

Second-Order Base-Catalyzed Elimination Reactions. A solution, 0.05 *M* in *p*-toluenesulfonate and approximately 0.1 *M* in base, was prepared in the following manner. The desired compound (0.0025 mole) was weighed accurately into a 50-ml. volumetric flask. After equilibration at the reaction temperature, it was diluted to the calibration mark of the volumetric flask with 0.1 *M* base also equilibrated at the same temperature. The flask was shaken until homogeneity was obtained. Kinetic runs were made at 30, 50, and 70°, and all solutions were equilibrated and pipetted at those temperatures.

The kinetics were measured by quenching a 5-ml. aliquot in 50 ml. of distilled water and titrating the excess base with standard hydrochloric acid. Infinity points were taken experimentally and checked well with calculated values. The base was standardized by this procedure at each reaction temperature.

All rates were second order and the integrated form of the second-order rate equation was applied to the data. Rates were calculated from each experimental point.

Pseudo-First-Order Base-Catalyzed Elimination Reactions. A solution, 0.005 *M* in desired compound and 0.1 or 0.3 *M* in base, was prepared in the following

manner. The proper *p*-toluenesulfonate (0.00025 mole) was weighed accurately into a 50-ml. volumetric flask and placed in the constant temperature bath. After equilibration of base at the reaction temperature, the volumetric flask was filled to the calibration mark and shaken until homogeneity was observed. The kinetics were followed by quenching a 5-ml. aliquot in 40 ml. of 95% ethanol in a 50-ml. volumetric flask. After diluting to the calibration mark and shaking, the solution was diluted 1:10 with 95% ethanol in a 50-ml. volumetric flask. The olefin concentration of this dilution was measured.

The pseudo-first-order rate constants were obtained from the measured absorbances by use of the following equation

$$k = \frac{2.303}{t} \log \frac{A_{\infty} - A_0}{A_{\infty} - A_t}$$

wherein A_{∞} is the measured infinity absorption after 10 or more half-lives, A_0 is the absorbance at $t = 0$, and A_t is the absorbance at time t . In each kinetic run at least eight points were determined and the rate constant is the numerical average of six or more points. In almost all cases, the runs were duplicated and errors listed are the standard deviation between runs.

Extraordinary Dipositive Carbonium Ions. A Re-examination of the Evidence for Their Formation in Sulfuric Acid¹

R. J. Gillespie² and E. A. Robinson

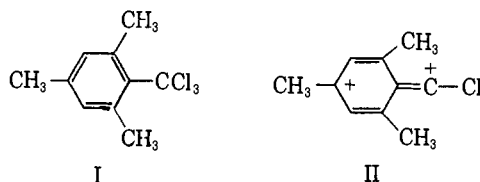
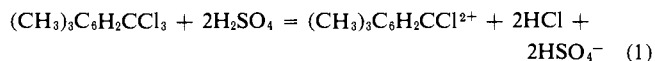
Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, and the Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada. Received January 29, 1965

Cryoscopic and conductometric studies of solutions of trichloromethylmesitylene and mesitoyl chloride in sulfuric acid show that in each case reaction occurs to give five particles in solution ($\nu = 5$), two of which are hydrogen sulfate ions ($\gamma = 2$). Conductometric titrations with dilute oleum and proton n.m.r. measurements have also been carried out for solutions of both solutes. The n.m.r. and ultraviolet spectra of solutions of mesitoyl chloride in sulfuric acid show that the mesitoyl cation is formed quantitatively. It is concluded that mesitoyl chloride and trichloromethylmesitylene react with sulfuric acid according to eq. 3 and 7. Thus trichloromethylmesitylene gives rise to a monopositive carbonium ion rather than a dipositive ion as has been claimed previously. The almost quantitative reaction of hydrogen chloride with sulfuric acid according to eq. 2 is confirmed by cryoscopic and conductometric measurements on dilute solutions of HCl in sulfuric acid.

(1) For a preliminary communication see R. J. Gillespie and E. A. Robinson, *J. Am. Chem. Soc.*, **86**, 5676 (1964).

(2) Department of Chemistry, McMaster University, Hamilton, Ontario.

Hart and Fish³⁻⁵ have presented evidence that trichloromethylmesitylene (I) ionizes in sulfuric acid with the formation of the dicarbonium ion II (eq. 1)



and that pentamethyltrichloromethylbenzene and trichloromethylprehnitene behave in a similar manner. They claim that all three compounds give a fivefold depression of the freezing point of sulfuric acid, that conductance measurements show the formation of two hydrogen sulfate ions from each molecule of solute,

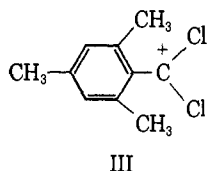
(3) H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **80**, 5894 (1958).

(4) H. Hart and R. W. Fish, *ibid.*, **82**, 5419 (1960).

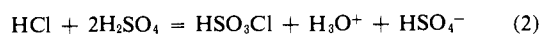
(5) H. Hart and R. W. Fish, *ibid.*, **83**, 4460 (1961).

and that 2 moles of hydrogen chloride are swept from the sulfuric acid solutions by a current of dry nitrogen.

