or ferrocyanide anions. Thus, complexation between either of these complex ions and **8** is either very weak or else does not significantly perturb the absorption spectrum of **8**.

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Mechanism for the Reaction Involving Dimethyl Sulfoxide and Acetyl Chloride Studied by Nuclear Magnetic Resonance Spectroscopy

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The kinetics of the reaction between dimethyl sulfoxide (Me_2SO) and acetyl chloride (AcCl) have been studied using the nuclear magnetic resonance spectroscopy of both static and flowing liquids at 30 °C in either benzene or methylene chloride solutions. The decay of Me_2SO and AcCl follows mainly second-order kinetics, first order each in Me_2SO and AcCl. The growth of the main products, acetic acid and chloromethyl methyl sulfide, appears to be mainly second order also, although the overall reaction is complicated by several side reactions that compete to a lesser extent with the main path. These side reactions generate three previously unreported compounds in small amounts, namely, acetoxymethyl methyl sulfide, acetic anhydride, and chlorodimethylsulfonium chloride. Both the anhydride and the sulfonium salt are unstable under the reaction conditions and eventually disappear, with the salt having the faster rate. When Me_2SO-d_6 replaces Me_2SO, a primary deuterium isotope effect is observed, indicating the presence of an intermediate. This conclusion is supported by the observation that acetic anhydride and the sulfonium salt appear to be generated by trapping reactions. A mechanism to account for these observations is proposed.

Introduction

The chemistry of dimethyl sulfoxide (Me_2SO) has been under study for a number of years, and much is known about its nucleophilic properties.[1b] However, in the case of addition to acyl halides, conclusions concerning the reaction mechanism are based on only the nature of the products that could be identified.[2] No kinetic data seem to be available, and none of the proposed intermediates have been detected in solution at room temperature. In the present paper, we report a study of the kinetics of the reaction between Me_2SO and acetyl chloride (AcCl) in benzene and in methylene chloride, studied using nuclear magnetic resonance spectroscopy (NMR). In each solvent the rate of reaction appears to be second order, first order each in Me_2SO and ACT. The main products of this reaction are acetic acid (AcOH) and chloromethyl methyl sulfide (CMMS), as reported earlier.[2] However, small amounts of two other compounds, acetoxymethyl methyl sulfide (AMMS) and acetic anhydride (Ac_2O), are also generated during the reaction, and their amounts depend on the reaction conditions. In addition, a transient signal is observed in the frequency region expected for a dimethylsulfonium salt. A mechanism is proposed to account for these observations as well as the occurrence of a primary deuterium isotope effect for the disappearance of the reactants and the growth of the products.

Experimental Section

Chemicals. Me_2SO, Me_2SO-d_6, AcCl, benzene, and methylene chloride were obtained from commercial sources. Me_2SO and AcCl were distilled immediately before solution preparation. Benzene and methylene chloride were dried over molecular sieves, distilled, and stored over additional molecular sieves.

Kinetic Studies. The time dependence of the proton NMR spectrum was measured at 30 ± 2 °C using a Varian A-60 or HA-100-15 for the slower rates and an HA-100-15 equipped with a flow system[3] for the faster rates. Solutions of each reactant were prepared gravimetrically, and equal volumes were mixed (outside the magnet for the static runs and inside the magnet via a mixing chamber for the flow runs). Temperature regulation was not as precise as for other studies using the HA-100 flow system because the thermostated reservoir was left out to decrease solution volume.

In a complementary study, a Beckman IR-12 was used to measure the time dependence of infrared absorption bands due to Me_2SO-d_6 (1050 cm^{-1}) and ACT (950 and 1900 cm^{-1}) at about 25 °C after mixing equal volumes of a benzene solution containing 0.4 M Me_2SO-d_6 and one containing 0.4 M ACT.

Results

The CH_3 region of the proton NMR spectra of a nonspinning sample obtained at 100 MHz after mixing but before completion of the reaction is given in Figure 1 to illustrate the solvent dependence of the reactant and product signals. The series of spectra given for benzene solvent consists of five consecutive scans from left to right with pauses ranging from 30 s to several minutes. The first scan (labeled 1) gives CH_3-proton resonances for Me_2SO (labeled d) and AcCl (labeled a). Scan 2 illustrates an additional central signal (labeled c,h), which is a superposition of the AcOH (labeled h) and CMMS (labeled c) CH_3-proton resonances. The AcOH signal position as well as its intensity is time dependent moving upfield in scans 2, 3, 4, and 5, in which it is at higher field than the ACT signal. Its final position is upfield from the AcCl

