > 10$) appeared, attributable to HOTf. Control experiments showed that at these temperatures methyl triflate does not survive in sulfolane; it is converted to triflic acid. The reaction is plausibly the sequence of reactions 4 and 5 with the step (4) reversible, with an equilibrium constant at 35 °C $<7 \times 10^{-5}$ (the equilibrium constant with benzophenone).[10] This is analogous to an acid-catalyzed version of the observed base instability of sulfolane,[2] and the second step, an $\mathrm{E_2}$ elimination by the base triflate ion, is rea-

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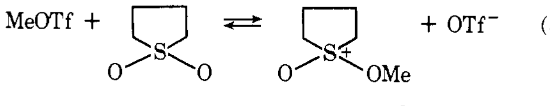
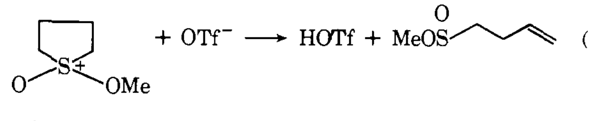
Table I. Rate Constants, Equilibrium Constants, Activation Energies, and Enthalpy Changes for Reaction 1

	methylating agent						
nucleophile[b]	1[c]	2[c]	3[d]	4	5	6	8
1[c]	—	—	—	—	—	5.9×10^{-8}	1.8×10^{-8}
	1	2.9×10^{-1}	2.3×10^{-3}	2.3×10^{-4}	2.2×10^{-6}	2.9×10^{-7}	3.7×10^{-8}
	—	—	—	—	—	—	—
	0	—	—	—	—	—	—
2[c]	—	—	—	3.6×10^{-7}	3.2×10^{-7}	6.8×10^{-8}	2.2×10^{-8}
	3.4×10^{0}	1	7.7×10^{-3}	7.5×10^{-6}	7.7×10^{-6}	1.0×10^{-6}	1.3×10^{-7}
	—	—	—	—	31.2	—	32.5
	—	0	—	+15.2	+19.1	—	+20.4
3[d]	—	—	—	7.9×10^{-8}	—	—	—
	4.5×10^{2}	1.3×10^{2}	1	1.3×10^{-1}	1.05×10^{-3}	1.5×10^{-4}	1.8×10^{-5}
	—	—	—	25.3	—	—	—
	—	—	0	4.9	—	—	—
4	—	3.7×10^{-3}	6.1×10^{-7}	—	1.8×10^{-8}	—	—
	3.5×10^{3}	1.01×10^{3}	7.8	1	8.2×10^{-3}	1.2×10^{-3}	1.4×10^{-5}
	—	—	20.4	—	23.5	—	—
	—	−15.2	−4.9	0	+4.3	—	+5.7
5	—	4.2×10^{-2}	—	2.2×10^{-6}	—	—	1.7×10^{-8}
	4.5×10^{5}	1.3×10^{5}	9.4×10^{2}	1.2×10^{2}	1	1.4×10^{-1}	1.8×10^{-2}
	—	12.1	—	19.2	—	—	21.7
	—	−19.1	—	−4.3	0	—	+1.4
6	2.0×10^{-1}	6.7×10^{-2}	—	—	—	—	2.2×10^{-8}
	3.4×10^{6}	9.8×10^{5}	6.6×10^{3}	8.4×10^{2}	7	1	1.3×10^{-1}
	12.2	12.7	—	—	—	—	24.6
	—	—	—	—	—	0	0
7	2.5×10^{-1}	9.5×10^{-2}	—	—	—	—	—
	—	—	—	—	—	—	—
	12.7	12.8	—	—	—	—	—
	—	−18.9	—	—	—	—	—
8	4.9×10^{-1}	1.7×10^{-1}	—	—	9.8×10^{-7}	1.7×10^{-7}	—
	2.7×10^{7}	7.8×10^{6}	5.4×10^{4}	6.9×10^{3}	5.6×10^{1}	8	1
	12.3	12.1	—	—	20.3	24.6	—
	—	−20.4	—	−5.7	−1.4	0	0
9	8.5×10^{-1}	2.7×10^{-1}	—	—	—	—	—
	—	—	—	—	—	—	—
	13.1	12.4	—	—	—	—	—
	—	−20.6	—	—	—	—	—
10	1.2	—	—	—	—	—	—
	—	—	—	—	—	—	—
	13.3	—	—	—	—	—	—
	—	—	—	—	—	—	—

