The broadening of the δ 63.13 signal (ca. 10 Hz) is the result of three-bond coupling to the fluorine atoms.

Preparation of 2,2-Bis[(trifluoromethyl)thio]acetic Acid (7b). To a mixture of 48% hydrobromic acid (90 mL) and acetic acid (10 mL) was added 1,1,1-triethoxy-2,2-bis[(trifluoromethyl)thio]ethane (**6**, 14.5 g, 0.04 mol) along with sodium iodide (0.5 g, 0.003 mol). The dark solution was refluxed for 20 h. The reaction solution, after cooling to room temperature, was saturated with sodium chloride and extracted with dichloromethane (3 × 75 mL). The combined organic extracts were dried over magnesium sulfate and concentrated under reduced pressure at 30 °C. The residual oil was purified by distillation yielding 5.36 g (51%) of **7b**: bp 101 °C (33 mmHg); IR (neat) 3000, 1725, 1400, 1260, 1125, 815, 760 (CF_3S) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.13 (s, CH); ^{13}C NMR ($CDCl_3$) δ 46.86, 129.78 (q, $J_{^{13}C-^{19}F}$ = 309 Hz), 173.34; ^{19}F NMR ($CDCl_3$) δ 43.4. Anal. Calcd for $C_4H_2F_6O_2S_2$: C, 18.46; H, 0.77; F, 43.81; S, 24.65. Found: C, 18.49; H, 0.89; F, 43.98; S, 24.78.

Preparation of Ethyl [(Trichloromethyl)thio]acetate (11b). To a solution of triethyl orthoacetate (36.6 g, 0.226 mol) in carbon tetrachloride (100 mL) was added portionwise trichloromethanesulfenyl chloride (21.3 g, 0.115 mol), and the reaction was warmed to 80 °C. While the mixture refluxed for over 4 h, 2,2′-azobis(2-methylpropionitrile) (0.4 g, 0.003 mol) was added portionwise. Volatiles formed during the course of the reaction were removed through a short-path distillation apparatus. After the mixture cooled to 60 °C, methanesulfonic acid (2–3 mL) was added and the stirring continued at 60 °C for 30 min. The reaction was cooled and then quenched in ice water (200 mL). The resultant two-phase mixture was extracted with chloroform (3 × 100 mL). The combined chloroform extracts were washed with water (until the water washings were pH 5–6) followed by saturated sodium chloride. The chloroform solution was dried over magnesium sulfate and concentrated, yielding a crude liquid which weighed 26.1 g (stench). Short-path distillation yielded 16.0 g (59%) of **11b**: bp 105 °C (0.2 mmHg); η^{25}_D 1.4992; IR (neat) 3000, 1740, 1300, 1270, 1180, 1140, 1020, 805, 765 (C–S), 715 (CCl_3) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (3 H, t, CH_3), 3.93 (2 H, s, CH_2), 4.21 (2 H, q, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 14.04, 39.00, 62.14, 97.06, 167.16; mass spectrum, *m/e* (relative intensity) 236 (M^+, 2), 201 (M^+ – Cl, 15), 163 (M^+ – $COOC_2H_5$, 10), 137 (25), 109 (15), 79 (33), 29 (100). Anal. Calcd for $C_5H_7Cl_3O_2S$: C, 25.28; H, 2.97; Cl, 44.78; S, 13.50. Found: C, 25.50; H, 3.08; Cl, 44.76; S, 13.77.

The initially formed [(trichloromethyl)thio]orthoacetate **10b** could not be obtained in pure form. As indicated, it was converted directly to the ester **11b** by heating with methanesulfonic acid or hydrogen chloride.

Preparation of 1,1,1-Trimethoxy-2-[(trichloromethyl)thio]ethane (10a). Compound **10a** was prepared by reacting trimethyl orthoacetate with trichloromethanesulfenyl chloride in carbon tetrachloride in the presence of 2,2′-azobis(2-methylpropionitrile). The reaction conditions were the same as those for preparing **11b**. However, in this case, the resulting ortho ester was isolated by quenching in ice water instead of hydrolyzing the product with methanesulfonic acid. The product was extracted into dichloromethane. The organic layer was dried (sodium sulfate) and the solvent removed to afford an oil (**10a**): IR (neat) 3000, 1450, 1260, 1210, 1150, 1075, 1050, 1010, 990, 810, 785, 710 (CCl_3) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.40 (9 H, s, CH_3), 3.65 (2 H, s, CH_2).