It is the purpose of this paper to show that trichloromethylmesitylene reacts with sulfuric acid to give the monopositive carbonium ion III rather than a dipositive ion.



Hart and Fish misinterpreted their experimental data mainly because they considered that hydrogen chloride does not react with sulfuric acid. It is shown that at low concentrations HCl reacts quantitatively with sulfuric acid to form chlorosulfuric acid and water. Since the latter is extensively ionized in sulfuric acid the over-all reaction may be represented by eq. 2.



Results

Hydrogen Chloride. The specific conductances of solutions of hydrogen chloride are given in Table I and in Figure 1 where they are compared with the conductances of solutions of water in sulfuric acid. If HCl reacts quantitatively with sulfuric acid according to eq. 2 the conductivities should be very similar to those of solutions of water,⁶ whereas if HCl behaves as a nonelectrolyte as was previously claimed,³⁻⁵ little change in the conductivity is expected. In fact, HCl increases the conductivity considerably and at low concentrations the conductance curve is close to that for water. Comparison of concentrations of HCl and water which give equal conductivities enables γ , the number of moles of hydrogen sulfate ions produced per mole of HCl, to be calculated (Table I).⁷ Up to 0.06 *m* the conversion of HCl to HSO_3Cl is essentially complete, while at 0.1 *m* it is 90% complete, and at 0.2 *m* about 77% complete. A value of $K = 0.07$ mole² kg.⁻² was calculated for the equilibrium constant

$$K = \frac{[\text{HSO}_3\text{Cl}][\text{H}_3\text{O}^+][\text{HSO}_4^-]}{[\text{HCl}]} = \frac{\gamma^3 m^2}{(1 - \gamma)}$$

These results were confirmed by cryoscopic measurements. A 0.148 *m* solution of HCl in H_2SO_4 was found to have f.p. 8.260°, which corresponds to a ν -factor of 2.59 and 80% reaction to give HSO_3Cl , (cf. 82% reaction from conductometric measurements), while a 0.0395 *m* solution had f.p. 9.842°, and a ν -factor of 2.99, corresponding to essentially complete reaction to give HSO_3Cl . In the experiments on organic chlorides, cryoscopic measurements were carried out on solutions in which the concentration of HCl formed did not exceed 0.06 *m* so that its conversion to HSO_3Cl may be regarded as complete. In the conductance measurements somewhat more concentrated solutions were studied.

Mesitoic Acid and Mesitoyl Chloride. Treffers and Hammett⁸ showed that mesitoic acid gives a fourfold

(6) S. J. Bass, R. H. Flowers, R. J. Gillespie, E. A. Robinson, and C. Solomons, *J. Chem. Soc.*, 4315 (1960).

(7) R. J. Gillespie and C. Solomons, *ibid.*, 1789 (1957).

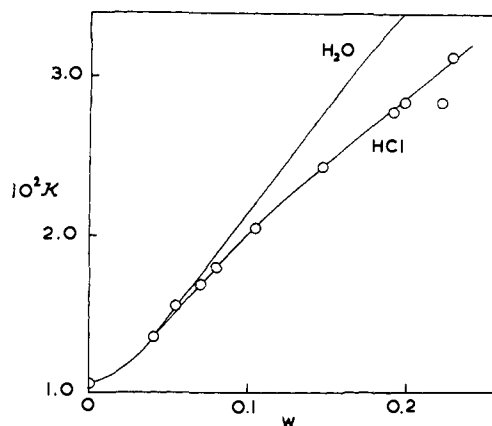


Figure 1. The specific conductance of solutions of hydrogen chloride in 100% H_2SO_4 at 25°.

depression of the freezing point of sulfuric acid. On dilution of the solution with water mesitoic acid was recovered and on dilution with methyl alcohol methyl mesitoate was obtained. These authors suggested

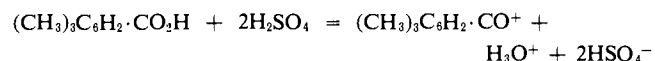
Table I. Conductivities of Solutions of Hydrogen Chloride in Sulfuric Acid at 25°

w^a	$10^2 K$	w^a	$10^2 K$
0.069	1.675	0.079	1.785
0.222	2.835	0.104	2.038
0.192	2.77	0.147	2.427
0.198	2.82	0.039	1.360
0.228	3.12	0.054	1.554

w^a	γ^b	K^c	w^a	γ^b	K^c
0.02	1.00	...	0.14	0.83	0.06
0.04	1.00	...	0.16	0.81	0.07
0.06	0.97	0.11	0.18	0.79	0.07
0.08	0.94	0.09	0.20	0.77	0.07
0.10	0.89	0.06	0.22	0.77	0.08
0.12	0.86	0.06			
Mean					0.07

^a Moles per 1000 g. of solution. ^b 100 γ = per cent reaction ($\text{HCl} + 2\text{H}_2\text{SO}_4 \rightleftharpoons \text{HSO}_3\text{Cl} + \text{H}_3\text{O}^+ + \text{HSO}_4^-$). ^c $K = \frac{[\text{HSO}_3\text{Cl}][\text{H}_3\text{O}^+][\text{HSO}_4^-]}{[\text{HCl}]} = \frac{\gamma^3 w^2}{(1 - \gamma)}$.

that the mesitoyl ion is formed quantitatively according to the equation



This interpretation has been supported by later work^{9,10} and it has been shown, for example, that both 2,3,5,6-tetramethyl- and pentamethylbenzoic acids give ν -factors of 4 and ionize in a similar manner to mesitoic acid. Our conductometric measurements, which show that mesitoic acid ionizes to give two hydrogen sulfate ions per molecule of mesitoic acid (Table II and Figure 2), confirm this reaction. The mesitoyl cation is readily identified from its characteristic ultraviolet spectrum for which we found a maximum absorption at 2820 Å. ($\epsilon_{\text{max}} 20,800^{10}$).

