interaction between antipodes in the monolayer under conditions of equilibrium with the bulk phase.

Summary

This study highlights the importance of a tightly packed crystalline surface phase for the onset of detectable chiral molecular recognition between enantiomers in monolayer films. The Π/A isotherms and surface shear viscosities indicate that there are only scant differences between the ionized films *cast* from *solutions* of enantiomeric and racemic stearoyltyrosine. By comparison with previously established data of Zeelen,[17a] we interpret this as a reflection of repulsive coulombic interactions between ionized tyrosine headgroups which tend to fluidize the monolayer system. In direct contrast, the thermodynamic treatment of films in equilibrium with their *crystals* over a temperature range indicate that the presence of the bulk solid phase in the surface system allows for expression of enantiomeric discrimination at a transition point between the ionized monolayer and the bulk crystalline phase. Enantiomeric discrimination is also reflected in the thermodynamics of transition between film types which are in equilibrium with each other and the bulk phase. These experiments constitute, to our knowledge, the first *quantitative* description of the dependence of chiral molecular recognition on the surface phase of the surface film system of a chiral amphiphile as an ionized monolayer.

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Methyl Transfers. 14. Nucleophilic Catalysis of Nucleophilic Substitution

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Abstract: Nucleophiles X^- can catalyze the substitution $Nu^- + RY \rightarrow NuR + Y^-$ by adding the faster pathway $X^- + RY \rightarrow XR + Y^-$ followed by $Nu^- + XR \rightarrow RNu + X^-$. New examples include catalysis by I^- of the exchange of methyl between two dialkyl sulfides and the transfer of methyl from an arsonium salt to a phosphine. The individual reactions are separately studied, and some equilibrium information is presented. Iodide is ineffective in the transfer of methyl between two phosphines, which is not detected with or without iodide. The Marcus equation treatment of this catalysis is shown to require that the identity transfer of R between two X^- groups be far faster than that for transfer of R between two Nu^- groups. Nucleophiles other than I^- are discussed. The possibility that some "supernucleophiles" may have fast identity rates is discussed, and literature evidence that this is indeed the case is presented. Stereochemical studies using chiral methyl derivatives have shown that vitamin B_{12} does provide a nucleophilic catalysis to methyl transfer in living systems. Thus, the apparently superfluous participation of B_{12} in some biological methyl transfers is explained.

The S_N2 mechanism for reaction 1 is not always a fast process. The catalysis by electrophiles which make Y^- a better leaving group is well-established, and many protic nucleophiles can be rendered far more nucleophilic by loss of a proton to a base. In this paper the catalysis by X^- through the mechanism of (2) followed by (3) is discussed, and the reasons for the apparent rarity are presented.

$$\mathrm{Nu^- + RY \rightarrow NuR + Y^-} \tag{1}$$

$$\mathrm{X^- + RY \rightarrow XR + Y^-} \tag{2}$$

$$\mathrm{XR + Nu^- \rightarrow X^- + RNu} \tag{3}$$

Implied by the notation is the fact that since each step occurs with inversion of configuration, the catalytic sequence must involve a net retention of configuration. This successive displacement mechanism is described by Hammett,[1] who notes that it constitutes an example of the failure of a rate–equilibrium correlation. Hammett's two examples are the hydrolysis of methyl bromide catalyzed by iodide ion and the ethanolysis of active α-phenylethyl toluenesulfonate, which has predominent retention of configuration only in the presence of high concentrations of chloride ion. Curiously, the first example is not catalytic because (contrary to Hammett's statement) the hydrolysis of iodomethane, which is indeed formed, is somewhat slower than that of bromomethane.[2] In the second, catalysis is not demonstrated, although we shall see that this stereochemical criterion is nevertheless valuable.

However, authentic examples do exist. The transfer of methyl between tertiary amines has been shown to be catalyzed by iodide ion, as has the attack of enolate ions on alkyl bromides.[3] The Finkelstein reactions of alkyl halides with halide ions in acetone give rate constants, corrected for degree of dissociation of the lithium salts,[4] as shown for reactions 4–6. Thus the path through

$$\mathrm{Cl^- + MeBr \rightarrow ClMe + Br^-} \qquad k_4 = 0.595 \tag{4}$$

$$\mathrm{I^- + MeBr \rightarrow IMe + Br^-} \qquad k_5 = 0.70 \tag{5}$$

$$\mathrm{IMe + Cl^- \rightarrow I^- + MeCl} \qquad k_6 = 4.70 \tag{6}$$

IMe is somewhat faster than the direct path of eq 4. I^- is thus a catalyst, and because iodides are more dissociated than chlorides, the practical effects are larger. In the present work we add to these examples and show, in terms of the Marcus equation treatment of these reactions,[5] the criteria for the existence of catalysis, and we point out directions to find new examples.

Results

Reaction 7 with R = octyl and R′ = decyl is slow at 120 °C, when the counterion is trifluoromethanesulfonate (OTf^-) or the

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monomethyl sulfate anion. However, equilibrium is established easily at 35 °C in the presence of iodide. The rate and equilibrium of the component reactions of the catalytic process, reaction 8 and its reverse, have been studied in two solvents, acetonitrile and chloroform.