Attempted purification of **10a** by vacuum distillation resulted in extensive decomposition.

Preparation of Methyl [(Trichloromethyl)thio]acetate (11a). Compound **11a** was prepared from trimethyl orthoacetate in the same manner as for the preparation of the ethyl ester **11b**. Distillation of the crude product gave a 55% yield of **11a**: bp 95 °C (0.2 mmHg); η^{25}_D 1.5136; IR (neat) 3000 (v w), 1750, 1425, 1300, 1260, 1160, 1140, 1010, 810, 770 (C–S), 720 (CCl_3) cm^{-1}; ^1H NMR δ 3.84 (2 H, s, CH_2), 4.00 (3 H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ 38.69, 52.90, 97.02, 167.59; mass spectrum, *m/e* (relative intensity) 187 (M^+ – Cl, 100), 133 (74), 113 (82), 105 (M^+ – CCl_3,48), 79 (54). Anal. Calcd for $C_4H_5Cl_3O_2S$: C, 21.50; H, 2.25; Cl, 47.59; S, 14.35. Found: C, 21.70; H, 2.26; Cl, 46.16; S, 14.39.

Acknowledgment. We are grateful to J. Fitzpatrick, D. Lane, E. Reich, D. Staiger, and G. Zuber for spectral interpretation and microanalyses. Continued support for this project by Dr. Dale Blackburn and Dr. Charles Berkoff is deeply appreciated.

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Equilibria and Reactions in the Systems Aluminum Chloride–Acetyl Chloride–Aromatic Hydrocarbon in Sulfur Dioxide as Solvent

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Equilibrium constants are obtained for 1:1:1 complexes of $AlCl_3$–acetyl chloride–aromatic hydrocarbon with benzene, *p*-xylene, and mesitylene. The magnetic resonance spectra suggest that these are σ complexes. The rates of Friedel–Crafts acetylation are proportional to the concentration of the σ complex.

There have been many investigations of the mechanism for the Friedel–Crafts acetylation reaction. The rate study of Brown et al. on the acetylation of benzene and toluene with $AlCl_3$ in ethylene dichloride as solvent at 0 and 25 °C showed that the rate was dependent upon the concentrations of the aromatic hydrocarbons and the 1:1 $AlCl_3$–acetyl chloride complex.[2] Complicated kinetic results on the same system at 30 °C were accounted for by the intervention of three acylating species: a 1:1 complex, a complex with two $AlCl_3$'s for each acetyl chloride, and an acetylium ion.[3]

A generalized mechanism for the Friedel–Crafts reaction proposed by Brown and Stock considers the rate-determining step to be the formation of a σ complex by the attacking reagent and the aromatic hydrocarbon.[4] Olah

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et al. suggest that the transition state of highest energy may vary from one late in the reaction coordinate, resembling a σ complex, to an early one, resembling a π complex, depending upon the particular system considered.[5] However, the controversy continues with recent data being cited to claim that the σ complex alone is the reaction intermediate.[6,7]

Until now there has been no direct experimental evidence for the existence or structure of stable intermediate complexes in the Friedel–Crafts acetylation reaction. σ complexes have been identified with hydrogen halide, Lewis acid, and aromatic hydrocarbon.[8,9] It has been possible by ^1H and ^{13}C magnetic resonance studies to identify and obtain equilibrium constants for the formation of 1:1 and 2:1 complexes of $AlCl_3$ and acetyl chloride.[10] Complex formation between acetophenone, the product of the acetylation reaction with benzene and $AlCl_3$, has also been investigated.[11] It therefore seemed possible to study, via magnetic resonance, the formation of the hypothetical σ complex and to follow with time the concentrations of all reactants and products in the acetylation of some simple aromatic hydrocarbons.