(8) H. P. Treffers and L. P. Hammett, *J. Am. Chem. Soc.*, 59, 1788 (1937).

(9) M. S. Newman, H. G. Kuivila, and A. B. Garrett, *ibid.*, 67, 704 (1945).

(10) M. S. Newman and N. C. Deno, *ibid.*, 73, 3651 (1951).

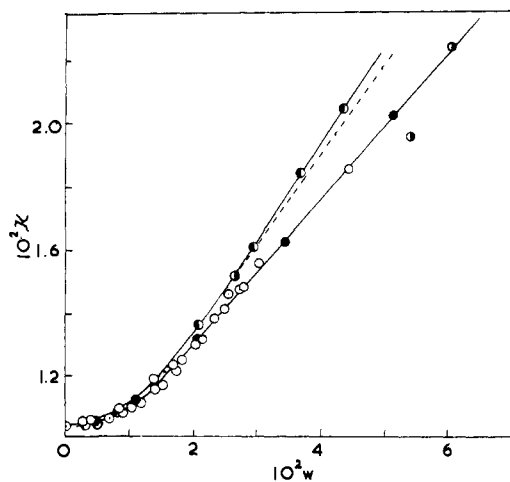


Figure 2. Specific conductances in 100% H_2SO_4 at 25°: ●, $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{COCl}$; ○, $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CO}_2\text{H}$; ○ (our results) and ○ (Hart and Fish), $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CCl}_3$; - - - - , $2\text{H}_2\text{O}$.

Mesitoyl chloride dissolves readily in sulfuric acid. The ultraviolet spectrum shows that the mesitoyl cation is formed quantitatively (λ_{max} 2820 Å. (ϵ_{max} 20,900)). The results of our conductometric and cryoscopic measurements are given in Tables II and III and Figures 2 and 3. The cryoscopic results indicate a

Table II. Results of Conductivity Measurements at 25°

Mesitoic acid		Mesitoyl chloride	
w^a	$10^2\kappa$	w^a	$10^2\kappa$
0.0000	1.043	0.0000	1.043
0.0031	1.047	0.0042	1.065
0.0080	1.077	0.0104	1.142
0.0138	1.185	0.0206	1.319
0.0209	1.359	0.0344	1.621
0.0295	1.604	0.0516	2.022
0.0367	1.838	0.0708	2.444
0.0434	2.044	0.0917	2.814 ^b

Trichloromethylmesitylene					
w^a	$10^2\kappa$	w^a	$10^2\kappa$	w^a	$10^2\kappa$
0.0000	1.043	0.0000	1.043 ₃	0.0000	1.043
0.0041	1.062	0.0030	1.045	0.0022	1.045
0.0080	1.101	0.0067	1.064	0.0046	1.053
0.0165	1.235	0.0103	1.102	0.0086	1.082
0.0277	1.480	0.0140	1.154	0.0116	1.114
0.0444	1.852	0.0172	1.216	0.0149	1.183
0.0634	2.461 ^c	0.0203	1.294	0.0180	1.251
		0.0232	1.382	0.0215	1.311
		0.0256	1.456	0.0248	1.414
		0.0256	1.511 ^d	0.0273	1.477
				0.0302	1.552
				0.0302	1.683 ^e

^a Moles per 1000 g. of solution. ^b After 36 hr. ^c After 24 hr. ($\gamma = 2.0$). ^d After 16 hr. ($\gamma = 2.1$). ^e After 6 hr. ($\gamma = 2.2$).

fivefold depression of the freezing point and the conductometric measurements, the production of approximately two hydrogen sulfate ions per molecule for both mesitoyl chloride and trichloromethylmesitylene at concentrations up to 0.02 *m*, although at higher concentrations γ falls to about 1.8. The decrease in γ may be attributed to the incompleteness of the reaction of HCl with H_2SO_4 . These results are consistent with the following reaction for mesitoyl chloride (eq. 3).