$$\mathrm{RMe_2S^+ + R'MeS \rightleftarrows RMeS + R'Me_2S^+} \qquad (7)$$

$$\mathrm{RMe_2S^+ + I^- \rightleftarrows RMeS + MeI} \qquad (8)$$

The rate constants for reaction 7 at 120 °C are $k_7 = 1.8 \times 10^{-4}$ $\mathrm{M^{-1}\ s^{-1}}$ in acetonitrile and 5.4×10^{-4} $\mathrm{M^{-1}\ s^{-1}}$ in chloroform. In the presence of iodide, the equilibrium constant in both solvents is 1.00 ± 0.01 at 35 °C. The rate of reaction 8 is, unlike that of reaction 7, sensitive to solvent. In acetonitrile at all concentrations, the equilibrium lies to the left; in chloroform in dilute solution the equilibrium lies far to the right. Quantitative rate information is complicated, because of ion pairing. In acetonitrile, conductivity measurements give an ion-association constant, K = [ion pair]/[$\mathrm{RS^+Me_2}$][$\mathrm{I^-}$] = 178 at 35 °C, comparable to that for the triflate salt of 220. These constants resemble those for trimethylsulfonium bromide with K = 320 in ethanol[6] and 233 in dimethylacetamide.[7]

In chloroform, conductivity was not detected except in the most concentrated solutions of the triflate salt, where the identity of the species contributing to the very low conductivity is unknown. The rate constants are expressed as unimolecular reactions of the ion pair, in acetonitrile calculated from the association constant, in chloroform assuming only ion pairs to be present. The rate constants were determined from HPLC analyses allowing for the presence of reverse reaction. In acetonitrile, the forward rate constant $k_8 = 3 \times 10^{-6}\ \mathrm{s^{-1}}$, the equilibrium constant is about 0.01 M, giving a reverse rate constant of $3 \times 10^{-4}\ \mathrm{M^{-1}\ s^{-1}}$. In dilute (0.0012 M) solution in chloroform the forward rate constant is 3.8×10^{-4}, and the equilibrium constant is too large to measure (>35). But in more concentrated solution in chloroform (0.33 M sulfonium iodide), the reaction is significantly reversible, $k_8 = 2.5 \times 10^{-5}\ \mathrm{s^{-1}}$, $K_8 = 3.1$, $k_{-8} = 8 \times 10^{-6}\ \mathrm{M^{-1}\ s^{-1}}$. The precision is low in both solvents, in acetonitrile largely because the extent of reaction is small, and in chloroform the salt concentration drops as the reaction proceeds, causing an increase in rate constant. Salt effects were less conspicuous in acetonitrile, partly because there was little change in electrolyte concentration. In view of the ion pairing, we did not try in interpret the effect of adding other electrolytes. Certainly, the iodide catalysis of reaction 7 is conspicuous.

Reaction 9 is also subject to catalysis by iodide ion. The reaction is very slow or absent without iodide, and with iodide the rate is independent of the concentration of triphenylphosphine. The rate determining step is apparently reaction 10, followed by a fast reaction 11.

$$\mathrm{Ph_3P + MeAsPh_3^+ \rightarrow Ph_3PMe^+ + AsPh_3} \qquad (9)$$

$$\mathrm{MeAsPh_3^+ + I^- \rightleftarrows AsPh_3 + MeI} \qquad (10)$$

$$\mathrm{MeI + Ph_3P \rightarrow MePPh_3^+ + I^-} \qquad (11)$$

The value of k_{10} was measured with excess $\mathrm{PPh_3}$ by $^{31}\mathrm{P}$ NMR in propylene carbonate following the production of methyltriphenylphosphonium ion. Rather concentrated solutions of the arsonium triflate and sodium iodide were required; the iodide dependence is confused by salt effects; hence the precision is low. However, even at the lowest iodide concentrations, the reaction is at least 10 times faster than any uncatalyzed reaction, which may not occur at all. Approximate values of k_{10} are 8.9×10^{-6} at 75 °C, 3.2×10^{-4} at 100 °C, and 1.3×10^{-3} at 120 °C, all at an ionic strength of 0.2 M, in the unit $\mathrm{M^{-1}\ s^{-1}}$. Extrapolating gives $k_{10} = 7.5 \times 10^{-9}\ \mathrm{M^{-1}\ s^{-1}}$ at 25 °C. In this solvent at 25 °C we find (by conductivity) $k_{-10} = 8.7 \times 10^{-5}\ \mathrm{M^{-1}\ s^{-1}}$, and $K_{10} = 8.6 \pm 6 \times 10^{-5}$. The rate of reaction 10 in the solvent acetone has been measured,[8] with $k_{10} = 1.6 \times 10^{-4}\ \mathrm{s^{-1}}$ at 95 °C. There was extensive reverse reaction in this case. The first-order rate constant was used to reflect extensive ion pairing in this much less polar solvent; the ion-pairing association was determined conductometrically. The earlier suggestion that an ion pair is an obligatory intermediate was attacked by Pocker and Parker[6] in a different system. They showed that this is not kinetically demonstrable; as usual the rate law only gives the transition-state composition.

Table I. Rates and Equilibria for Formation of MeI from $\mathrm{MeAr_3As^+I^-}$

t (°C)	Ar	k ($\mathrm{M^{-1}\ s^{-1}}$)	K
151	p-tolyl	1.5×10^{-4}	0.1
141	phenyl	2.1×10^{-4}	0.4
151	p-chlorophenyl	4.7×10^{-2}	2.3

Independent measurements of the rate constant k_{11} and k_{-10} shows indeed that triphenylphosphine should compete with triphenylarsine effectively for iodomethane. At 25 °C in propylene carbonate $k_{11} = 1.20 \times 10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$ and $k_{-10} = 8.68 \times 10^{-5}\ \mathrm{M^{-1}\ s^{-1}}$, a ratio of 138 favoring the phosphine reaction. In acetonitrile, the ratio is reported as 189 at 25 °C,[9] and in acetone at 15 °C, the ratio is 263.[10]

The equilibrium and rate problem has been attacked directly. When methylarsonium iodides were heated in sulfolane solution to elevated temperatures, the free arsine and iodomethane were formed. Analysis at various times provided kinetic data from initial rates and ultimately equilibrium results, expressed as K = [MeI][$\mathrm{Ar_3As}$]/[$\mathrm{MeAr_3As^+}$][$\mathrm{I^-}$]. These are summarized in Table I, with estimated errors on the rate constants of 10–20%. These data are too sparse and imprecise to give a meaningful rate–equilibrium relation.