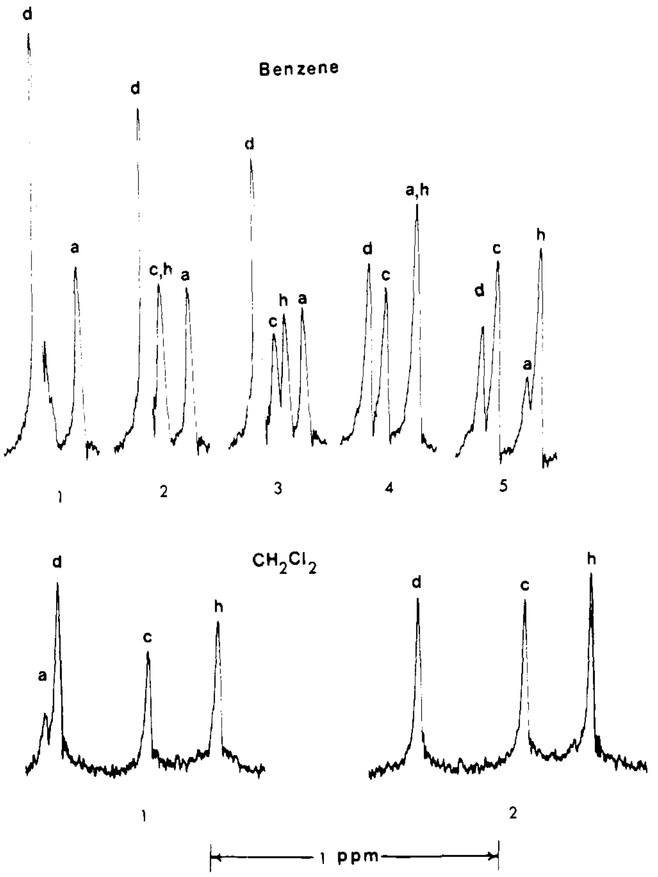


Figure 1. Successive scans of the CH_3-proton resonance region at 30 °C and 100 MHz during the reaction after the flow had been stopped with pauses from 30 s up to several minutes obtained without spinning. For each solvent, the first scan is labeled 1. For benzene, the initial concentrations were 0.070 M Me_2SO and 0.066 M AcCl. For methylene chloride, the initial concentrations were 0.103 M Me_2SO and 0.091 M AcCl, and the spectra were obtained at lower rf power than that used for the benzene solution. The assignments of these CH_3-proton resonances are: Me_2SO, d; AcCl, a; CMMS, c; add AcOH, h.

Table I. Chemical-Shift Values (Hz) for the CH_3-Proton Resonances of Me_2SO and AcOH Relative to *tert*-Butyl Alcohol in Benzene at 30 °C

[AcOH], M	[Me_2SO], M	δ_{AcOH}	δ_{Me_2SO}
0.202		83	
	0.07		93.2
	0.31		99.5
	0.92		108.4
0.100	0.146	98	102.5
0.104	0.501	103	111.2
0.106	0.820	104	115.8

position by about 10 Hz. This time dependence for the AcOH signal position results from the fact that the AcOH chemical shift in benzene depends on the concentration of Me_2SO, as illustrated in Table I, which lists the chemical shifts for Me_2SO and AcOH relative to *tert*-butyl alcohol. Thus, as the reaction progresses the concentration of Me_2SO decreases and the AcOH signal moves upfield. This conclusion is also supported by the fact that the position of the CH_3-proton resonance of AcOH is fixed downfield if a sufficient excess of Me_2SO-d_6 is present.[4] The CH_3- and CH_2-proton resonances due to CMMS appear to be independent of Me_2SO concentration, and the CH_2-proton resonance is observed at lower field at 2.43 ppm from the CH_3-proton resonance. In addition a transient signal is observed 1.48-ppm downfield from the CH_3-proton resonance of CMMS. No other transient signals were observed. Because the AcOH signal moves into other signals, its time dependence could not be determined accurately in benzene. For this reason, the reaction was also studied in methylene chloride, a solvent in which the AcOH signal position is only slightly dependent on Me_2SO concentration. As illustrated in Figure 1, the chemical shifts for AcCl and Me_2SO are very close in this solvent. In fact, the Me_2SO signal position is somewhat concentration dependent and it moves into the AcCl signal as the reaction progresses. However, the time dependence for the Me_2SO and AcCl signals could still be determined as accurately as in benzene when spinning samples were used to provide better resolution. The proton resonance (not illustrated) of a transient could also be observed 1.48-ppm downfield from the CMMS CH_3 signal. The CMMS CH_2-proton signal could be observed, although it is close to the methylene chloride signal, 0.6-ppm upfield. The higher resolution spectra obtained with spinning samples permit the observation of additional signals. Sample spectra obtained during the reaction are illustrated in Figure 2 for the reaction of AcCl with Me_2SO (Figure 2A) and with Me_2SO-d_6 (Figure 2B). In addition to the signals identified above, three