[a] The first line is the rate constant at 35 °C in $M^{-1}\,s^{-1}$, the second is the equilibrium constant, the third is the activation energy, the fourth is ΔH, in kcal/mol. [b] Nucleophiles (and their conjugate methylating agents) follow: 1, dimethyl ether (trimethyloxonium ion); 2, trifluoromethanesulfonate ion (methyl triflate); 3, methyl sulfate ion (dimethyl sulfate); 4, diphenyl sulfide; 5, methyl 3,4-dichlorophenyl sulfide; 6, methyl 3-chlorophenyl sulfide; 7, methyl *p*-chlorophenyl sulfide; 8, methyl phenyl sulfide; 9, methyl *p*-tolyl sulfide; 10, methyl *p*-methoxyphenyl sulfide. [c] All equilibria and reverse rate constant data for trimethyloxonium ion and methyl triflate use a combination of Jackman's data[10] with that presented here. Many of the rate constants are from ref 5, corrected to 35 °C. [d] The reaction of dimethyl sulfate with diphenyl sulfide leads to a significant amount of C-alkylation, especially at the higher temperatures. Thus there are larger errors in this equilibrium, the basis of all equilibrium and reverse rate constant data of this methylating agent.



(4)



(5)

sonable given that the methylated sulfolane is more stable with the counterion hexafluoroantimonate than with the presumably more basic tetrafluoroborate.[10] The reaction of methyl triflate with sulfolane is too slow below 50 °C to have been noticed before. In spite of the failure of this method in this case, the use of such exchange methods to follow the rate of thermodynamically unfavorable slow methyl transfers remains viable, as long as side reactions do not interfere, and alternate exchange mechanisms are too slow.

We do not yet have enthalpy data for very many cases. Some related data are available from the literature. Thus, a few rates and equilibria are available for the methylation with methyl iodide of substituted dimethylanilines,[11a] in several solvents, not including sulfolane. Equilibrium has also been measured for the reaction of trimethylsulfonium ion with bromide.[11b] Dr. R. Alder has also shown us unpublished results of calorimetric measurements of the reaction of methyl fluorosulfonate with numerous nucleophiles, also in another solvent.[12] The literature contains much data on rates, but very little on equilibria, with studies of substituent effects,[11] solvent effects,[11,13] and pressure effects[14] useful in characterizing the transition state. Abraham[15] notes that with limited data the plot of log *k* vs. log *K* has a slope somewhat less than 0.5. The results on the methyl transfers between thiophenoxides[4] are in principle very relevant, but they do not have much of a range of *K*, and are in a different solvent. There are in Table I 20 cases for which both

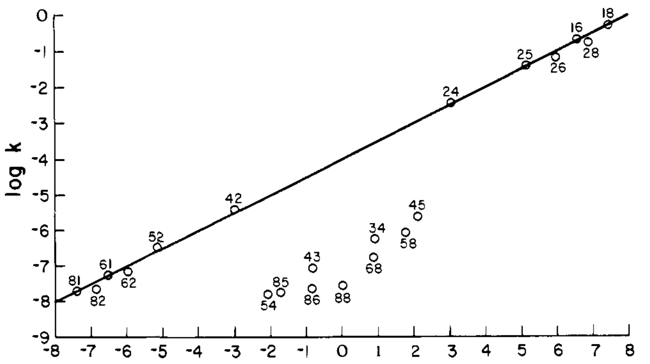


Figure 1. Logarithmic plot of rate constants for various methyl transfer reactions against the equilibrium constants. Experimentally measured rates are those with log $K > 0$. The first number in each pair denotes the leaving nucleophile (as in Table I); the second is the attacking nucleophile. The line drawn is log $k = -4 + 0.5$ log K.