The reaction of the salt is so extensive that in the arsenic analogy of eq 7, for example, the reaction of tri-p-tolylarsine with methyltriphenylarsonium iodide, while readily detectable, gave far less than a quantitative yield of methyltri-p-tolylarsonium iodide. The equilibrium constant for methyltriphenylarsonium iodide is measured at such a very different temperature from the estimate above of K_{10}, that comparison is not useful, although the value of K_{10} from these data of 1/0.4 = 2.5 is plausibly much closeer to unity than the 25 °C value of 1.2×10^4. Treatment of the equilibrium as if all the salt were ion paired gave very concentration-sensitive values; clearly, the extent of ion pairing in sulfolane at this temperature is not great.

The study was briefly extended to methyltriphenylstibonium ion. Triphenylstibine has long been known to be inert to iodomethane.[11] This lack of reactivity can be now attributed to a thermodynamic problem, rather than merely a slow rate. Thus, on treatment with methyl triflate in acetonitrile, a salt was readily obtained. This triflate salt with sodium iodide in acetonitrile was quantitatively converted to triphenylstibine after several hours at room temperature, confirming the large equilibrium constant of the antimony analogue of reaction 10.

Reaction 9 with iodide catalysis was readily observed, but the analogous reaction 12 could not be detected at all, even when clearly thermodynamically favored. Thus, with Ar = p-tolyl and Ar′ = Ph, no detectable reaction occurred with either $\mathrm{Br^-}$ or $\mathrm{I^-}$ as the counter ion. In the extreme case, the iodide salt was melted

$$\mathrm{Ar_3P + MeAr'_3P^+ \rightleftarrows MePAr_3^+ + Ar'_3P} \qquad (12)$$

with the free phosphine together for several hours at 250 °C, no triphenylphosphine could be detected by thin layer chromatography. This agrees with the observation of Gavrilov and Rakhmatullin[8] that methyltriphenylphosphonium iodide shows no

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perceptible reaction in 10 h at 180 °C in acetone. Pyrolysis of the same salt at >500 °C has been reported to produce some MeI, but the mechanism was believed to be different from the S_N2.[12] Reaction 12 was also studied with more extreme cases with iodide ion catalysis. However, with $Ar' = p\text{-}CF_3C_6H_4$ and even C_6F_5, and Ar = Ph in solution in sulfolane, no $Ar_3'P$ could be detected by HPLC after up to 3 weeks at 100 °C for the first case. The triphenylphosphine disappears slowly, presumably by oxygen abstraction from sulfolane. In the latter case the methyltris(pentafluorophenyl)phosphonium salt is unstable, and disappears (30% in 20 h at 100 °C) without producing any free phosphine.

Discussion

The presence of iodide ion catalysis is now firmly established both by prior results[3] and by the current results on several different reactions, e.g. reactions 7 and 9. It is not, however, general, for reaction 12 does not go at a perceptible rate even when the equilibrium is highly favorable.

The efficacy of the iodide arises from its very low identity barrier for methyl transfer, lower than any other studied nucleophile in water[13] or in sulfolane.[14] This comes from a consideration of the Marcus equation treatment of reactions 1–3. If all three reactions had identical intrinsic barriers (and these are high enough to allow neglect of the Marcus quadratic term), then the rate constants would be in the ratio $K_1^{1/2}:K_2^{1/2}:K_3^{1/2}$. The only way that k_2 could be substantially greater than k_1 would be that $K_2 > K_1$. Since $K_2K_3 = K_1$, this would require that $K_3 < 1$, and thus the corresponding rate constant k_3 would be too small. This is the failure of the rate–equilibrium correlation which Hammett noted[1] and is an inevitable consequence of the constant intrinsic barrier assumption.

It is clear that we may avoid this if the intrinsic barrier for reaction 2 is much lower than that for reaction 1. This requires that X^- have a very low methyl transfer identity barrier, since the intrinsic barrier is the mean of the identity barriers. Then both reactions 2 and 3 will necessarily have lower intrinsic barriers than reaction 1, and they can both be faster than 1 without the equilibrium inconsistencies. The function of iodide ion as the catalyst X^- is then obvious.

The equilibrium constants are nevertheless still important. Thus if K_1 is much less than unity, then k_1 can not be very large (and even if XR is formed at a significant rate, it can be destroyed by a faster reaction with Y^- as well as by Nu^-). Similarly, if K_3 is less than unity, then XR can be formed, but it will persist in the solution.

The case of the catalysis of the near-identity rate 7 shows that the overall equilibrium constant K_1 need not be large; the catalysis arises entirely from the low iodide identity barrier. The catalysis of the transfer between arsines likewise has a small equilibrium constant, as shown by the similar and near unity values of the equilibrium constants in Table I. However, there is an inefficient scavenging of the intermediate MeI by any of the arsines.

The failure to detect any reaction in the methyl transfer between phosphines tells us that this reaction itself has a very high intrinsic barrier and that the individual identity barriers are very high. The fact that iodide does not catalyze the reaction tells us that since triphenylphosphine will efficiently scavenge iodomethane, it must not be there and that the reverse of reaction 11 must be fast in order to prevent catalysis of reaction 12 even at 250 °C.