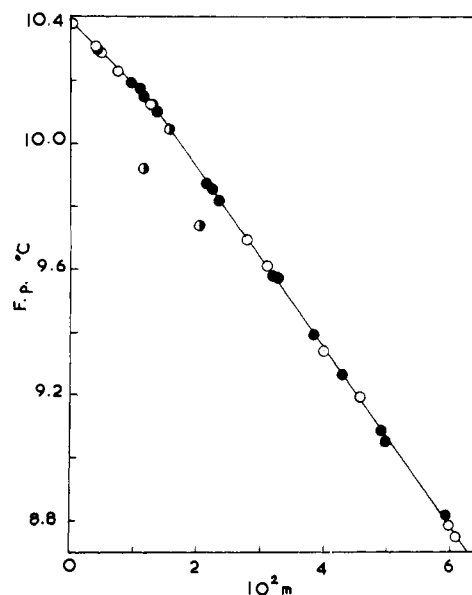
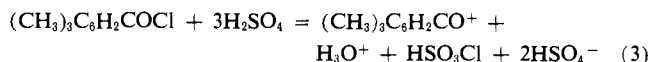


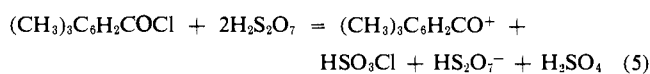
Figure 3. Freezing points: ○, $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{COCl}$; ● (our results) and ○ (Hart and Fish), $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CCl}_3$.



If HCl behaved as a nonelectrolyte in sulfuric acid reaction 4, for which $\nu = 3$ and $\gamma = 1$, would be expected; this is quite inconsistent with the experimental results.

On pouring a solution of mesitoyl chloride in sulfuric acid onto ice, mesitoic acid was obtained.

Confirmation of reaction 3 was obtained by conductometric titrations with dilute oleum.¹¹ For ionization of mesitoyl chloride according to eq. 3 we can represent the reaction in oleum as eq. 5. This differs from a simple acid-base titration, *e.g.*, eq. 6, in that



from a simple acid-base titration, *e.g.*, eq. 6, in that



each mole of added base removes an additional mole of $\text{H}_2\text{S}_2\text{O}_7$ in the formation of HSO_3Cl . For an initially 0.1 *m* solution of $\text{H}_2\text{S}_2\text{O}_7$ titrated with a strong base, *e.g.*, KHSO_4 , a minimum in the conductivity occurs at $r = 0.56$ (where r is the ratio of the number of moles of added base to initial moles of acid¹¹). Thus for mesitoyl chloride reacting according to eq. 2 the minimum conductivity in a titration with 0.1 *m* $\text{H}_2\text{S}_2\text{O}_7$ would be expected to occur at $r = 0.56/(1 + 0.56) = 0.36$. (Similarly for a strong base- $\text{H}_2\text{S}_2\text{O}_7$ titration, where the initial molality of acid is 0.05, $r_{\text{min}} = 0.60$, so that for mesitoyl chloride added to 0.05 *m* oleum $r_{\text{min}} = 0.38$ would be predicted.) The results of our titration experiments are given in Table IV and Figure 4. The observed conductivity minima occur very close to the theoretically predicted positions.

(11) R. H. Flowers, R. J. Gillespie, and E. A. Robinson, *Can. J. Chem.*, **38**, 1363 (1960).

Table III. Results of Cryoscopic Measurements

Mesityl chloride							
<i>m</i>	F.p., °C.	<i>m</i>	F.p., °C.	<i>m</i>	F.p., °C.	θ	ν
0.0000	10.368	0.0000	10.369	0.01	10.175	0.450	5.08
0.0039	10.300	0.0044	10.287	0.02	9.920	0.705	5.04
0.0129	10.115	0.0077	10.224	0.03	9.637	0.988	4.97
0.0278	9.688	0.0126	10.116	0.04	9.348	1.277	4.93
0.0400	9.339	0.0311	9.606	0.05	9.065	1.560	4.85
0.0598	8.769	0.0457	9.190	0.06	8.780	1.845	4.76
0.0598	8.765 ^a	0.0619	8.739				

Trichloromethylmesitylene					
<i>m</i>	F.p., °C.	<i>m</i>	F.p., °C.	<i>m</i>	F.p., °C.
0.0000	10.370	0.0000	10.360	0.0000	10.370
0.0115	10.138	0.0098	10.187	0.0042	10.292
0.0224	9.855	0.0141	10.095	0.0109	10.171
0.0378	9.387	0.0217	9.866	0.0236	9.813
0.0488	9.081	0.0325	9.571	0.0315	9.574
0.0594	8.806	0.0423	9.267	0.0315	9.196 ^b
0.0594	8.283 ^a	0.0495	9.050		
0.0594	8.075 ^c	0.0495	8.410 ^d		

<i>m</i>	F.p., °C.	θ	ν	<i>m</i>	F.p., °C.	θ	ν
0.01	10.175	0.450	5.08	0.01	10.175	0.450	4.30
0.02	9.920	0.705	5.04	0.02	9.920	0.705	4.47
0.03	9.637	0.988	4.97	0.03	9.637	0.988	4.53
0.04	9.348	1.277	4.93	0.04	9.348	1.277	4.58
0.05	9.065	1.560	4.85	0.05	9.065	1.560	4.56
0.06	8.780	1.845	4.76	0.06	8.780	1.845	4.53
				<i>c</i>	0.0594	8.075	6.72
				<i>d</i>	0.0495	8.401	7.02
				<i>b</i>	0.0315	9.574	7.06

^a After 24 hr. ^b After 72 hr. ^c After 98 hr. ^d After 96 hr. ^e m_d calculated for reaction according to eq. 3. ^f m_d calculated for reaction according to eq. 9. ^g m_d calculated for reaction according to eq. 8. ^h m_d calculated for reaction according to eq. 11 or 12.