Experimental Section

Chemicals. Aluminum chloride was purified by repeated vacuum sublimation, sealed in glass under vacuum, and used shortly thereafter. Acetyl chloride, benzene, toluene, and mesitylene were dried over 4A molecular sieves and then fractionally distilled at atmospheric pressure. *p*-Xylene was recrystallized from methanol at 5 °C, dried with Drierite, and twice fractionally distilled. All these liquids were again dried (acetyl chloride and mesitylene with 4A molecular sieves and benzene, toluene, and *p*-xylene with $LiAlH_4$) and transferred under vacuum to storage vessels closed by Teflon or stainless steel high-vacuum stopcocks. Sulfur dioxide was dried with phosphorus pentoxide and stored over mercury. Neopentane was transferred directly from the suppliers cylinder to a storage container on the vacuum line.

Sample Preparation. Some $AlCl_3$ was transferred, in a drybox, into an NMR tube closed with a Teflon high-vacuum stopcock. After the $AlCl_3$ was weighed, the appropriate quantities of sulfur dioxide, neopentane, and acetyl chloride, all measured as vapors, were condensed into the NMR tube. The contents were thawed and mixed, and the walls of the tubes were washed by distillation of solvent from the solution in the lower part. Finally a known quantity of aromatic hydrocarbon, also measured as vapor, was condensed into the sample tube which was then sealed under vacuum. The tube was quickly thawed, mixed, and stored at −80 °C. The vapor pressure of mesitylene was not high enough for accurate measurements. Therefore it was added to a side arm separated from the NMR tube by a second Teflon high-vacuum stopcock and weighed. The sample preparation then continued as with the more volatile hydrocarbons.

Equilibrium Measurements. Proton and ^{13}C resonance spectra were obtained in the Fourier transform mode on a Varian Associates XL100 spectrometer equipped with a Nicolet 1180 computer and associated pulsing and power amplifier components. The variable temperature controller was calibrated with a methanol sample. Neopentane, inert under the experimental conditions, was used as an internal reference, and chemical shifts were converted to tetramethylsilane as zero in the manner previously reported.[11] All concentrations are reported as mole fractions and all calculations are in this unit. The sample was equilibrated for 15 min at −64 °C in the NMR probe before the spectrum was obtained. Chilling and storing the sample and then rerunning it by using the same procedure gave reproducible results.

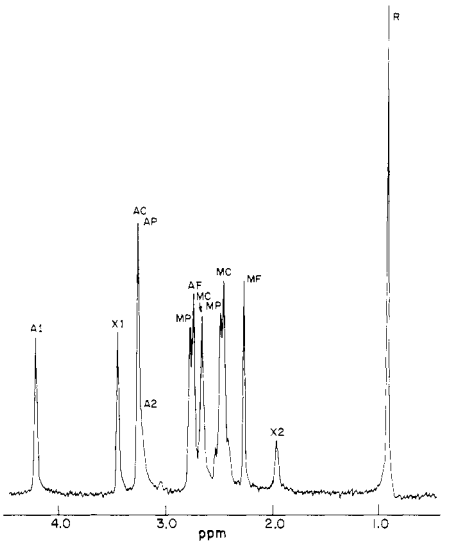

Figure 1. Proton resonance spectrum at −64 °C of a sulfur dioxide solution of $AlCl_3$, acetyl chloride, and *p*-xylene.

Kinetic Measurements. Samples were equilibrated in a bath at −30 ± 1 °C for each reaction period, and then the spectra were taken at −64 °C as described for the equilibrium measurements. This procedure provided sharp lines, without exchange broadening among the various species, and ensured negligible reaction during spectral acquisition. The concentrations of the various species were calculated directly from the integrals of their resonance signals by using the signal from neopentane as an intensity standard in each case.

Results and Discussion

In the first part of this section we will present the spectral evidence for the existence and structure of the 1:1:1 $AlCl_3$–acetyl chloride–hydrocarbon complexes. From the relative intensities of the appropriate lines, equilibrium constants for their formation will be calculated. In the second part the kinetics and mechanism of the reaction will be analyzed from the time dependance of the concentration of the various species in these systems.

The equilibria involving the various complex species may be represented by eq 1–3, with equilibrium constants given

$$AlCl_3 + CH_3COCl \rightleftharpoons AlCl_3{\cdot}CH_3COCl \quad (1)$$

$$AlCl_3 + AlCl_3{\cdot}CH_3COCl \rightleftharpoons (AlCl_3)_2{\cdot}CH_3COCl \quad (2)$$

$$AlCl_3{\cdot}CH_3COCl + ArH \rightleftharpoons AlCl_3{\cdot}CH_3COCl{\cdot}ArH \quad (3)$$

by the concentration of product divided by those of reactants. Table I lists the concentrations and equilibrium constants for several samples.