The contrast between the relative ease of breaking the methyl–arsenic bond compared to the failure to break the methyl–phosphorus bond is manifested in other ways. In the Wittig reaction the carbon–phosphorus bond in the intermediate betaine is broken only in a reaction forming the very strong phosphorus–oxygen bond. In the arsenic analogue, along with the alkene-forming reaction, the betaine suffers an internal nucleophilic substitution, yielding an epoxide and arsine.[15] This is analogous to the reaction of the sulfonium ylide with a carbonyl, in which internal nucleophilic attack liberates a free sulfide.[16]

Thus the equilibrium constant for eq 13 is very large for Q = P, is not very far from unity for Q = As or S, and is very small for Q = Sb, and is also small for Q = Se.[17]

$$R_nQ + MeI \rightarrow MeR_nQ^+ + I^- \qquad (13)$$

One must ask: Is iodide ion the only general and effective nucleophilic catalyst? It does have an apparently uniquely low identity barrier, but there have not been that many measured. The trend in methyl transfer identity barriers I < Br < Cl, $Ph_3As < Ph_3P$, $RSe^- < RS^-$ leads to the suggestion that At^-, RTe^-, and RPo^- (if it exists) might have still lower identity barriers, but none of these is an attractive potentially useful catalyst.

Possible catalysts are the "supernucleophiles", low-oxidation-state metal complexes which react very rapidly with iodomethane. Among the best are some Co^I complexes, notably the cobaloximes and vitamin B_{12s}, which have n_{MeI} values[18] of up to more than 14,[19] and cobalt(I) phthalocyanine, with $n_{CH_3I} = 10.8$.[20] These very high reactivities toward iodomethane imply either a very strong thermodynamic driving force or a low intrinsic barrier, or both.

The equilibrium constant for reaction of iodomethane with B_{12s} or the cobaloximes is not known, but it can be bracketted. Thiolates, such as thiophenoxide, are reported to be able to remove the methyl group from the methyl cobalt complex, implying that the equilibrium constant for that reaction is greater than unity. Correspondingly, the equilibrium constant for the reaction of B_{12s} or a cobaloxime with methyl iodide must be smaller than that for the reaction of iodomethane with the thiolate. The n_{CH_3I} value of thiophenoxide ion is 9.9, that for B_{12s} is 14.8. This nearly 10^5 greater rate, coupled with a smaller equilibrium constant, implies a much faster identity rate for the methyl transfer between cobalt complexes.

This identity rate has not been measured, but there is strong evidence that it is very fast. Thus Dodd, Johnson, and Lockman[21a] measured the rate constant for ethyl transfer from $EtCo^{III}$ dioxime complex to Co^I complexed with a slightly different dioxime ($k = 0.11\ M^{-1}\ s^{-1}$ at 0 °C in methanol), but the methyl compound was much faster, only a lower limit was set, $k \geq 17\ M^{-1}\ s^{-1}$ at 0 °C in methanol. Since there is little difference in the two dioximes, this estimate must be reasonably close to the identity rate.

Similarly, in an attempt to prepare methyl B_{12} with a chiral methyl group, Imhoff[21b] observed that conversion of the methyl group to acetic acid by a presumably stereospecific path gave a racemic product, which was attributed to a rapid transfer of methyl from one B_{12}s to another during the methylation. In contrast, optically active deuteroethyl B_{12} was degraded to active propionic-*d* acid. However, when tritium labelled B_{12s} was allowed to react with methyl B_{12} at 0 °C for 15 s, the activity in the methyl B_{12} and in the B_{12s} (isolated after oxidation to the Co^{III} state) were nearly equal, showing that the exchange was rapid under these conditions. Again the rate of ethyl transfer was much slower and measurable.

There are other examples of fast identity or near-identity transfers of alkyl groups between complexes of other metals. Thus, in a well-established case, alkyl transfer between two almost identical Rh^I species differing only in the nature of the ligands was observed,[22a] and rates were measured.[22b] Racemization of

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optically active secondary alkyl metal complexes by the unalkylated form has also been suspected in a manganese case,[23a] and a $\mathrm{Pd^0}$ case.[23b]

Casey and co-workers[24] have observed rather facile transfer of methyl between a number of low-valent-metal complexes in tetrahydrofuran, and a sequence of equilibrium stabilities was proposed. Several further examples of metal complexes leaving alkyl by nucleophilic attack are noted in that interesting article.

These alkyl transfers are formally oxidation-reduction reactions, in the same sense that in any S_N2 reaction the nucleophile increases its oxidation number by two, and the leaving group suffers the same loss in oxidation state.

Regarding these reactions as oxidation-reduction processes brings up the question of single-electron-transfer processes. The distinction between SET and S_N2 has been recently clarified;[25] there is no compelling reason to call these reactions SET processes.

The lower limit for the methyl transfer near-identity rate between $\mathrm{Co^I}$ complexes is much faster than that for the iodide iodomethane reaction in the same solvent at 35 °C with $k = (1-2) \times 10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$.[26] Thus these cobalt complexes have the requisite character of being both fast nucleophiles and leaving groups, and hence should be capable of nucleophilic catalysis.

The fact that the cobalt complexes have the necessary rate constants to act as nucleophilic catalysts hardly shows that they in fact do have this action. There are however some examples from the biochemical literature which can be interpreted as showing exactly this role.