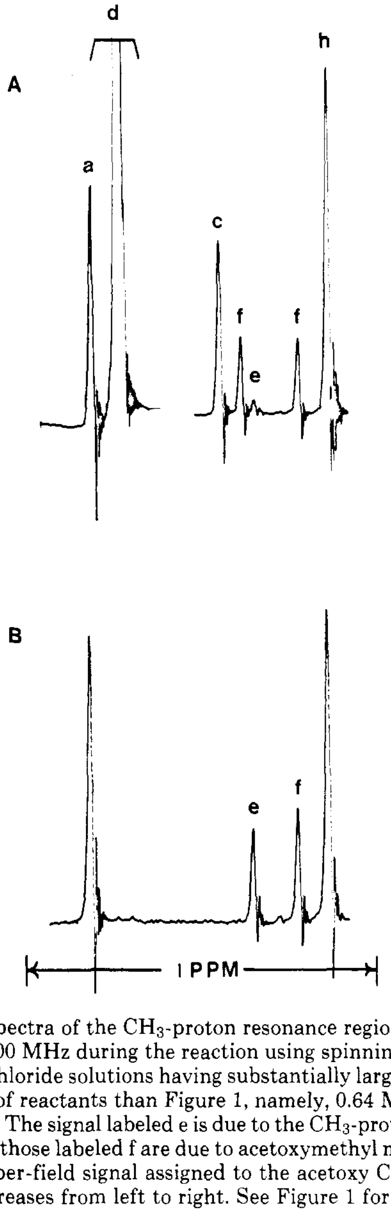


Figure 2. Spectra of the CH_3-proton resonance region obtained at 30 °C and 100 MHz during the reaction using spinning samples for methylene chloride solutions having substantially larger initial concentrations of reactants than Figure 1, namely, 0.64 M Me_2SO and 0.32 M AcCl. The signal labeled e is due to the CH_3-proton resonance of Ac_2O and those labeled f are due to acetoxymethyl methyl sulfide with the upper-field signal assigned to the acetoxy CH_3. The field strength increases from left to right. See Figure 1 for the other assignments.

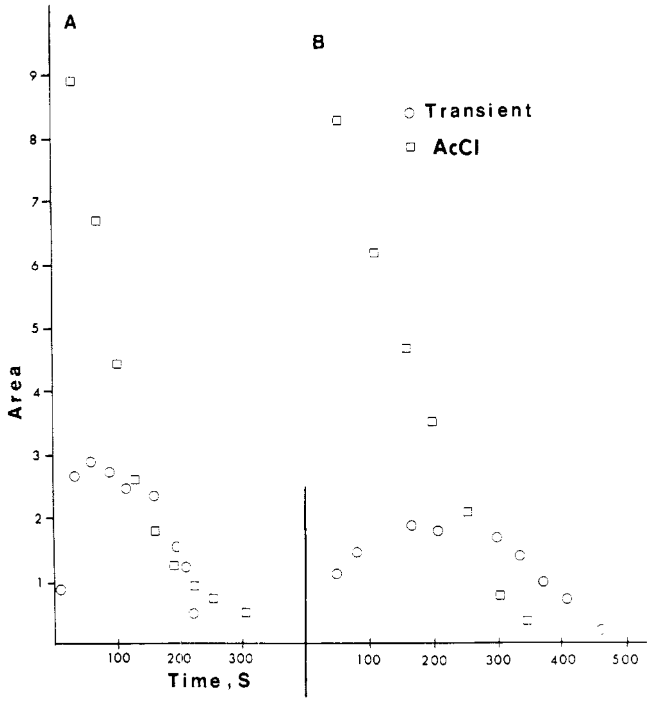


Figure 3. Integrated areas of the signals due to AcCl and the transient at various times during the reaction in methylene chloride at 30 °C. The initial concentrations were: A, 0.64 M Me_2SO and 0.32 M AcCl; B, 0.256 M Me_2SO and 0.128 M AcCl.

new signals are observed, and they are assigned to the CH_3-proton resonances of acetic anhydride (Ac_2O) (labeled e) and acetoxymethyl methyl sulfide (labeled f) (AMMS). The assignment for AMMS was confirmed by reacting Me_2SO with Ac_2O. Di-*tert*-butyl ketone is used as an internal reference. The intensity of these signals depends on the conditions employed. Thus, the intensity of the signals due to AMMS increase relative to the AcOH signal as the concentration of Me_2SO is increased. For example, if the initial AcCl concentration is held constant at 0.126 M, the intensity ratio, AMMS/AcOH, after AcCl has disappeared is 0.06 and 0.10 for initial Me_2SO concentrations of 0.146 and 0.256 M, respectively. Further, when these solutions contain HCl, AMMS is not detected, and when Me_2SO is replaced by Me_2SO-d_6 the downfield signal of AMMS disappears but the AMMS/AcOH concentration ratio remains about the same as that for undeuterated Me_2SO.