Table IV. Conductometric Titrations

Mesityl chloride			
$m_{\text{H}_2\text{S}_2\text{O}_7}^i = 0.0507$	$10^2 \kappa$	$m_{\text{H}_2\text{S}_2\text{O}_7}^i = 0.115$	$10^2 \kappa$
0.000	1.258	0.000	1.564
0.081	1.202	0.033	1.504
0.215	1.129	0.110	1.381
0.443	1.079	0.208	1.245
0.711	1.152	0.247	1.200
0.835	1.238	0.279	1.174
0.928	1.326	0.312	1.155
0.984	1.383	0.334	1.144
		0.364	1.137
		0.388	1.136
		0.412	1.139
		0.436	1.148
		0.470	1.165
		0.518	1.202

Trichloromethylmesitylene			
$m_{\text{H}_2\text{S}_2\text{O}_7}^i = 0.0514$	$10^2 \kappa$	$m_{\text{H}_2\text{S}_2\text{O}_7}^i = 0.1044$	$10^2 \kappa$
0.000	1.262	0.000	1.521
0.044	1.233	0.036	1.468
0.016	1.209	0.062	1.429
0.122	1.179	0.093	1.384
0.160	1.155	0.136	1.328
0.217	1.128	0.176	1.283
0.247	1.112	0.222	1.244
0.256	1.098	0.258	1.215
0.328	1.085	0.291	1.195
0.365	1.080	0.325	1.184
0.414	1.076	0.362	1.178
0.449	1.080	0.397	1.181
0.486	1.087	0.432	1.192
0.547	1.107	0.523	1.243
0.622	1.139	0.604	1.331

The chemical shifts of the lines observed in the n.m.r. spectra of mesitoic acid and mesityl chloride in 96 and 100% sulfuric acid and in carbon tetrachloride are shown in Table V. The spectra in 100% acid are due

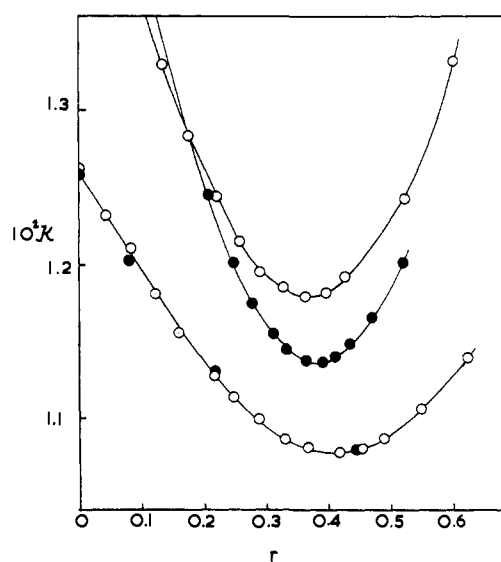


Figure 4. Conductometric titrations of oleum: O, $(\text{CH}_3)_2\text{C}_6\text{H}_2\text{COCl}$; ●, $(\text{CH}_3)_2\text{C}_6\text{H}_2\text{CCl}_3$.

to the acyl ion RCO^+ while in 96% acid they are due to the conjugate acid RCO_2H_2^+ .¹² N.m.r. spectra also

(12) N. C. Deno, N. Friedman, and J. Mockus, *J. Am. Chem. Soc.*, **86**, 5676 (1964).

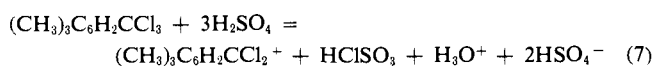
Table V. N.m.r. Spectra^a

	Solvent											
	CCl ₄			H ₂ SO ₄			HSO ₃ Cl			HSO ₃ F		
Mesitoic acid	6.81	2.41	2.27	7.22	2.52	2.37 ^b
Mesitoyl chloride	6.77	2.30	2.23	7.22	2.52	2.37 ^b	7.24	2.52	2.38	7.24	2.54	2.39
Trichloromethylmesitylene	6.88	2.78	2.27	7.29	2.73	2.39 ^d	7.32	2.75	2.40	7.32	2.73	2.38
				7.23	2.53	2.39 ^e						

^a Chemical shifts in p.p.m. from an external standard consisting of a dilute solution of (CH₃)₄Si in CDCl₃. The shifts have been corrected for the difference in susceptibility of CDCl₃ and the solvent; they were obtained by exchanging the sample and reference tubes while running the spectra. ^b 100% H₂SO₄. ^c 96% H₂SO₄. ^d Initial red solution in 100% H₂SO₄. ^e Final yellow solution in 100% H₂SO₄.

show that stable solutions of the acyl ion are obtained from mesitoyl chloride in chlorosulfuric and fluorosulfuric acid (Table V).