The synthesis of methionine in nature has a methyl group transferred from methyltetrahydrofolate to homocysteine, and in anaerobic systems B_{12} plays a part; methyl B_{12} has been identified as an intermediate which then passes the methyl onto the homocysteine.[27a] The use of the chiral methyl shows, in contrast to most methyl transfers, that the methyl group of the product methionine has the same configuration as the starting methyltetrahydrofolate, demonstrating a double inversion.[27b] Another related example is the double inversion in the conversion of methanol to acetic acid (by an extract of the methanogen *Methanosarcina barkeri* using the slightly different corrinoid MTI).[28] Similarly, the conversion of 5-methyltetrahydrofolate to acetic acid by a path requiring both B_{12} and a CO dehydrogenase by *Clostridium thermoaceticum* involves two inversions in a complex process.[29]

In two other examples from Floss and co-workers,[30] methyl transfer from methionine (presumably vis *S*-adenosylmethionine) also gave retention of configuration, but the participation of a cobalt species was not firmly implicated. In all other studied methylations by methionine, the reactions showed inversion of configuration.[27b]

It appears that the cobalt catalysis of nucleophilic methyl transfers is occasionally the efficient way to accomplish this substitution. All the reactions are enzymatic, so that there are many factors contributing to rate; yet the expected high rates of the $\mathrm{Co^I}$-catalyzed reactions offer a very plausible explanation of the occurrence of these otherwise obscure participations of cobalt enzymes as way stations on the route to a net S_N2 substitution.

One further possibility should be noted. Although the transfer to and from cobalt in the methionine synthesis is well-established, it has been claimed[31] that even thiolates are ineffective in accomplishing nucleophilic substitution on methyl B_{12} or methyl cobaloximes.

The efficacy of $\mathrm{MeCo^{III}L}_n$ as a methylating agent can be enhanced (as with all leaving groups) by putting the leaving group in a higher oxidation state, and it has been observed that $\mathrm{MeCo^{IV}L}_n{}^+$ is a more powerful methylating agent than $\mathrm{MeCo^{III}L}_n$.[32]

Thus the reaction of the $\mathrm{MeCo^{IV}}$ species with nucleophiles can be expected to be much faster than that of the $\mathrm{MeCo^{III}}$ species. Since many of these enzymatic systems are complicated, it is not inconceivable that a one-electron oxidation precedes or is coupled with the demethylation. This possibility does not argue against the existence and possible generality of nucleophilic catalysis in general, but it does have the potential to confuse any specific case.

Nevertheless, the role of cobalt complex enzymes as intermediates in methyl transfers appears to be entirely in accord with the idea that $\mathrm{Co^I}$ complexes, by virtue of the low identity barrier, can be nucleophilic catalysts for methyl transfers, even in nonenzymatic systems.

Experimental Section

Materials. Iodomethane, 1-octanethiol, 1-decanethiol, dimethyl sulfide, and methyl triflate were all obtained from Aldrich. The methyl triflate was freshly distilled before use. Propylene carbonate and iodomethane were purified by distillation as before.[33] Triphenylphosphine was recrystallized from methanol before use, mp 79–80 °C. Triphenylarsine was recrystallized from petroleum ether before use, mp 58–58.5 °C. Tetrahydrothiophene 1,1-dioxide (sulfolane) was purified by repeated distillation from sodium hydroxide and then from calcium hydride as before.[34]

Tri-*p*-tolylarsine. Arsenic trichloride in ether was added slowly to a solution of *p*-tolylmagnesium bromide in ether. Workup with aqueous acetic acid and removal of the ether led to a syrup, which turned to a white solid on extended stirring with ethanol. Recrystallization from methanol (or acetonitrile) gave white crystals, mp 150–152 °C, in 55% yield.

Tri-*p*-chlorophenylarsine. This was similarly made from *p*-chlorobromobenzene, in 45% yield after recrystallization from petroleum ether.

Methyltriphenylphosphonium Iodide. This salt was prepared by dropwise addition of iodomethane to a solution of triphenylphosphine in anhydrous ether under nitrogen. The white precipitate is rinsed with ether and recrystallized from ethanol/ether, mp 184.5–185.5 °C.

Methyltriphenylarsonium Iodide and Triflate. The arsonium salt was similarly prepared by a slower reaction. Methyltriphenylarsonium iodide was recrystallized from ethanol/ether, mp 182.5–183.5 °C (lit.[35] mp 171.5–172 °C). Methyltriphenylarsonium triflate was used without purification due to its hygroscopic nature.

Methylation of Other Arsines. The triarylarsines were boiled with iodomethane under reflux, the salt products were washed with ether to remove unreacted arsine. The yields were poor, probably because the equilibrium is unfavorable in this rather nonpolar solvent.

Octyldimethylsulfonium Iodide. Attempts to prepare sulfonium salts in one pot from the thiol were generally unsuccessful; they were therefore prepared via methyl octyl (or decyl) sulfide. Methyl octyl sulfide and decyl methyl sulfide were made from the corresponding thiol following the literature procedure of Ingold et al.[36] To 2.40 g of octyl methyl sulfide in a Schlenk tube under argon was added 1.1 mL of iodomethane. After 1 of stirring, an oil began to separate. Acetonitrile (1 mL) was added and stirring continued for 24 h. The acetonitrile was pumped away from the semicrystalline mass of product, and 5 mL of ether was added to produce complete crystallization. The crystals were filtered in the Schlenk apparatus. Low-temperature recrystallization from an ether/ethanol mixture gave pure white crystals, deliquescent on exposure to air.[37]

Octyldimethylsulfonium Triflate. In a dry 50-mL round-bottom flask was placed 1.390 g of octyl methyl sulfide. The flask was cooled in ice,

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and 1.0 mL of freshly distilled methyl trifluoromethanesulfonate was added slowly with stirring. A vigorous reaction resulted in formation of a solid mass within 1 min. The mixture was allowed to sit overnight and was then recrystallized from an ethyl ether/ethanol mixture to yield a white solid, mp 71–72 °C. Yield was 2.6 g (92%). This salt is not deliquescent and can be handled in air.