Although acetic anhydride reacts with Me_2SO, a similar intensity comparison is possible because its rate of reaction is substantially slower than that for AcCl; i.e., the AcCl reaction is essentially complete before an appreciable amount of acetic anhydride has reacted. In this case, we find that the acetic anhydride intensity increases relative to the AcOH intensity as the AcCl concentration increases. For example, when the initial Me_2SO concentration is fixed at 0.15 M, the intensity ratio, Ac_2O/AcOH, is 0.020 and 0.048 for initial concentrations of 0.13 and 0.32 M AcCl, respectively. In addition, replacing Me_2SO by Me_2SO-d_6 causes an increase in this ratio from 0.017 to 0.080 when the initial concentrations of AcCl and Me_2SO are held constant at 0.32 and 0.64 M, respectively. As in the case of AMMS, acetic anhydride is not detected when HCl is present in the solution.

The intensity of the transient signal and its time dependence also depend on the initial concentration of each reactant, as illustrated in Figure 3, which presents the area rather than intensity as a function of time. Areas are used because the line width of the transient increases as the concentration of each reactant is increased. As illustrated in this figure, doubling the concentration of each reactant not only increases the maximum area observed for the transient, but also decreases the time period in which the maximum is attained. This rate of growth of the transient appears related to the rate of disappearance of AcCl and Me_2SO, as can be seen from the time dependence for the intensity of AcCl; i.e., AcCl disappears more rapidly at the higher concentration. Furthermore, the rate of disappearance of the transient increases relative to that for AcCl when the excess concentration of Me_2SO is increased. In the presence of HCl, the transient appears to reach a larger maximum in a shorter time, and it disappears faster after AcCl has disappeared. However, the signal is substantially broader than in the absence of HCl and these results must be considered qualitative. The spectrum obtained using Me_2SO-d_6 in place of Me_2SO provides information concerning the structure of the compound responsible for this transient signal. First, the transient signal is not observed in this case. Second, no acetoxy-CH_3 signal is observed for this transient compound under these conditions, which provide a better opportunity for its detection than the Me_2SO mixtures do, since the CH_3 signals due to Me_2SO and CMMS are absent. To further probe the structure of this transient, a spectrum was obtained for a solution of Me_2SO in CH_2Cl_2 containing various amounts of dry HCl. Aside from the CH_2Cl_2 signal and one due to the reference (di-*tert*-butyl ketone), the spectrum consists of only one signal that moves downfield as the concentration of HCl is increased. However, even at the highest concentration of HCl employed, this signal has not reached the same chemical shift as observed for the transient generated by reaction of AcCl with Me_2SO. In addition, under these conditions, in the absence of AcCl Me_2SO appears to react slowly; i.e., after about 2 h approximately 4% of the Me_2SO has been converted to CMMS.

In another control experiment, 0.16 M AcCl was mixed with 0.13 M AcOH. These compounds react with each other to form acetic anhydride. After approximately 5 min equilibrium is attained, and the equilibrium constant is 2.2×10^{-3} at 30 °C.

The time dependence for the growth of AcOH does not coincide exactly with that for the growth of CMMS, as indicated in Table III, which illustrates the ratio (AcOH/CMMS) of concentrations as a function of time. For a solution containing 0.32 M AcCl and 1.28 M Me_2SO, the concentration of AcOH increases more rapidly and reaches it maximum value sooner than the CMMS concentration does, even though the final AcOH/CMMS concentration ratio is close to 1. Thus, AcOH grows at a somewhat larger rate than does CMMS. This difference in rates between AcOH and CMMS is enhanced when HCl is present, as illustrated in Table II, which indicates

Table II. AcOH/CMMS Concentration Ratio at Various Times during the Reaction of AcCl with Me_2SO at 30 °C

Time,	AcOH/CMMS[a]	
s	HCl absent[b]	HCl present[c]
20	1.42	
30		2.16
40	1.50	
50		3.11
60	1.25	
80	1.12	
100	1.10	1.61
120	1.05	
150		1.35
200		1.24
300		1.15

[a] Concentration ratio. [b] 0.32 M AcCl, 1.28 M Me_2SO initially. [c] 0.128 M AcCl, 0.256 M Me_2SO initially.