Table II. Calculation of Rates from Equation 7

ij	log k_{ij} calcd[a]	log k_{ij} obsd	log k_{calcd} − logk_{obsd}
12	−0.69		
14	−2.11		
15	−0.65		
16	−0.53	−0.70	+0.17
18	−0.46	−0.31	−0.15
24	−2.60	−2.43	−0.17
25	−1.14	−1.38	+0.24
26	−1.02	−1.17	+0.15
28	−0.95	−0.77	−0.18
45	−5.66	−5.66	0
46	−5.66		
48	−5.38		
56	−6.10		
58	−6.02	−6.01	−0.01
68	−6.77	−6.77	0
88	−7.60	(−7.60)[b]	(0)

[a] The rate constants are expressed in $M^{-1}\,s^{-1}$, and refer to 35 °C. [b] This is not a measured value, but derived from substituent effects as described in the text.

rates and equilibria are measured and these are plotted logarithmically in Figure 1, which also shows the line log $k = -4.00 + 0.5$ log K. These, however, represent only ten measurements of rate and equilibrium; the other ten represent the reverse reactions, calculated from the forward reaction rates and equilibrium constants. One further point has been added by extrapolating a line through the two points closest to log K = 0 to this axis. This extrapolation is effectively the calculation of the rate of the identity reaction

$$\mathrm{PhSMe_2^+ + PhSMe \rightleftarrows PhSMe + PhS^+Me_2} \qquad (6)$$

for which log $K_{88} \equiv 0$, from the rates and equilibria of the reactions of the m-chloro substituted and the 3,4-dichloro substituted sulfonium salts with the unsubstituted phenyl methyl sulfide. The extrapolation to $\sigma = 0$ by a two-point Hammett plot gives essentially the same value.

The fit of the line to several of the points of positive log K is significant and will be discussed below. The further fit to points of negative log K is without significance, for the logarithms of the forward and reverse rate constants differ by log K, but the equilibrium constants for the forward and reverse processes differ by 2 log K; thus each point with positive log K can be connected by a line of slope $1/2$ to the corresponding point for the reverse reaction.

The deviation from linearity of the rest of the points in the plot is significant, and does not seem to be related to experimental error either in our measurements or in the combination of these with those of Jackman.[10]

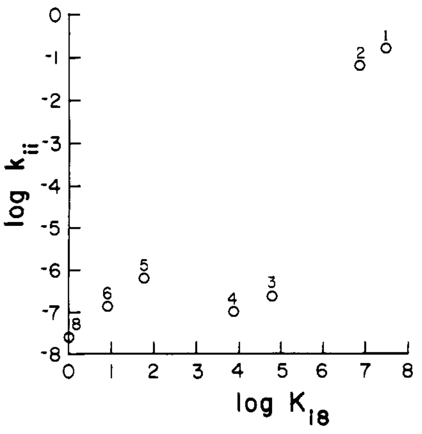


Figure 2. Plot of the calculated barriers for symmetrical methyl transfers vs. the equilibrium constant for transfer to methyl phenyl sulfide. The numbers next to the points refer to the leaving nucleophile as in Table I.

Starting with Marcus' idea of an "intrinsic barrier" [16] which is the arithmetic mean of the barriers for identity reactions, and neglecting (or implicitly including) the w terms, we can calculate the rate constants by the expression for the rate of reactions:

$$\log k_{ij} = (\log k_{ii} + \log k_{jj})/2 + \tfrac{1}{2} \log K_{ij} \qquad (7)$$

where k_{ii} is the rate constant for the identity reaction

$$\mathrm{Nu}_i{}^+\mathrm{Me} + \mathrm{Nu}_i \underset{k_{ii}}{\overset{k_{ii}}{\rightleftarrows}} \mathrm{Nu}_i + \mathrm{Me}^+\mathrm{Nu}_i \qquad (8)$$

The only value of k_{ii} available is the extrapolated value for eq 2, i.e., log $k_{88} = -7.60$, and the remaining values, selected to fit the data, are as follows: log $k_{11} = -0.76$, log $k_{22} = -1.18$, log $k_{33} = -6.66$ (based on only one rate), log $k_{44} = -7.00$, log $k_{55} = -6.20$, log $k_{66} = -6.84$.

Using these values, and eq 7, Table II can be calculated. The values for dimethyl sulfate (**3a**) are not included; if included the agreement with experiment would of course be perfect. It can be seen that there are no major discrepancies.

