A Study of the 1,3,5-Trialkylbenzenes with Aluminum Chloride-Hydrogen Chloride Systems

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The "red-oil" complex layers of systems of 1,3,5-trialkylbenzenes (Me_3B, Et_3B, i-Pr_3B, and s-Bu_3B) with $AlCl_3$–HCl were prepared and studied by means of ^1H NMR and ^{13}C NMR spectroscopy. The results show that the 2,4,6-trialkylbenzenium ion is evidently formed in the complex layer of the $AlCl_3$–HCl system, much as in other superacid systems, and that those ions from i-Pr_3B and s-Bu_3B are substantially stable, even at room temperature. The molar ratios of i-Pr_3B and s-Bu_3B to HAl_2Cl_7 are almost 1. On the other hand, the molar ratios of Me_3B and Et_3B to HAl_2Cl_7 are 4.5 and 1.9 respectively. These two complex layers are considered to be formed by both 1,3,5-trialkylbenzene and its protonated product, and to be in a certain equilibrium state as a result of proton exchange at room temperature.

Many investigations of benzenium ions by using NMR have been reported in recent years,[1] and most of them have been carried out in various superacids, such as HF–BF_3, HSO_3F, and HF–SbF_5, at low temperatures. In the Friedel-Crafts reaction, alkylbenzene–$AlCl_3$–HCl systems are frequently used in commercial processes. However, the structures and compositions of the above systems have not yet been ascertained. The reasons for this are that the measurement of the NMR spectrum is difficult at low temperatures because of the solidification of the system, and that it is hard to obtain at room temperature because of the disproportionation process.

In a previous paper,[2] we reported that some of the methylbenzenes are stable in the system at room temperature, and are scarcely disproportionated even at room temperature. In order to obtain further information about the structure and composition of the "red-oil" complex layer (complex layer) in the system, we will now deal with the system of 1,3,5-trialkylbenzenes with $AlCl_3$–HCl and the formation of the stable benzenium ions by using NMR.

Experimental

Materials. The mesitylene (Me_3B) was commercially available in a high purity. The 1,3,5-trialkylbenzenes were known; they were prepared from mono- or di-alkylbenzene by Friedel-Crafts type reactions. The purities of the 1,3,5-triethyl-, 1,3,5-triisopropyl-, and 1,3,5-tri-s-butylbenzenes (Et_3B, i-Pr_3B, and s-Bu_3B respectively) were 96, 100, and 98% respectively, as determined by means of VPC analysis. All the alkylbenzenes dried over metallic Na were distilled just before use.

Preparation of Complex Layers. The complex layers of the systems of 1,3,5-trialkylbenzenes with $AlCl_3$ were prepared by the method reported previously.[2] After the reaction had been completed, the complex layer was separated as a lower layer, leaving colorless hydrocarbon as an upper layer. The volumes of the two layers were almost equal. The lower layer was then pipetted out and measured. This layer is substantially stable and keeps for several days at room temperature.

Measurements. The ^{13}C NMR spectra were obtained using a JNM-PS-100/EC-100 spectrometer equipped with a Fourier transform recorder at 25.15 MHz under a complete proton decoupling. The pulse width and repetition time were 12 μs (about $\pi/4$ pulse) and 6s respectively. The spectra were observed at 6250 Hz (data point 8191) in a 10 mmϕ tube with an external lock standard contained in a 3 mmϕ tube, holding acetone-d_6 and TMS, coaxially centered. All chemical shifts are referred to this TMS standard. The ^1H NMR spectra were also obtained using a JNM-PS-100 spectrometer, with external TMS (capillary) as the reference.

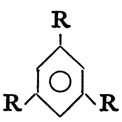
Analyses of Hydrocarbons. Hydrocarbons in both the upper and lower (complex) layers were analyzed by means of VPC after each layer had been decomposed with water. The analyses were made on a Shimadzu GC-3AF apparatus, fitted with a 3 m × 3 mm column packed with Apiezon grease L 10% and with an ionization detector, at 160 and 200 °C.

Analyses of Aluminum and Chlorine.[3] The aluminum and chlorine in the complex layer were determined by the oxine and mercury-titration methods respectively.