Table III. Second-Order Rate Constant for the Reaction of Me_2SO with AcCl at 30 °C

$[Me_2SO]$,[a] M	[AcCl],[a] M	$k_{obsd} \times 10^2\ M^{-1}\ s^{-1}$		
		Me_2SO	AcCl	AcOH
		Benzene		
0.067	0.108	d_6[b]	1.0 ± 0.2	1.1 ± 0.3
0.067	0.216	d_6	1.2 ± 0.2	
0.086	0.069	d_6	1.8 ± 0.4	1.7 ± 0.4
0.127	0.063	d_6	1.6 ± 0.2	1.5 ± 0.4
0.175	0.075	d_6	1.6 ± 0.4	1.6 ± 0.4
0.050	0.038	9 ± 1.5	9.4 ± 0.8	
0.070	0.077	6.0 ± 0.9	5.7 ± 0.9	
0.070	0.173	7.8 ± 0.7	6 ± 1	4.9 ± 0.7[c]
0.103	0.070	6.0 ± 0.8	8 ± 1	
0.125	0.066	9.3 ± 0.8	7.3 ± 0.7	
0.151	0.111	5.4 ± 0.9	5.0 ± 0.7	
0.202	0.156	4.8 ± 0.7	4.5 ± 0.6	
		Methylene chloride		
0.64	0.32	d_6[b]	0.53	0.43
0.146	0.128	2.2	2.5	2.8
0.297	0.128	2.3	2.9	2.7
0.64	0.32			2.6
0.256[d]	0.128	12.3	12.0	8.6
0.256[e]	0 128	0.99	0.80	0.92

[a] Initial concentration after mixing equal volumes of solutions. [b] Me_2SO-*d_6*. [c] AcOH signal overlaps with several signals during the reaction. Consequently, this value is obtained from only four intensity values and should be considered to be only an approximation. [d] Lower concentration of HCl present. [e] Higher concentration of HCl present. Based on downfield shift of Me_2SO resonance.

that the maximum value for the ratio AcOH/CMMS is substantially larger than that obtained in the absence of HCl. This relative acceleration by HCl may be somewhat larger than indicated in the table because HCl reacts with Me_2SO to form CMMS as mentioned above. In fact, if the solution is allowed to stand overnight, the concentration of CMMS continues to grow and exceeds that for AcOH. In addition, the rate of disappearance of Me_2SO and AcCl as well as the rate of growth of AcOH and CMMS are affected by the presence of HCl in a complicated manner. Thus, when present at a lower concentration, HCl accelerates the rate for the reactants and products relative to that in its absence. On the other hand, at a higher concentration of HCl, the rate is retarded somewhat and becomes smaller than that measured at the lower concentration of HCl, as can be seen from the rate constants presented below. The quantitative effect of HCl on the rates cannot be determined from our results because the absolute concentration of HCl was not measured. Instead, the relative concentration of HCl in each solution was determined qualitatively from the extent of the downfield shift of the Me_2SO CH_3-proton resonance.

The time dependence of the various signals has been used to calculate first- and second-order rate constants. For reasons presented in the discussion, we conclude that the rate has mainly a second-order dependence, and values are listed as k_{obsd} in Table III. The values listed for benzene are averages of at least two runs, whereas those given for methylene chloride are calculated from one each.

Discussion

As mentioned above, the data were analyzed in terms of first- and second-order rate expressions, and the results indicate that the reaction is more consistent with second-order kinetics, first order each in Me_2SO and AcCl. This conclusion is based on the fact that the second-order rate constant exhibits no systematic concentration dependence, whereas the first-order rate constant does. For example, when the initial concentration of Me_2SO is held constant at 0.070 M, doubling the AcCl concentration from 0.077 to 0.173 M has only a slight effect on the value for the second-order rate constant (see Table III) whereas the first-order rate constant increases from 4.4×10^{-3} to $12 \times 10^{-3}\ s^{-1}$ when benzene is the solvent. When methylene chloride is the solvent and the initial concentration of AcCl is held constant at 0.128 M, doubling the Me_2SO concentration from 0.146 to 0.297 M has little effect on the second-order rate constant (Table II) but increases the first-order rate constant by a factor of 2.1.