Trichloromethylmesitylene. This solute behaves in an analogous way to mesitoyl chloride giving a cryoscopic ν -factor of 5 (Table III and Figure 3), a conductometric γ -factor of 2 (Table II and Figure 2), and conductivity minima in titrations with oleum close to $r = 0.38$ (Table IV and Figure 4). These results are consistent with the ionization shown in eq. 7. The n.m.r. spectra of solu-



tions of mesitoyl chloride and trichloromethylmesitylene in sulfuric acid are, however, different, which is consistent with the formation of the acyl ion RCO⁺ from the former and the dichlorocarbonium ion RCCl₂⁺ from the latter. The n.m.r. spectra of solu-

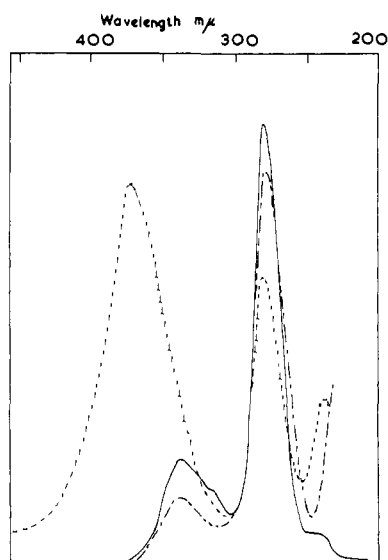


Figure 5. Absorption spectra: - - - -, (CH₃)₃C₆H₂CCl₃ in 100% H₂SO₄ (red solution); - · - · -, (CH₃)₃C₆H₂CCl₃ in 100% H₂SO₄ (yellow solution); —, (CH₃)₃C₆H₂COCl in 100% H₂SO₄.

tions of trichloromethylmesitylene in chlorosulfuric and fluorosulfuric acid, are the same as that of the solution in sulfuric acid, indicating that the RCCl₂⁺ ion is also formed in these solution. Although solutions of mesitoyl chloride in sulfuric acid are stable those of trichloromethylmesitylene change slowly with time. Initially the solutions have the characteristic red color previously reported⁵ but on standing the

color changes to yellow. The change is more rapid at 25° (conductivity experiments) than at 10° (cryoscopic experiments), and while only a very slow change was observed for dilute solutions at 10°, the reaction is quite rapid in the concentrated solutions used to obtain the n.m.r. spectra at 25°. The color change is accompanied by a change in ν from 5 to approximately 7 and an increase in γ from 1.8 to slightly greater than 2. Simultaneously, the absorption spectrum changes as shown in Figure 5 and the n.m.r. spectrum as shown in Figure 6. The solutions of trichloromethylmesitylene in chlorosulfuric and fluorosulfuric acid are more stable than those in sulfuric acid.

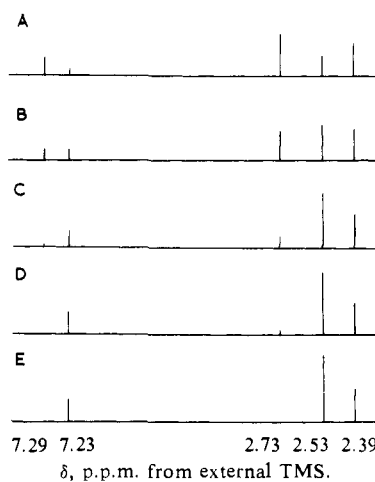
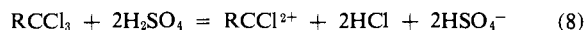
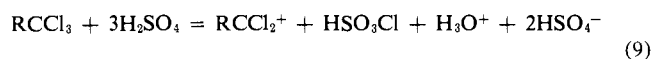


Figure 6. The n.m.r. spectrum of trichloromethylmesitylene in 100% H₂SO₄: A, after 15 min. (red solution); B, after 40 min.; C, after 50 min.; D, after 90 min.; E, after 6 hr. (yellow solution).

While both the mode of ionization claimed previously for trichloromethylmesitylene (eq. 8) and that



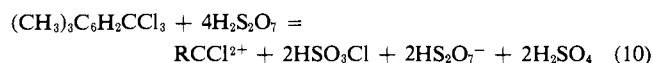
put forward in the present work would give $\nu = 5$ and $\gamma = 2$, the following five arguments can be given in support of reaction 9.



1. The conductometric and cryoscopic experiments described above clearly demonstrate that HCl reacts with 100% H₂SO₄ to give HSO₃Cl according to eq. 2, and the experiments with mesitoyl chloride show that, as expected, the hydrogen chloride produced from the reaction of an organic chloride with sulfuric acid reacts in just the same way.

2. The value of γ for trichloromethylmesitylene decreases from 2 at low concentrations to 1.8 at higher concentrations. This result is difficult to account for on the basis of reaction according to eq. 8 as this should give two hydrogen sulfate ions independent of concentration. However it is consistent with reaction according to eq. 9 which would be expected to give somewhat less than two hydrogen sulfate ions per molecule of solute as a consequence of the equilibrium between hydrogen chloride, chlorosulfuric acid, and water.

3. The close similarity of the conductometric titration curves clearly shows that the ionizations of mesitoyl chloride and trichloromethylmesitylene must also be very similar, *i.e.*, they must be represented by eq. 5 and 9. Even if HCl did not react with H₂SO₄ it is known that it reacts with oleum and therefore in oleum eq. 8 must be written in the form



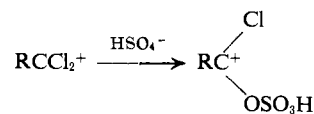
For this reaction a minimum in the conductance would be expected at $r = 0.28/[1 + 2(0.28)] = 0.18$, which is not in accord with the experimental observations.