Methyltris[*p*-(trifluoromethyl)phenyl]phosphonium Iodide. Into a test tube were weighed 210 mg of tris[*p*-(trifluoromethyl)phenyl]phosphine and 157 mg of iodomethane. An amount of acetonitrile was added sufficient to give a clear solution, and the tube was stoppered tightly. After 48 h, no free phosphine was detectible by HPLC, and the solution was evaporated to give a yellow oil. Crystallization from a mixture of chloroform and hexane gave 0.22 g (77%) pale yellow crystals, mp 294–296 °C dec: ^{1}H NMR ($CDCCl_3$) δ 3.55 (d, J = 14 Hz, 3 H), 7.8–8.2 (m, 12 H).

Methyltris[*p*-(trifluoromethyl)phenyl]phosphonium Trifluoromethanesulfonate. Into a 1-mL volumetric flask were weighed 140 mg of tris[*p*-(trifluoromethyl)phenyl]phosphine and 65.2 mg of 1,1,2,2-tetrachloroethane (as NMR internal integration standard). A small amount of either trideuterioacetonitrile or deuteriochloroform was added and then 20 μL of methyl trifluoromethanesulfonate from a freshly opened ampule was added by syringe. The flask was filled to the mark, and the contents were mixed and transferred to an NMR tube equipped with a ground joint. The solution was degassed on the vacuum line, and the tube was sealed. Monitoring by NMR indicated that the reaction in acetonitrile was complete by the time the tube was sealed. The solution in chloroform reacted more slowly; the "half-life" was estimated at 30 min.

After opening, the tube's contents were transferred to a small flask, and the solvent was evaporated under a nitrogen stream to yield white crystals. Recrystallization from chloroform gave a 67% yield of white crystals, mp 231–234 °C dec. Concentration gave a second crop but with a substantially lower melting point. The proton NMR was indistinguishable from that of the iodide salt except that the chemical shift of the methyl group was a few hundredths of a parts per million to higher field.

Methyltris(pentafluorophenyl)phosphonium Triflate. In a small test tube were placed 190 mg of tris(pentafluorophenyl)phosphine, about 0.2 mL of chloroform, and 90 μL of methyl triflate from a freshly opened ampule. The mixture was transferred to a jointed ampule, degassed on the vacuum line, and sealed. Heating to 100 °C caused initial dissolution of the weakly soluble phosphine and after a few hours produced a heavy precipitate of salt. On cooling, the ampule was opened, and the contents were rinsed out by repeated washings with chloroform. The white crystalline solid was refluxed with several portions of dichloromethane and then pumped dry on the vacuum line at 0.01 mmHg. Freshly dried crystals had a melting point of 262–263 °C. The crystals were too insoluble in chloroform to use it for an NMR solvent. In deuterioacetonitrile, the ^{1}H NMR showed two signals, each apparently a doublet of quintets (J = 2 and 14 Hz), one at δ 2.40 (a heptet is expected from the 6 *ortho* fluorines, but the extreme signals are easily missed), and the other at δ 3.25 in a ratio of 1:1.74. The ^{31}P NMR showed two signals in the same ratio at δ −13.2 and −15.5 (H_3PO_4 capillary standard). The latter signal was the lesser in area and became reversibly broadened as the temperature was raised. The ^{19}F NMR showed signals at δ −79.3 (triflate), −126.7, −137.1, and −157.3 (relative to CF_3Cl with a capillary of CF_3COOH at −76.5). The nature of this equilibrium is not established. The reversible addition of a nucleophile to one of the three pentafluorophenyl rings is a possibility, not quite compatible with the ^{19}F NMR, but our instrument is not very sensitive to fluorine, so minor peaks could have been overlooked. On exposure to air after several days, the crystals became sticky and had a lower melting point.

Methyltriphenylstibonium Triflate. In 3 mL of dry acetonitrile were dissolved 0.35 g of methyl triflate from a freshly opened ampule and 0.81 g of triphenylstibine. The reaction was monitored by removing a small amount of the solution and checking its NMR spectrum, which also showed the spectrum (a 1,1,1 triplet) for $CH_3CNCH_3^+$.[38] The reaction appeared to be complete (no methyl triflate remaining) after about a day. The solution was diluted with chloroform to which a few drops of methanol had been added (to destroy any traces of methyl triflate) to produce a yellow oil. The oil on sitting in air for two weeks became largely crystalline. A first crystallization from 2:1 $CCl_4/CHCl_3$ gave white crystals with a small amount of yellow oil; washing with cold chloroform freed the crystals from most of the oil with minimal loss. A second crystallization from the same solvent mixture gave pure white product: mp 116.5–119 °C; NMR ($CDCl_3$) δ 2.45 (s, 3 H), 7.60 (m, 15 H).

Attempted Methyl Transfers to Tri-*p*-tolyphosphine. The reaction in sulfolane of methyltriphenylphosphonium bromide with tri-*p*-tolylphosphine with or without added iodide and the reaction of the iodide salt in a melt at 250 °C were studied by searching for triphenylphosphine with the use of thin-layer chromatography on silica with a cyclohexane solvent. No triphenylphosphine was ever detected, although it was easily seen in controls.