The second-order rate of reaction indicates that the time dependence of the signals assigned to the reactants is, in fact, the dependence for the respective reactants. In other words, the observed CH_3-proton resonances labeled d and a are not due to an intermediate arising from a rapid addition of Me_2SO to AcCl, since the decay of such an intermediate would be expected to exhibit a first-order dependence, which does not appear to be the case. This conclusion is supported by the chemical shifts of the resonances. If an intermediate were formed, the signals labeled d and a should be shifted relative to the Me_2SO and AcCl CH_3 signals. However, as can be seen in Figure 1, no additional signal is observed when Me_2SO is present in excess. Likewise, no additional signal is observed when AcCl is present in excess. As an additional check of this conclusion, the reaction was studied using infrared spectroscopy. One minute after mixing equal volumes of 0.4 M AcCl in benzene with 0.4 M Me_2SO-*d_6* in benzene, the infrared spectrum contained the 950- and 1900-cm^{-1} bands for AcCl and the 1050-cm^{-1} band for Me_2SO-*d_6*. These bands decay with a time dependence that is very close to that observed in the NMR study. To our knowledge, the only reported kinetic study concerning acid halides is one involving the reaction of Me_2SO with 5-dimethylaminonaphthalene-1-sulfonyl chloride in ethyl ether.[5] The ultraviolet spectrum was followed as a function of time for a solution containing a large excess of Me_2SO, and it was concluded that the reaction is bimolecular.

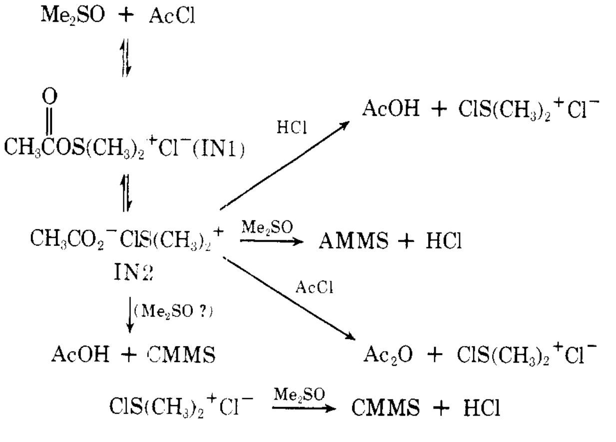
Comparison of the k_{obsd} values for Me_2SO and Me_2SO-*d_6* in Table II indicates the occurrence of a deuterium isotope effect in both solvents. Although the values for k_{obsd} fluctuate to some extent for both types of determinations, the ratio k_H/k_D is at least 4 or greater, indicating a primary deuterium isotope effect for the disappearance of the reactants and the formation of AcOH (and also CMMS). Consequently, the rate-limiting step for the disappearance of reactants and the formation of AcOH involve a transfer of the SCH_3 proton. This information along with the time dependence for the transient relative to that for AcCl indicate that the transient is not an intermediate in the main path of the reaction and is generated by a minor competitive pathway. This conclusion is based on the following argument. If the transient is an intermediate resulting from the reaction of AcCl with Me_2SO, the rate-limiting step in the formation of products must occur after the formation step for this transient; i.e., an intermediate would not be observed if its formation were involved in the rate-limiting step. Consequently, the deuterium isotope effect would be associated with the decomposition of the transient. As a result, to account for the fact that the decay of reactants is subject to this isotope effect, the reactants would have to be in equilibrium with the transient if it were an intermediate. However, the reactants are not in equilibrium with the transient, since a fixed relationship is not maintained between their concentrations during the reaction; i.e., the concentrations do not conform to an equilibrium constant during the period of reaction, as can be seen in Figure 3. Thus, at the lower initial concentration of reactants, the transient has a smaller concentration than AcCl during most of the reaction but can still be detected after AcCl has disappeared completely. This crossover in concentrations would not be expected if the transient were in equilibrium with the reactants. At a higher initial concentration for the reactants, no crossover occurs because the decay of the transient is faster, presumably because it is catalyzed by Me_2SO. For convenience, the structure of this transient will be discussed after the proposed mechanism is presented.

Since this transient is not an intermediate in the main path for product formation, the mechanism given in Scheme I is proposed to account for all of the observations given above. In this scheme, IN1 and IN2 are intermediates that are in equilibrium with the reactants. On the basis of product studies, the possibility that these intermediates could occur in this reaction was suggested previously.[2b] IN1 is suggested to be an ion pair; however, it could have a sulfurane structure similar to that suggested for the analogous *tert*-butoxy compound[6] and no alteration in the mechanism would be required. The ion pair structure indicated for IN2 is suggested because it provides a chemically reasonable route to Ac_2O as discussed below. Neither IN1 nor IN2 are observed, requiring that the equilibrium constant be small. The rate-limiting step in this mechanism, the decomposition of IN2, is consistent with the observations presented above. Thus, the main path is the formation of AcOH plus CMMS according to the left-hand step, which involves the removal of the SCH_3 proton and, therefore, is consistent with the primary deuterium isotope effect observed for the formation of the products. Furthermore, the preequilibrium can explain why this isotope effect is also observed for the decomposition of the reactants.