The proton resonance spectra of benzene-containing solutions do not have any lines directly attributable to the 1:1:1 complex. A weak line at δ 162.4 in the ^{13}C spectrum is assigned as the exchange-averaged signal of the aromatic carbons in the complex. Because of the slight extent of complex formation only an approximate K_3 of 0.5 ± 0.2 at −64 °C can be obtained. Toluene reacts readily to give ketonic products under these conditions, and the problems of signal overlap and exchange preclude positive identification of the intermediate complex.

The high-field region of the proton resonance spectrum of a 1:1:1 ratio of $AlCl_3$–acetyl chloride–*p*-xylene solution in SO_2 at −64 °C is shown in Figure 1. This solution has

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Table I. Concentrations and Equilibrium Constants for Complex Species in Friedel-Crafts Acetylation

reagents added, mmol			species concn, mole fraction			
$AlCl_3$	CH_3COCl	C_6H_6	$AlCl_3 \cdot CH_3COCl$	C_6H_6	$AlCl_3 \cdot CH_3COCl \cdot C_6H_6$	K_3
2.502	2.556	1.250	0.0298	0.0410	0.001 06	0.87
2.512	2.513	2.512	0.0242	0.0641	0.000 64	0.41
0.557	2.572	3.832	0.0267	0.119	0.001 97	0.62
4.799	7.194	7.205	0.0204	0.0741	0.000 29	0.19
2.680	7.580	5.460	0.05	0.102	0.002 68	0.53

reagents added, mmol			species concn, mole fraction					
$AlCl_3$	CH_3COCl	*p*-xylene	$AlCl_3 \cdot CH_3COCl$	*p*-xylene	$AlCl_3 \cdot CH_3COCl$-*p*-xylene	$(AlCl_3)_2 \cdot CH_3COCl$	K_3	K_2/K_1
0.257	0.260	0.118	0.004 20	0.006 24	0.001 78	0.006 07	68	1.8
0.295	0.316	0.118	0.004 57	0.006 36	0.001 78	0.007 16	61	2.6
0.247	0.250	0.236	0.004 42	0.008 38	0.002 24	0.003 63	61	0.63
0.222	0.220	0.236	0.003 41	0.013 9	0.002 10	0.003 22	44	1.1
0.325	0.454	0.354	0.004 80	0.018 4	0.005 06	0.011 8	57	5.6
0.262	0.395	0.236	0.005 72	0.008 05	0.002 99	0.002 11	65	0.76
0.253	0.382	0.236	0.007 43	0.005 65	0.003 55	0.001 85	85	0.56
0.274	0.546	0.118	0.006 03	0.005 76	0.002 19	0.004 71	63	3.1
0.246	0.253	0.354	0.003 60	0.014 9	0.002 54	0.002 70	48	1.0
0.222	0.230	0.472	0.003 80	0.026 7	0.004 80	0.001 39	47	0.5
0.253	0.260	0.708	0.002 68	0.029 8	0.005 15	0.001 47	65	0.56
0.289	0.237	0.236	0.003 30	0.013 7	0.002 44	0.004 56	54	2.2

reagents added, mmol			species concn, mole fraction			
$AlCl_3$	CH_3COCl	mesitylene	$AlCl_3 \cdot CH_3COCl$	mesitylene	$AlCl_3 \cdot CH_3COCl$-mesitylene	K_3
0.325	0.328	0.338	0.0007	0.000 21	0.0146	99 000

Table II. Chemical Shifts of Species Present in the Systems $AlCl_3$-Acetyl Chloride-ArH