4. Although both reactions 8 and 9 give $\nu = 5$ they would represent the self-ionization of the solvent in different ways since eq. 9 gives an H₃O⁺ ion while eq. 8 does not. This difference can be used to distinguish between them. Thus if repression of the self-ionization of the solvent is allowed for on the basis of eq. 8 the calculated ν -values are in the range 4.30 to 4.53, whereas repression of the self-dissociation according to eq. 9 gives values in the range 5.08 to 4.76, which are more constant and much closer to the theoretically predicted value of 5. Thus although both give $\nu \approx 5$, ionization according to eq. 9 is in fact in better agreement with the experimental freezing points than ionization according to eq. 8.

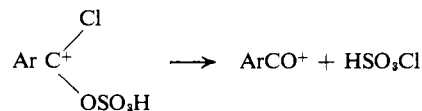
5. The n.m.r. spectra of both II and III would be expected to be rather similar except that the probably greater charge delocalized in the ring of the supposed dicarbonium ion might be expected to cause greater downfield shifts of the methyl groups and ring protons. However the downfield shifts of the methyl groups when the ion is formed from the neutral molecule are very comparable with those observed in the mesitoyl ion, which suggests that the ion formed from I is in fact a monocarbonium ion rather than a dicarbonium ion.

The nature of the yellow species, formed slowly from the red ion, is not completely certain. Its n.m.r. spectrum is very similar to that of the mesitoyl cation¹² (Table V), and its ultraviolet absorption spectrum (Figure 5) is similar to that of mesitoyl chloride in sulfuric acid. Thus it seems likely that the dichloro-carbonium ion reacts further to give the mesitoyl ion, although the yellow color of the solution cannot be explained in this way. However, colored solutions in sulfuric acid often arise from a minor impurity. Hart and Roobol¹³ have claimed that hydrolysis of RCCl_2^+ gives an acylium ion. Since water is present almost entirely as H₃O⁺ in slightly aqueous sulfuric acid, further reaction of RCCl_2^+ in this medium is unlikely to be due to nucleophilic attack by water. More likely is a reaction with HSO₄⁻ which is present in relatively high

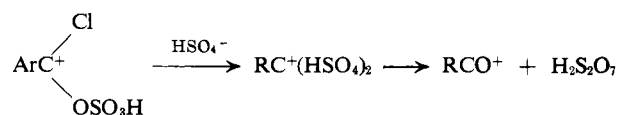
concentration. Indeed we find that the rate of the color change from red to yellow is enhanced enormously by adding KHSO₄ to a solution of RCCl_3 in 100% H₂SO₄.



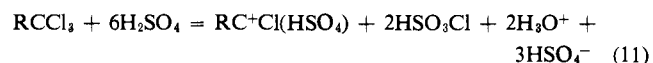
which is presumably followed by



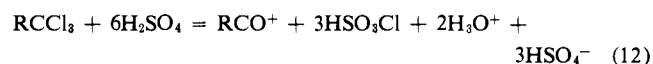
or by



For the over-all reactions we have



($\nu = 8$, and $\gamma = 3$) and



($\nu = 9$, and $\gamma = 3$). However, HSO₃Cl will not be formed quantitatively because of the equilibrium with HCl, H₃O⁺, and HSO₄⁻, so that both ν and γ would be expected to be somewhat smaller than these limiting values. On the basis of the equilibrium constant obtained above for the reaction of HCl with H₂SO₄ the expected ν - and γ -factors for reaction according to eq. 11 and 12, respectively, may be calculated. The results of these calculations are shown in Table VI.

Table VI. Calculated Values of ν and γ for Solvolysis of RO^+Cl_2

m	Eq. 11		m	Eq. 12	
	γ	ν		γ	ν
0.02	3.0	8.0	0.02	2.9	8.8
0.03	2.9	7.8	0.03	2.8	8.6
0.04	2.8	7.6	0.04	2.7	8.4
0.05	2.7	7.4	0.05	2.6	8.2
0.06	2.6	7.2	0.06	2.5	8.0
0.08	2.5	7.0	0.08	2.3	7.6
0.10	2.4	6.8	0.10	2.2	7.4

The observed results ($\nu = \sim 7$, and $\gamma = \sim 2$) are in reasonable agreement with those expected for reaction to give $\text{RCCl}(\text{HSO}_4)^+$ but in only fair agreement with those expected for reaction to give RCO^+ . Presumably the formation of acyl ion had not gone to completion in any case. Further investigations are clearly necessary in order to fully understand this reaction.