Attempted Methyl Exchange Reactions between Other Phosphines. In a typical case 30–40 mg of the phosphonium salt was weighed out and a known volume of a solution of triphenylphosphine and tetrachloroethylene standard in dry sulfolane was added to give a solution 0.01 M in the salt and having a similar amount of triphenylphosphine. The solution was transferred to ampules and sealed under nitrogen. Ampules were heated to 35 °C in a water bath, or to 100 °C by immersion in a flask of refluxing water, or placed in a 195 °C oil bath. Upon cooling, the ampules were opened and checked by HPLC using a C18 column, water/acetonitrile azeotrope as eluant at 1.5 mL/min flow rate, and a 250-nm UV monitor. Under these conditions, the initial salt had a retention time of 1.35 min (essentially the solvent retention time) the tetrachloroethylene standard 4.00 min, triphenylphosphine 6.60 min, and tris[*p*-(trifluoromethyl)phenyl]phosphine 10.5 min. Relative to the tetrachloroethylene standard, the response factor for triphenylphosphine was 12.7 and for the tris[*p*-(trifluoromethyl)phenyl]phosphine 10.6. No tris[*p*-(trifluoromethyl)phenyl]phosphine was ever observed in any of the reaction ampules. Introduction of an equimolar amount of tetrabutylammonium iodide during the weighing only increased the rate of an undetermined alternate decomposition of the salt and phosphine. The procedure for the methyltris(pentafluorophenyl)phosphonium salt used was the same as for the methyl tris[*p*-(trifluoromethyl)phenyl]phosphonium salts. Again, either no reaction or only destruction of salt and phosphine were observed.

Methyltriphenylarsonium Ion–Triphenylphosphine Reaction. Solutions of methyltriphenylarsonium triflate, tetra-*n*-butylammonium iodide, and triphenylphosphine in propylene carbonate were heated in a thermostat to 75, 100, or 120 °C in NMR tubes containing a capillary of benzene-d_6 (for locking) and trimethyl phosphate as an internal standard. The tubes were removed periodically and placed in an ice bath, and their ^{31}P spectra were recorded on a JEOL FX 90Q spectrometer. The formation of methyltriphenylphosphonium salt followed a first-order course, since the iodide ion concentration is constant. Second-order rate constants were obtained by dividing the first-order rate constants by the concentration of iodide salt.

Methyl Transfers between Arsines. These reactions occurred readily in hot sulfolane solution as seen by TLC, but there was a net loss of methyl groups, presumably as iodomethane.

Methyltriarylarsonium Iodide Reactions. Decomposition of methyltriarylarsonium salts were followed by HPLC using samples in sulfolane solution sealed in an ampule and heated to 141 or 151 °C. HPLC analysis (C18 reversed-phase column, acetonitrile/water azeotrope solvent) at early stages gave initial rates at various initial concentrations, and samples kept for longer times gave equilibrium values, somewhat uncertain because of iodomethane in the void space in the ampules.

Methyltriphenylstibonium Triflate with Iodide. Methyltriphenylstibonium triflate (65.6 mg), 1,1,2,2-tetrachloroethane (16 mg), and dried NaI (18.6 mg) were placed in a 1-mL volumetric flask. CD_3CN was added to the mark, and the solution was well mixed, transferred to a jointed NMR tube, degassed, and sealed. The mixture turned dark yellow immediately upon addition of the NaI. The NMR spectrum was taken periodically, but the tube was kept in a 35 °C water bath at all other times. Some iodomethane and triphenylantimony were observable immediately, but reaction was not over until 2 days had passed. Integration with the tetrachloroethane as standard indicated that the yield of iodomethane was quantitative. The yellow solution faded to colorless over the first day of reaction.

Methyl Transfer between Sulfides, Kinetics. A large excess of decyl methyl sulfide was weighed into one volumetric flask; the dimethyloctylsulfonium triflate was weighed into a second volumetric flask; acetonitrile was added to the latter, and this solution was diluted serially with the final transfer into the flask containing the sulfide. The decyl methyl sulfide was also used as the internal integration standard. The response of the octyl sulfide relative to the decyl compound was 1.01 at 220 nm. Ampules were filled and sealed in the same way. Because the decyl methyl sulfide was found to contain 0.3% of octyl methyl sulfide (from octanethiol in the original decanethiol) a correction for the amount of octyl methyl sulfide found in the initial unheated solution was applied in the case of the more concentrated solutions.

At 120 °C there was some reaction between the free sulfides and both chloroform and acetonitrile. This was slow enough not to interfere with kinetic measurements for the first few half-lives but seriously interfered with determination of the equilibrium constant for the near-identity

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exchange. However, the exchange was subject to iodide ion catalysis, so equilibrium constants were determined at 35 °C by mixing the triflate salt, sulfide, and tetrabutylammonium iodide plus internal standard in acetonitrile or chloroform in sealed ampules.

Dimethyloctylsulfonium Iodide Kinetics. With use of a Schlenk adapter, a small amount of the sulfonium iodide was transferred to a volumetric flask. Tetrachloroethylene was weighed in (as an internal standard), and the flask was filled with acetonitrile. After mixing, 10–15 small ampules were charged with the solution, cooled in dry ice, and sealed.

The ampules were placed in a 35 or 15 °C water bath. Upon removal, each ampule was immediately cooled to −25 °C and promptly opened and checked by HPLC using a C18 reversed phase column and the acetonitrile/water azeotrope solvent.

Because dissociation of sulfonium iodide to iodomethane and octyl methyl sulfide in chloroform is a much more rapid reaction when the salt is dilute (concentrations below 0.01 M), a slightly different method of solution preparation was necessary. The sulfonium salt was weighed into a dry, argon-purged round-bottom flask equipped with a magnetic stirrer and a Schlenk adapter. The internal standard was weighed into a volumetric flask, and the chloroform was added and mixed to give a solution at the desired final concentration of standard. The round-bottom flask was cooled to −25 °C in a dry ice/CCl_4 bath, and the solution of the internal standard was pipetted in very gradually with vigorous stirring. The initial concentration of salt and products was determined, a few milliliters of the solution was transferred to a small flask, and this tightly stoppered flask was then immersed in the water bath. HPLC analysis of the initial solution showed that even at 0.0009 M salt, where the half-life for dissociation is under 40 min at 35 °C, less than 2% dissociation had occurred before immersion in the water bath. Analysis of individual points was done by withdrawing a few microliters of the solution by syringe and immediately injecting them into the HPLC.