We do not ascribe enormous significance to the fit of Table II, in view of the five (i = 1, 2, 4, 5, 6) adjustable parameters (k_{ii}), but feel that the general plausibility of eq 7 at least justifies the attempt. If the predictions in Table II are experimentally confirmed, then there may be a little more reason to believe in this treatment. If we could obtain new values of log K_{ij} and log k_{ii}, then we could make many more predictions. The values of log k_{ii} appear to be largest for the very powerful methylating agent. Figure 2 shows a plot of log k_{ii} vs. log K_{i8}, that is, the equilibrium for methylation of phenyl methyl sulfide, and a rather poor correlation does exist. It is clear that only in rather closely related systems (such as the points 5, 6, and 8) can a somewhat reliable prediction be made of log k_{ii} from log K_{i8}. Nevertheless a guess can be made from this figure. Tetramethoxyphosphonium ion and trimethyloxonium ion are equally strong methyl donors.[10] Thus the rate of reaction of tetramethoxyphosphonium ion with triflate ion in sulfolane should be about as fast as we predict for trimethyloxonium ion with triflate ion (log $k = -0.69$, $k \approx 2 \times 10^{-1}\ M^{-1}\ s^{-1}$). Experimentally, in several different media methyl triflate and trimethyl phosphate equilibrate as soon as a good NMR spectrum can be obtained.[17] The peaks are all quite sharp; thus the transfer rate is slow compared to the NMR time scale. These observations do not determine the rate constant but roughly suggest that $-2 < \log k < +2$, in agreement with the above estimate.

The low reactivity of dimethyl sulfate is not easily explained; so far only the rate and equilibrium with diphenyl sulfide are established. The low rate constant is not of high precision since it was done by NMR, there were side reactions, and it was extrapolated from higher temperature measurements, but errors of more than 20–30% appear unlikely. It is perhaps not now fruitful to discuss this case without further data, except to note that the nature of the leaving atom does not here appear to be the major factor.

The equilibrium constant for reaction of dimethyl sulfate with triflate ion in Table I is small, but perceptible. This is compatible with the syntheses of methyl triflate and methyl fluorosulfonate suggested by Alder,[18] in which triflic acid or fluorosulfonic acid is added to dimethyl sulfate, and the equilibrium is shifted by removal of the more volatile ester by distillation.

The use of eq 7 specifically excludes the higher order term in the Marcus equation, exploited by Albery and Kreevoy,[8] and therefore corresponds to the limit near $K = 1$, with $\alpha = \frac{1}{2}$. The exclusion of terms leading to a downward concavity in Figure 1 is in part due to the absence of evidence for it, but is also prompted by the earlier lack of evidence of much loss of selectivity even with highly reactive systems.[3] It appears that without experimental data on the various identity reactions that we cannot yet say whether the Albery and Kreevoy use of the Marcus equation is applicable to our data. However, the current results, together with more data of the same sort using experimental equilibrium constants, have the potential of providing a very firm base for testing this theory.

The absence of downward concavity for the branch $\log K > 0$ in Figure 1 is not in accord with the behavior expected from operation of the reactivity-selectivity principle. This principle, the Hammond postulate, the Marcus equation, or other simple relations[19] between $\log k$ and $\log K$ all lead to a slope $+\frac{1}{2}$ at $\log K = 0$, approaching unity for $\log K \ll 0$ and approaching zero with large $\log K$. The arguments leading to this form of curve are virtually irrefutable; we must therefore conclude that not only are other factors operative (such as variable intrinsic barriers) but that the range of $\log K$ is not large enough to produce curvature in the expected direction.

The statement that no evidence for curvature exists is not strictly true. If we consider only the points 25, 26, and 28 corresponding to the reactions of methyl triflate with the three aryl methyl sulfides, the slope through these is clearly less than $\frac{1}{2}$. In Hammett equation terms, the forward reaction rate has $\rho^+ = -1.1$ (based on five points[5]) and the equilibrium has $\rho_{eq} = -2.9$ (based on three points from this work). Thus $\rho^+/\rho_{eq} = 0.38$, and this is of course also the slope of a line through these three points only in Figure 1. This observation may be taken as partial although not convincing evidence of curvature; a quantitative treatment is not yet justified.