	^1H NMR, δ		^{13}C NMR, δ		
species	acetyl	methyl	acetyl	aromatic	methyl
CH_3COCl	2.73		33.7		
$AlCl_3 \cdot CH_3COCl$	4.25		48.2		
$(AlCl_3)_2 \cdot CH_3COCl$	3.25		28.6		
C_6H_6				121.6	
$AlCl_3 \cdot CH_3COCl \cdot C_6H_6$				162.4	
$C_6H_4(CH_3)_2$		2.28		128.1 (C_1) 125.4 (C_2)	21.3
$AlCl_3 \cdot CH_3COCl \cdot C_6H_4(CH_3)_2$	3.25	2.48 2.69	27.8	130.7 138.9 ($C_{1,4}$) 126.4, 126.6, 131.8, 137.1 ($C_{2,3,5,6}$)	20.8 25.2
$C_6H_3(CH_3)_2COCH_3$ $AlCl_3$	3.28	2.50 2.78	29.3	120.3 130.7, 135.3 ($C_{1,3,4}$) 126.6, 131.8, 137.1 ($C_{2,5,6}$)	24.7 25.2
$C_6H_3(CH_3)_3$		2.23		131.2 (C_1) 120.8 (C_2)	21.3
$AlCl_3 \cdot CH_3COCl \cdot C_6H_3(CH_3)_3$	3.38	2.47 (H_7) 2.72 (H_8)	32.2	146.2 (C_1) 140.5 (C_3) 125.5 (C_2) 124.5 (C_4)	23.4 (C_7) 25.2 (C_8)
$C_6H_2(CH_3)_3COCH_3 \cdot AlCl_3$	3.21	2.39 (H_7) 2.56 (H_8)	34.0	140.6 (C_1) 121.4 (C_4) 135.1 (C_3) 124.5 (C_2)	22.4 (C_7) 22.6 (C_8)

reacted to some extent, and the assignments of the lines to reactants and products are listed in Table II along with those for the other hydrocarbons. Signal R is from the neopentane reference, MF is from the methyl groups of free (uncomplexed) *p*-xylene, AF is from free acetyl chloride, A1 and A2 are from the 1:1 and 2:1 complexes of $AlCl_3$ with acetyl chloride, AC and AP are from the acetyl methyl signals of the 1:1:1 complex and of the product complexed with $AlCl_3$, and MC and MP are from the aryl methyl groups of the 1:1:1 complex and product. X1 and X2 are unidentified products in the reaction. The signal labeled X1 does not come from a 1:1:1 complex of acetyl chloride, product ketone, and $AlCl_3$. The product ketones are found to be stronger Lewis bases than acetyl chloride in competition experiments. The growth of X1 with reaction time parallels that of product ketone. Signal X2 is also observed in the absence of aromatic hydrocarbons and is attributed to the reaction product of an impurity in the $AlCl_3$ with acetyl chloride.

Carbon-13 resonance spectra are in agreement with the assignments of the proton resonance spectra, and peak assignments are also listed in Table II. Assignments were aided by the simple determination of the number of hydrogens directly attached to each carbon.[12] These assignments are listed in Table II.

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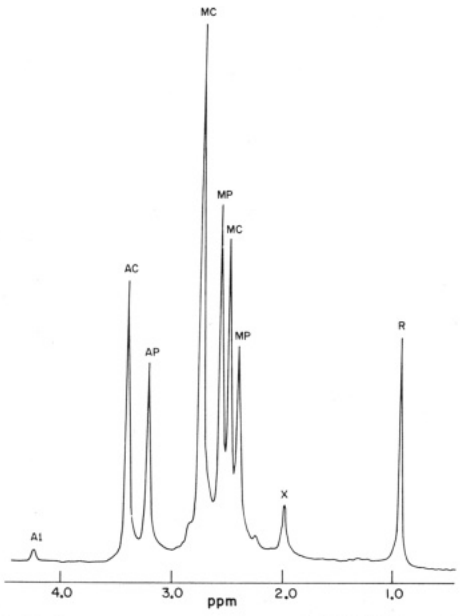

Figure 2. Proton resonance spectrum at −64 °C of a sulfur dioxide solution of $AlCl_3$, acetyl chloride, and mesitylene.