Experimental

Mesitoic acid (Aldrich Chemical Co.) was recrystallized from ethanol-water and had m.p. 155–156°. *Mesitoyl chloride* (b.p. 128° at 24 mm.) was prepared by refluxing 40 g. of mesitoic acid with 40 g. of thionyl chloride for 1.5 hr. and then distilling off the excess thionyl chloride, followed by distillation under reduced pressure. On hydrolysis with NaOH

(13) H. Hart and N. R. Roobol, *J. Am. Chem. Soc.*, **86**, 1373 (1964).

solution it gave mesitoic acid, m.p. 155°. *Trichloromethylmesitylene* was prepared according to the method of Hart and Fish⁴ by slowly adding 30 g. of mesitylene in 50 ml. of carbon tetrachloride to a mixture of 67 g. of aluminum chloride in 100 ml. of carbon tetrachloride. The reaction was carried out at room temperature over a total period of 5 hr. The mixture was poured onto 5% HCl-ice water and dried over CaCl₂. The CCl₄ solvent was removed under reduced pressure and the compound was distilled *in vacuo* (b.p. 115° at 2 mm.). *Anal.* Calcd.: C, 50.56; H, 4.67; Cl, 44.77. Found (Bernhardt, Max Planck Institut): C, 50.7; H, 4.70; Cl, 47.7.

Anhydrous hydrogen chloride was prepared by bubbling HCl from a cylinder through 98% sulfuric acid, then through a tower packed with glass wool, and finally through a cold trap. The results obtained for HCl dried in this way were the same as those obtained when HCl was dried by passing it through a long tube packed with magnesium perchlorate. The concentration of HCl in the conductometric experiments was determined by weighing the conductivity cell before and after HCl was slowly bubbled into the sulfuric acid contained in it. Freezing point depressions of HCl solutions were determined in a conventional cryoscope on solutions which were transferred from the conductivity cell.

The preparation of 100% sulfuric acid, the apparatus, and the method of carrying out the cryoscopic and conductometric measurements and the acid-base conductometric titrations have been described previously.^{11,14,15}

(14) R. J. Gillespie, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2473 (1950).

Cryoscopic ν -factors were obtained as has been described previously¹⁶ from the equation

$$\nu = \theta(1 - 0.098ms)/(6.12m - m_d/m)$$

where m is the molal concentration of solute, θ is its freezing point depression calculated from the freezing point of hypothetical undissociated acid (10.625°), s is the number of moles of sulfuric acid used up in the ionization of 1 mole of solute, and $m_d = m_\alpha + m_\beta$, where m_α is the total concentration of autoprotolysis ions and m_β is the total concentration of ionic dehydration ions, resulting from incomplete repression of the self-dissociation of the solvent. The conductometric γ -factors were obtained by comparison of the concentrations of solute and potassium hydrogen sulfate or hydronium hydrogen sulfate which give equal specific conductivities.⁷

The ultraviolet-visible spectra were recorded on a Perkin-Elmer 250 spectrometer and a Bausch and Lomb 505 spectrometer. N.m.r. spectra were measured using a Varian Associates A-60 spectrometer.

Acknowledgments. The National Research Council of Canada and the Allied Chemical Co. is thanked for generous financial assistance. The help of Mrs. Diane Jones, Mr. R. Child, Mr. K. Ny, Mr. J. S. Hartman, and Mr. S. A. A. Zaidi in performing some of the experimental work is acknowledged and Professor Peter Yates of the Department of Chemistry, University of Toronto, is thanked for encouraging us to complete this work.

(15) R. J. Gillespie, J. V. Oubridge, and C. Solomons, *ibid.*, 1804 (1957).

(16) S. J. Bass, R. J. Gillespie, and E. A. Robinson, *ibid.*, 821 (1960)

The Effect of Pressure on the Hydrolysis of Chloroform, Chlorodifluoromethane, and 3-Chloro-3-methylbutyne. The Nature of the Intermediates¹

William J. le Noble

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York. Received February 5, 1965

The effects of hydrostatic pressure on the base-catalyzed hydrolysis of chloroform, chlorodifluoromethane, and 3-chloro-3-methylbutyne, as well as the neutral hydrolysis of the latter compound, have been measured over a range of 6-7 kbars. The activation volumes are +16, +8.5, +2, and -15 cm.³/mole, respectively. It is concluded that these values support the B1 mechanism, α -dehydrohalogenation, the B1 mechanism, and an S_N1 mechanism for these respective reactions; the positive, but rather small volume change accompanying the base-promoted reaction of 3-chloro-3-methylbutyne strongly suggests that the incipient intermediate carbene has a highly dipolar structure.

(1) For a preliminary account of this work, see W. le Noble and M. Duffy, *J. Am. Chem. Soc.*, 86, 4512 (1964).

In the past few years increasing use has been made of liquid-phase, high-pressure reactions as a tool for learning details of reaction mechanisms otherwise not easily accessible.² Among such details, particularly important are the progress of bond formation and breakage and concomitant compression or decompression in the solvent surrounding the reacting molecules. One of the problems that can thus be solved is whether or not the transition state leading to an unstable intermediate involves a solvent molecule covalently bound. In essence, the technique works

(2) For recent reviews, see (a) S. D. Hamann, "Physico-Chemical Effects of Pressure," Academic Press Inc., New York, N. Y., 1957, Chapters 8 and 9; (b) E. Whalley, "Advances in Physical Organic Chemistry," Vol. 2, V. Gold, Ed., Academic Press Inc., New York, N. Y., 1964; (c) S. D. Hamann, *Ann. Rev. Phys. Chem.*, 15, 349 (1964).