The calorimetric data are useful in conjunction with activation energies to compare the thermodynamic properties of the activated complex with those of the products. Such calculations might now be made for numerous combinations in Table I. The original plan was to see whether we could find a correlation between ΔH and ΔG, such as was found by Arnett[20] for proton transfers. The current limited data show the possibility of such correlations, but we prefer to postpone detailed treatment until we have further and more reliable data.

Experimental Section

Materials. The source and purification of the methyl trifluoromethanesulfonate (methyl triflate), dimethyl sulfate, the aryl methyl sulfides and sulfolane have been described before.[2,3,4] Commercial (Aldrich) trimethyloxonium tetrafluoroborate and diphenyl sulfide were used as supplied. The sulfonium salts were prepared as triflates by treatment of the sulfides with methyl triflate.

Rates were measured in the NMR by observing either the increase of the peak height of the methylated product or the decrease in the reagent methyl peak. Except for the methyl triflate-diphenyl sulfide reaction, which was followed in the NMR instrument, all samples were kept in an NMR tube (sealed for higher temperatures), in a good thermostat except while measurements were made. The measurement time was negligible. In the case of dimethyl sulfate reaction with diphenyl sulfide, the methyl groups of dimethyl sulfate, methyl sulfate anion, methyldiphenylsulfonium cation, and two peaks identified partially as C-S dimethylated material were at least partially resolved, although the *S*-methyl signal of the latter substance overlapped badly with that of the methyldiphenylsulfonium peak. Thus rates (and equilibria) with this combination were less precise than the others. In this case C-methylation was more serious at the higher temperatures, indicating a somewhat, although not well established, higher activation energy than for S-methylation. Rate constants were derived for irreversible reactions by conventional plots, using either one reagent at a large excess and the usual logarithmic plots or reagents at equal concentrations, using the usual reciprocal plot. When the reactions were significantly reversible, the reagents were held at equal concentrations, and the equation developed before[4] was used. The rates for methyl triflate and trimethyloxonium ion with the various aryl methyl sulfides, pyridine, and dimethylaniline are taken from earlier work[5] and corrected to 35 °C by the temperature dependencies given there when possible. All rates for combinations with $K < 1$ are calculated from the rate and equilibrium constant in the opposite direction.

Enthalpy Data. The values of ΔH in the table come from two sources. Where equilibrium constants are actually measured, the temperature dependence gives a value of ΔH. In other cases, using reactions with methyl triflate, they represent direct calorimetric measurements of the heat evolved when the nucleophile was added (by breaking a glass bubble containing it) to a solution of methyl triflate in sulfolane in a calorimeter. This calorimeter is the same as the one described by Turner[21] for measurement of heats of hydrogenation except that the hydrogen inlet tube was closed off, and a Kepco Model PCX 15-1.5 C power supply replaced the storage battery used as the power source for calibration heating. This calorimeter is being rather extensively altered, so that further details will not be given here.

Attempted Reverse Rate Measurement by Exchange. A sample of dimethylphenylsulfonium triflate was made from methyl phenyl sulfide and methyl triflate, followed by removal of volatile materials on the vacuum line. Methyl-d_3 triflate was prepared from commercial methyl-d_3 iodide and silver triflate, followed by decantation from the solid and distillation. In sulfolane only the methyl triflate NMR absorption (barely resolved quartet, δ 4.20) is well clear of sulfolane (triplet, δ 2.85, triplet, δ 2.0, $J \sim 6$ Hz) and its spinning sidebands and satellites. The sulfonium methyl group (δ 2.95) is difficult to treat quantitatively; its intensity did not appear to change. In spite of this clear region, no methyl triflate could be seen in a sulfolane solution of about 1 M sulfonium salt and a small amount of methyl-d_3 triflate after 20 min at 170 °C. Similar experiments at lower temperatures and longer or shorter times also failed to produce undeuterated methyl triflate. A peak at δ 14.9, attributed to triflic acid, appeared rapidly; when more concentrated solutions of ordinary methyl triflate in sulfolane were heated in the same way, the acid peak again appeared and there were clearly changes in the sulfolane absorption at about δ 2.0. The methyl triflate is apparently destroyed more rapidly than it can exchange.