From the relative areas of the peaks from the various species were obtained the concentrations of these species and the values for the equilibrium constant of the 1:1:1 complex, and these values are listed in Table I. The relatively constant value (60 ± 11) calculated for the equilibrium constant in solutions with significantly different concentrations confirms the assignment of proton resonance signals to the particular species. The behavior expressed by eq 1 and 2 should be independent of the presence of other species in the solution. The concentration and equilibrium constants (K_2/K_1) for these reactions are also listed in Table I. The average values from the present runs (1.7 ± 1.5) are in the same range as that previously reported (0.8 ± 0.2) in the absence of *p*-xylene.[10]

Although a 1:1:1 intermediate complex has long been postulated to explain the mechanism of the Friedel–Crafts reaction, this is the first quantitative measurement of such a complex under actual reaction conditions. The ^{13}C resonance spectrum of this complex has six separate aromatic carbon signals, four of which are directly bonded to a single hydrogen and two of which are quaternary. It follows that the $AlCl_3$–acetyl chloride moiety is associated with a particular hydrogen-bearing aromatic carbon. This strongly implies that in the present system the intermediate complex has σ and not π bonding.

With mesitylene as the aromatic hydrocarbon there are only weak signals from unreacted hydrocarbon in both the proton and ^{13}C resonance spectra. Signals in these spectra may be assigned to the 1:1:1 complex and to the product from their changes in intensity with time. These assignments are listed in Table II and indicated in the spectra of Figures 2 and 3 by using the same notation as described for Figure 1. Observation of two and one different methyl groups and of two and one aromatic carbons in both proton and carbon resonance spectra, respectively, for the intermediate complex strongly suggests that in this instance also it is a σ complex.

From the very weak signals of free mesitylene and the 1:1 $AlCl_3$–acetyl chloride complex an approximate K_3 of 10^5 may be calculated. The order of magnitude for the K_3 values for benzene, *p*-xylene, and mesitylene parallels their basicity as determined by the solubility of HBr[13] and extraction with HF and BF_3.[14] Assuming a linear relationship between K_3 and the basicity of the methylbenzenes gives a calculated K_3 of 8.4×10^4 for mesitylene, in excellent agreement with that observed in the present study.

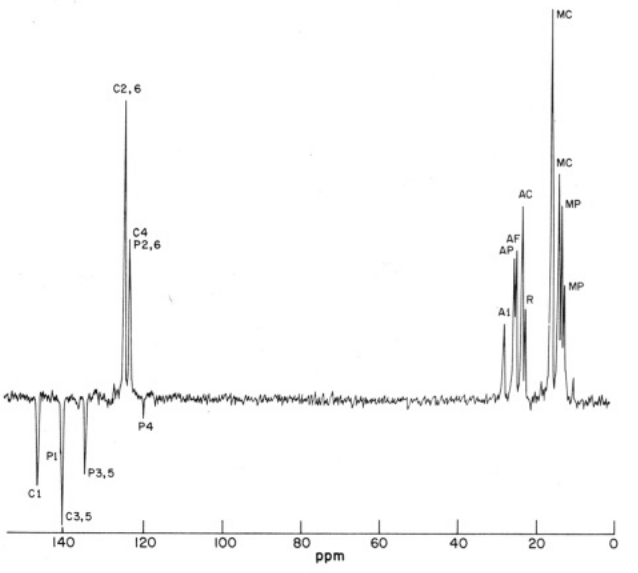

Figure 3. Carbon resonance spectrum at −64 °C of a sulfur dioxide solution of $AlCl_3$, acetyl chloride, and mesitylene.

Table III. Early Rate Data for the System $AlCl_3$–Acetyl Chloride–*p*-Xylene in SO_2 at −30 °C

initial composition, mmol			$10^4 \times$ d[product]/	rate
$AlCl_3$	CH_3COCl	*p*-xylene	d*t*	constant
0.247	0.250	0.236	3.15	63.4
0.246	0.253	0.354	3.20	45.5
0.253	0.260	0.708	6.58	49.5
0.262	0.395	0.236	2.63	33.9
0.253	0.382	0.236	5.53	58.1
0.237	0.724	0.236	6.05	52.0
0.112	0.230	0.118	0.57	58.3
0.157	0.158	0.236	1.13	58.6

We will now present and discuss the kinetic results. Their measurement is made more difficult since the initial product is a 1:2 complex of $AlCl_3$ and ketone. Therefore it is only meaningful to measure the rate early in the course of the reaction while there is still sufficient $AlCl_3$ to complex all the ketonic species and little $AlCl_4^-$ has been produced. Integrated rates after 4 min of reaction at −30 °C for a series of concentrations with *p*-xylene as the hydrocarbon are listed in Table III. The samples are described by the quantities of reagents used in their preparation. The rate constant is determined from eq 4. By

$$d[\text{product}]/dt = k[AlCl_3][CH_3COCl][ArH] \quad (4)$$

combining eq 1, 3, and 4 we get an equivalent equation (eq 5).