The reaction steps proceeding to the right can account for the formation of the minor products. Consequently, the observation of these products provides support for the occurrence of an intermediate. The formation of AMMS is accompanied by the formation of HCl, which is probably associated with Me_2SO. That Me_2SO acts as a base in this step is supported by the fact that the concentration ratio, AMMS/AcOH, increases as the concentration of Me_2SO is increased. This result also indicates that a base such as Me_2SO may be less important for proton removal in the main reaction path, i.e., the formation of AcOH plus CMMS. In addition, for the initial concentrations of 0.32 M AcCl and 0.64 M Me_2SO, this concentration ratio is unchanged at 0.19 when Me_2SO is replaced by Me_2SO-d_6, as might be expected for the mechanism in Scheme I since AMMS and AcOH are each formed via rate-limiting steps that involve removal of the SCH_3 proton. The fact that AMMS is not observed in the presence of added HCl provides additional support for an intermediate. Thus, the intermediate is trapped by HCl faster than it can react to form AMMS.

According to Scheme I, Ac_2O is formed by trapping IN2 with AcCl. This path is consistent with the fact that the concentration ratio Ac_2O/AcOH increases as the concentration of AcCl is increased. Furthermore, this path can account for the substantial increase in Ac_2O concentration when Me_2SO is deuterated. Thus, since the reaction of AcCl with IN2 does not involve proton removal, the rate of this reaction should be unaffected when Me_2SO is deuterated, whereas the rates for the formation of AcOH + CMMS and AMMS + HCl are retarded. Consequently, deuteration of Me_2SO makes the trapping of IN_2 by AcCl more competitive with the main path for the decomposition of IN2. Furthermore, at a fixed initial concentration of reactants, the fraction of Ac_2O in the products increases approximately by a factor of the deuterium isotope effect when Me_2SO is deuterated, as would be expected since the Ac_2O path makes a very small contribution in the nondeuterated case; i.e., the rate constant for this path is substantially smaller than those for the other paths in the nondeuterated case. The Ac_2O results are also the reason for the suggested structure for IN2. Thus, since these results indicate that AcCl traps an intermediate to generate Ac_2O, trapping IN2 seems more reasonable than trapping IN1 (or the chlorosulfurane) for which larger steric interactions are expected; i.e., AcO^- is expected to be better than IN1 as a nucleophile for AcCl.

Scheme I



The possibility that Ac_2O is formed via reaction between AcOH and AcCl must also be considered. As indicated above, this reaction proceeds to equilibrium, and it is possible to estimate an upper limit to the concentration ratio Ac_2O/AcOH.[7] For a solution containing 0.64 M Me_2SO and 0.32 M AcCl initially, this upper limit (0.022) is comparable to the observed value (0.017). Although the calculated and experimental results appear to agree in this case, the agreement is very poor when Me_2SO is replaced by Me_2SO-d_6 for which the observed ratio is 0.08, a factor of 3.6 larger than the calculated value. Furthermore, the disparity is larger if this analysis is made using data obtained earlier in the Me_2SO-d_6 reaction. Thus, after about 100 s of reaction, the calculated Ac_2O concentration is a factor of 4.6 smaller than the observed value, i.e., 0.0038 vs. 0.0173 M, indicating that the Ac_2O is formed somewhat more rapidly at the beginning of the reaction when AcCl is present in higher concentration, a result expected for a trapping reaction. Consequently, a reaction path involving AcCl and AcOH can, at best, account for only a small part of the Ac_2O formed when Me_2SO-d_6 is a reactant. Its contribution in the Me_2SO case may be smaller than indicated above, since the Me_2SO–AcCl reaction is almost complete in 3 min, a time shorter than the 5-min time period observed for the AcCl–AcOH–Ac_2O equilibration at comparable concentration, namely, 0.13 M AcOH and 0.16 M AcCl.

As indicated in Scheme I, chlorodimethylsulfonium chloride is generated in the same step as Ac_2O is generated. We suggest that the transient signal is due to the methyl protons of this sulfonium salt and will discuss the reasons for this conclusion below. This salt may also be generated along with AcOH via reaction of HCl with IN2 as indicated in Scheme I. This path is proposed to account for the observations that AcOH is generated slightly more rapidly than CMMS and that the presence of added HCl enhances this difference in rate (Table III). As indicated, the overall scheme is self-consistent, since HCl is generated in another step.[8] Furthermore, the bottom step in this scheme can account for the fact that CMMS eventually attains the same concentration as AcOH. Thus, the chloromethylsulfonium salt reacts more slowly than IN2 to form CMMS. Me_2SO is indicated as a base in this step, since the transient signal seems to disappear more rapidly at higher concentrations of Me_2SO (Figure 3). The effect of HCl on the overall rate of disappearance of reactants will be discussed below.