HPLC Analytical Method. Iodomethane and starting sulfonium salt concentrations were determined at 250 nm while octyl methyl sulfide was determined at 220 nm in a separately injected sample. Molar response factors relative to tetrachloroethylene were determined previously at the monitored wavelengths on solutions of the individual components plus standard. The response factors were 0.457 for iodomethane, 1.014 for the sulfonium iodide, and 0.112 for the sulfide. The solvent (acetonitrile/water as above) was pumped at 1.5 mL/min. Retention times are 1.08 min for the salt, 2.49 min for iodomethane (and also for chloroform), 3.00 min for tetrachloroethylene, and 4.35 min for octyl methyl sulfide.

Unless the salt and reacting ampules were kept in the dark, determination of the salt response factor and later measurements of its concentration were not trustworthy. In running the Hewlett-Packard integrator, the internal standard and the salt were treated as solvent peaks while the iodomethane and sulfide were tangent-skimmed. When chloroform was used as the solvent, the chloroform peak was also treated as a solvent but the internal standard peak was not, instead it was tangent-skimmed. The iodomethane peak was not separated from the chloroform and could not be quantitated in those runs.

Calculations

Concentrations of the starting sulfonium salts were calculated from the concentrations of liberated octyl methyl sulfide. With the iodide salt in acetonitrile, liberated iodomethane was also used for this purpose, and the numbers were found to agree to a few percent, although the sulfide numbers were usually used because of possible loss of the volatile iodomethane (iodomethane concentrations were almost always 0.1–1% lower than the measured sulfide concentrations). Direct measurement of the iodide salt could be done, but for runs in which the ampules were exposed to light for any length of time, the solutions became yellow and the directly measured concentrations were usually substantially higher than the indirectly determined ones and so were not used. A minor correction for a side reaction, the formation of 1-iodooctane and dimethyl sulfide was made since the iodooctane was separated in the chromatography.

Data were treated by linear least-squares fit to the integrated form of the appropriate rate equation (simple first- or second-order or reversible first-, mixed-, or second-order) taken from Moore and Pearson's text[39] and converted into a BASIC program. For reactions with equilibrium extents of reactions under 50%, alternate solutions to the differential equations were written into the program.

Conductivity of Sulfonium Salts. Conductivities were measured at 1000 Hz in a Fisher Scientific conductivity cell, with a General Radio Z-Y bridge and a Tectronics Model 6103N oscilloscope as a null detector. The cell constant was determined by measurement of the conductivity of an aqueous 0.01 M KCl solution. Acetonitrile used for dissolving the organic salts was purified by the literature method[40] and stored under nitrogen in serum-capped flasks.

Both the triflate and the iodide sulfonium salts were examined. An attempt was made to determine the conductivity of the triflate in chloroform but solutions below 0.05 M gave no measurable conductivity ($<1\ \mu\Omega^{-1}\ \mathrm{cm}^{-1}$). A 0.1008 M solution gave a specific conductivity of only 15 $\mu\Omega^{-1}\ \mathrm{cm}^{-1}$. The triflate was weighed into volumetric flasks and dissolved in the purified acetonitrile, and the flasks were filled to the mark. The more dilute solutions were prepared by serial dilutions, 25-mL samples being diluted to 100 mL. The iodide salt could not be so studied in chloroform because the reaction is much faster. The iodide salt was also weighed into volumetric flasks, but the flasks were first fitted with standard taper joints so that they could be attached to the Schlenk storage tube containing the iodide with a standard adapter; a nitrogen atmosphere was maintained until after the acetonitrile had been introduced (by syringe). Once dissolved, the solutions were no more moisture sensitive than the acetonitrile itself and brief exposure to air produced no measurable changes in conductivity, allowing all further handling to be done as with the triflate.

Plots of specific conductivity versus concentration were strongly curved over their entire range, but plots of molar conductivity versus the square root of concentration (Kohlrausch plots) were linear up to 0.028 M for the triflate (slope $-630 \pm 11\ \mu\Omega^{-1}\ \mathrm{cm}^{-1}\ \mathrm{M}^{-1/2}$) and up to 0.048 M for the iodide (slope $-534 \pm 13\ \mu\Omega^{-1}\ \mathrm{cm}^{-1}\ \mathrm{M}^{-1/2}$).

Ion pairing of the sulfonium salts in acetonitrile was calculated by the method of Davies.[41] Since the association constants determined were above 100, more sophisticated treatments were deemed unnecessary.

Conductivity Kinetics of Methylation. Reactions were run in propylene carbonate solution under either second-order or pseudo-first-order conditions. For all reactions, a calibration curve of conductivity versus concentration was constructed to insure that the equilibrium conductivity value corresponded to complete reaction and for the calculation of the second order runs. Over the concentration range studied in this solvent, these all fit a fairly good straight line ($r > 0.994$) whose intercept was approximately 0. The calculated limiting molar conductivities were as expected for a virtually completely dissociated electrolyte. The reaction of triphenylarsine with iodomethane were done under pseudo-first-order conditions with an excess of at least 7-fold in the arsine. The slope of a plot of ln ($\mathrm{Cond}_{\mathrm{inf.}} - \mathrm{Cond}_t$) versus time is the pseudo-first-order rate constant, k_{obs}. Division by the concentration of the nucleophile gave the second-order rate constants. All of these plots had correlation coefficients greater than 0.996. The faster runs on triphenylphosphine and iodomethane were done under second-order conditions, with no great excess of either reagent. Rate constants were obtained from conventional second-order plots.

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