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Specific Substituent Effects in the Dehalogenation of Halobenzene Derivatives by the Gaseous Bronsted Acid CH$_5^+$ [1]

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Abstract: In the methane chemical ionization mass spectra of chlorobenzene derivatives containing an electron-donating substituent meta to the chlorine, the protonated molecular ions, MH$^+$, formed in the initial protonation reaction undergo extensive loss of HCl to form substituted phenyl cations. This dehalogenation reaction is not observed when the substituent is ortho or para to the chlorine (except for the *p-N,N*-dimethylamino substituent) nor for electron-withdrawing substituents. For fluorobenzene derivatives loss of HF from MH$^+$ is observed when the substituent is meta or para to the fluorine but not when it is ortho to the fluorine. The origin of these unusual substituent effects is discussed. It is concluded that the substituents act to alter the carbon-halogen bond dipole. This bond dipole in turn exerts a kinetic effect which either alters the activation energy for elimination of the neutral hydrogen halide from MH$^+$ or, more likely, influences the extent of protonation at the halogen through localized ion-bond dipole interactions in the collision complex.

Introduction

In the methane chemical ionization (CI) mass spectra of fluorine- and chlorine-substituted benzenes and toluenes moderately abundant fragment ion peaks are observed[2,3] corresponding nominally to protonated toluene or the appropriate protonated xylene. The importance of these product ions decreased through the halogen series with the result that they were of minor importance for the bromo derivatives and were absent for the iodo derivatives.[2,3]

In the CI studies the formation of these products was attributed[2,3] to the direct reaction

$$\mathrm{CH_5^+ + YC_6H_4X \rightarrow YC_6H_4CH_3 \cdot H^+ + HX} \qquad (\mathrm{Y = H, CH_3;\ X = F, Cl}) \qquad (1)$$

while from radiolytic[4] and ICR[5] studies the two-step reaction sequence

$$\mathrm{CH_5^+ + YC_6H_4X \xrightarrow{-CH_4} YC_6H_4X \cdot H^+ \xrightarrow{-HX} YC_6H_4^+} \qquad (2)$$

$$\mathrm{YC_6H_4^+ + CH_4 \rightarrow YC_6H_4CH_3 \cdot H^+} \qquad (3)$$

was proposed. Pressure-variation studies[6] under CI conditions have shown that both the direct reaction (1) as well as the two-step sequence (2) plus (3) are operative, the relative importance of the two pathways being dependent on the identity of the halogen X and the nature and orientation of the substituent Y.

In both CI[2,3,6] and radiolytic[7] studies of the reaction of H$_3^+$ (or D$_2$T$^+$) with halobenzenes and halotoluenes a similar two-step dehydrohalogenation reaction, (4) plus (5), was observed. In addition, the CI studies showed that this reaction

$$\mathrm{H_3^+ + YC_6H_4X \xrightarrow{-H_2} YC_6H_4X \cdot H^+ \xrightarrow{-HX} YC_6H_4^+} \qquad (4)$$

$$\mathrm{YC_6H_4^+ + H_2 \rightarrow YC_6H_5 \cdot H^+} \qquad (5)$$

$$\mathrm{H_3^+ + YC_6H_4X \xrightarrow{-H_2} YC_6H_4X \cdot H^+ \xrightarrow{-X} YC_6H_5^{+\cdot}} \qquad (6)$$

mode was in competition with the alternative fragmentation of YC$_6$H$_4$X·H$^+$ (MH$^+$) by loss of a halogen atom (reaction 6). Loss of HX from MH$^+$ was the only fragmentation mode for X = F or Cl, both loss of HX and X were observed when X = Br, while loss of the halogen atom was the only fragmentation mode observed for X = I. In a more recent study[8] of the reaction of H$_3^+$ with a variety of substituted halobenzenes it was observed that the competition between loss of HX and loss of X· from MH$^+$ was strongly dependent on the substituent, with electron-releasing substituents enhancing fragmentation by reaction 6. The competition between the two fragmentation modes has been rationalized[3,8] in terms of reaction energetics.

The pronounced effect of substituents on the H$_2$ CI mass spectra of substituted halobenzenes[8] indicated that a similar study of substituent effects on the CH$_4$ CI mass spectra was desirable. As will be discussed below, unusual substituent orientation effects have been observed in that dehydrohalogenation of chlorobenzene derivatives is observed only when

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