The assignment of the CH_3-protons of the chloromethylsulfonium salt to the transient signal is based mainly on the fact that only one transient signal is observed with a chemical shift comparable to those for oxysulfonium salts. Thus, relative to tetramethylsilane, the transient chemical shift is 3.75 ppm in methylene chloride, and for the methyls of dimethyl-*tert*-butoxysulfonium salts they range from 3.43 to 3.78 ppm.[6] Although the SCH_3 proton resonance of IN1 is expected to lie in the same region, this structure is precluded because the corresponding acyl-CH_3 resonance expected for this structure is not observed. Furthermore, assignment of this structure to the transient is not consistent with the kinetic results discussed above, e.g., isotope effect and concentration dependence of some of the minor products. In addition, it is unlikely that the resonance assigned to Ac_2O could, in fact, be due to the acyl CH_3 of IN1. First, the ratio of intensities is not 2 to 1. Second, the Ac_2O signal remains long after the transient has disappeared. Third, the time period for this disappearance is similar to that observed when Ac_2O is mixed with Me_2SO. Thus, the chlorosulfonium salt seems more consistent with the experimental results than IN1 does. Furthermore, this type of salt has been suggested to be the intermediate isolated when sulfuryl chloride is allowed to react with an aryl methyl sulfide below 0 °C.[2b]

As mentioned above, the line width of the transient signal depends on the experimental conditions. Thus, it increases as the initial concentration of reactants is increased. The fact that the line width for each of the other signals remains unaffected by concentration changes indicates that the protons in the transient signal are undergoing an exchange process. The nature of this exchange process cannot be expressed conclusively. However, since the line width of the transient also increases as the concentration of HCl is increased, one possible explanation is that the methyl protons of the chlorosulfonium salt are exchanging with those of $(CH_3)_2S(OH)^+ Cl^-$ via a mechanism in which the OH group is replaced by Cl. The details of this mechanism must await the results of further investigation.

Since the presence of HCl alters the overall rate of reaction, it probably alters the mechanism in Scheme I to some extent. Thus, the initial increase in rate observed in the presence of small amounts of HCl could result from protonation of IN1 as well as trapping IN2. The retardation at higher concentrations of HCl may be due to a substantial reduction in the amount of unprotonated Me_2SO and, therefore, a reduction in the amount of IN1 since it is in equilibrium with the reactants.

Because of the low polarity of the solvents (as indicated by their dielectric constants), salts are expected to exist in the form of ion pairs or larger ion aggregates. For this reason, the sulfonium salts are indicated to be ion pairs in Scheme I. The polarity of the solvent also appears to affect the rate of reaction. Thus, methylene chloride, which has a larger dielectric constant than benzene (9.08 vs. 2.26) has a rate constant that is smaller by about a factor of 2 than the one for benzene. The proposed mechanism is consistent with this result, since the charge is destroyed when AcOH and CMMS are formed. However, a more extensive solvent study is needed to test this proposal. In addition, on the basis of the above discussion, it is clear that the reaction is not cleanly second order except at low concentration for which the minor products cannot be observed. However, even at the higher concentrations, the contribution made by the minor reaction paths is sufficently small to make a second-order fit possible. Finally, as also noted by other workers,[9] CMMS reacts with Me_2SO. Since this reaction is slower than the one involving Me_2SO and AcCl, it, therefore, was not studied.

Finally, because of the relatively low concentrations employed, no precautions were necessary. However, concentrated solutions of Me_2SO plus AcCl have been known to explode.[1a]

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Registry No.—Me_2SO, 67-68-5; AcCl, 75-36-5; AcOH, 64-19-7; CMMS, 23372-58-9; AMMS, 16437-69-7; Ac_2O, 108-24-7.

References and Notes

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(4) Me_2SO-d_6 was used instead of Me_2SO to avoid overlap of the AcOH signal with those of Me_2SO and CMMS.

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(7) This ratio is calculated at a time in the reaction when AcCl and AcOH have equal concentrations using the equilibrium constant ($K = 2.2 \times 10^{-3}$) and assuming the approach to equilibrium is instantaneous, which is not the case. Equilibration takes approximately 5 min with comparable concentrations of AcCl and AcOH whereas the reaction between Me_2SO and AcCl is essentially over in about 3 min at these concentrations. In addition, this ratio is probably slightly overestimated, since HCl is also generated in the step that produces AMMS.

(8) The downfield shift of the Me_2SO signal during the reaction is consistent with the formation of HCl, since addition of HCl causes a downfield shift.

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