$$\frac{d[\text{product}]}{dt} = \frac{k[AlCl_3 \cdot CH_3COCl \cdot ArH]}{K_1 K_3} \quad (5)$$

It is shown in Table III that the rate constant calculated according to eq 4 is in fact constant. Therefore eq 5 also describes the rate results. This is strong evidence, although not absolute proof, that the rate of product formation is directly proportional to the concentration of 1:1:1 complex. It is therefore quite likely that the σ complex observed in

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Table IV. Early Rate Data for Equivalent Systems with some Aromatic Hydrocarbons

ArH	initial composition, mmol			$10^4 \times$ d[product]/dt
	$AlCl_3$	ArH	CH_3COCl	
benzene	0.243	0.245	0.243	very slow
p-xylene	0.247	0.236	0.250	3.15
toluene	0.240	0.250	0.243	14.4
mesitylene	0.232	0.246	0.243	20.2

this study is the intermediate normally postulated in Friedel–Crafts acetylation.

There is always concern that conclusion from studies under a particular set of conditions may not be transferable to studies made under other conditions. To establish the generality of the preceding results, we also made comparitive rate studies with benzene, toluene, and mesitylene. The data are listed in Table IV. The differences in reactivity of toluene, *p*-xylene, and mesitylene are only slightly smaller than those listed for other aromatic substitutions.[15] The greater reactivity of toluene compared to *p*-xylene is unique, but a displacement of the position of mesitylene has been observed previously.[16] It thus appears that the present studies are within the range of values reported previously for other systems. The increase in rate constant from *p*-xylene to mesitylene is much less than the increase in equilibrium constant K_3. This implies that the more stable intermediate complex with mesitylene breaks down more slowly to give products than that of *p*-xylene. Therefore, the much larger range of values for the stability of σ complexes than for relative rates of reactions does not necessarily preclude σ complexes as intermediates in these reactions.[15]

Registry No. CH_3COCl, 75-36-5; $AlCl_3$, 7446-70-0; benzene, 71-43-2; *p*-xylene, 106-42-3; toluene, 108-88-3; mesitylene, 108-67-8.

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Phosphorus Hybridization in the Equatorial and Apical Directions of Trigonal Bipyramids. An Electron Spin Resonance Study

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The stereoisomers **1a** and **1b** open the possibility to determine the contribution of the 3s and 3p character of phosphorus in a trigonal-bipyramidal (TBP) configuration. The ESR experiments clearly show that there is a small excess of 3s spin density in the equatorial ligand in comparison with the apical one. Although this result does not conflict with the physical and chemical properties of phosphorus in a TBP, it refines the established idea that the sp^3d hybridization of phosphorus can be constructed from three equatorial sp^2 ligands and two apical pd ligands. This study was carried out by starting from the precursor **2**, present as a single crystal. By means of UV and X-ray irradiation the different stereoisomers could be obtained. The single-crystal experiments allowed us to obtain the directional information, i.e., location of the odd electron in the equatorial and apical location.

An important aspect of phosphorus five-coordination,[1] in contrast to four-coordination, is that the distribution of the ligands about the central atom cannot be spherically symmetrical; i.e., the ligands are not equivalent.[2,3] Two possible structural models are favored, as shown by X-ray analyses:[3-5] the trigonal bipyramid (TBP) and the tetragonal pyramid (TP). Usually, the TBP is encountered, although the energy difference between the TBP and TP is often very small.[2] In the TBP configuration, the apical bonds are longer and usually weaker than the equatorial bonds.[2,3,6,7] In addition, apical sites are preferred by electron-withdrawing ligands, whereas electron-donating ligands tend to occupy equatorial positions.[6-8] This polarity rule has been derived from many experimental data[9,10] and is supported by semiempirical calculations.[3-5,11-15] Furthermore, it has been found that small rings are easily accommodated in the TBP configuration if they span an apical and an equatorial position. This strain rule[16] is a result of the 90° angle between apical and equatorial bonds in the TBP. In fact, since the TBP is

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