Results and Discussion

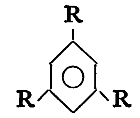
Analyses of Complex Layers. As was described in our previous paper,[2] the formation of a reaction system, that is, a complex layer and a hydrocarbon layer, requires a limited amount of HCl evolved by moisture contained in $AlCl_3$. In this study, when suitable amounts of alkylbenzene and $AlCl_3$ were used, it was

Table 1. Disproportionated products of 1,3,5-trialkylbenzenes at 2 °C

Starting material 	Layer	Products (mol%)				
		m-Di-R-C_6H_4	p-Di-R-C_6H_4	1,3,5-Tri-R-C_6H_3	1,2,4-Tri-R-C_6H_3	Tetra-R-C_6H_2 and unknown products
R=Me[a]	Upper	—	—	100	—	—
	Lower	—	—	100	—	—
R=Et[b]	Upper	2.7	0.7	88.5	4.8	3.3
	Lower	3.0	1.3	87.0	4.6	4.1
R=i-Pr	Upper	0.4	0.2	99.0	—	0.4
	Lower	0.6	0.3	98.5	—	0.6
R=s-Bu[c]	Upper	0.6	0.2	96.6	2.1	0.5
	Lower	0.6	0.3	96.1	2.2	0.8

a) Ref. 2. b) 1,3,5-Triethylbenzene: 1,2,4-triethylbenzene = 96.0: 4.0. c) 1,3,5-Tri-s-butylbenzene: 1,2,4-tri-s-butylbenzene = 98.0: 2.0.

Table 2. The constituents of the complex layers of 1,3,5-trialkylbenzenes with aluminum chloride–hydrogen chloride

Starting material 	Al (wt%)	Cl (wt%)	Hydrocarbon (wt%)	Molar ratios			
				Al[a]	Cl[a]	1,3,5-Trialkylbenzene	Hydrocarbon
R=Me	6.4	29.7	63.9	1	3.53	2.24	2.24
R=Et	8.3	38.2	53.5	1	3.50	0.93	1.07
R=*i*-Pr	9.4	43.2	47.4	1	3.50	0.66	0.67
R=*s*-Bu	9.2	42.3	48.5	1	3.50	0.56	0.58

a) Al: ±0.3 wt%, Cl: ±1.0 wt%.

possible to obtain two layers apparently equal in volume. The data of the disproportionated products of 1,3,5-trialkylbenzene obtained in the reaction with $AlCl_3$ and HCl at 2 °C are listed in Table 1. The contents of the hydrocarbons in both upper and lower layers, that is, the hydrocarbon layer and the complex layer respectively, were separately analyzed by means of VPC.

The results indicate that the disproportionation of 1,3,5-trialkylbenzene scarcely proceeds at all. These relations held constantly up to about 30 °C. To obtain the contents of $AlCl_3$ and HCl in the complex layer, Al and Cl were analyzed and the molar ratios of Al, Cl, and alkylbenzene were estimated, as is shown in Table 2.

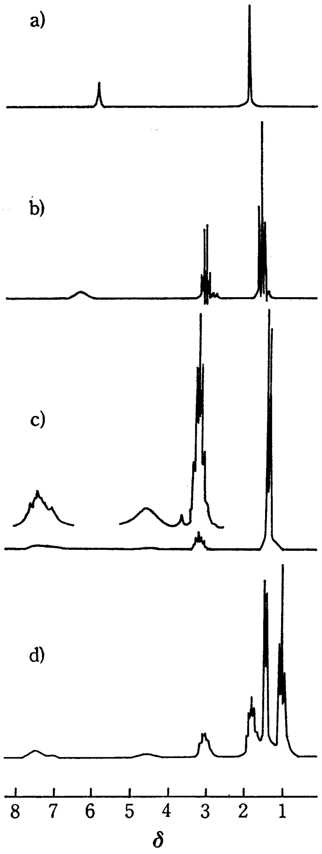


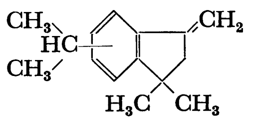
Fig. 1. 100 MHz ^1H NMR spectra of complex layers of 1,3,5-trialkylbenzenes with aluminum chloride-hydrogen chloride at 30 °C.
a) 1,3,5-Trimethylbenzene. b) 1,3,5-Triethylbenzene. c) 1,3,5-Triisopropylbenzene. d) 1,3,5-Tri-*s*-butylbenzene.

The molar ratio of Al/Cl was 1/3.5 for all the complex layers. This means that HAl_2Cl_7,[4] made up of 2 mol of $AlCl_3$ and 1 mol of HCl, plays an important role in the formation of the complex layer. The molar ratio of 1,3,5-trialkylbenzene/HAl_2Cl_7 decreased with an increase in the alkyl carbon numbers as follows; 4.5 for Me_3B, 1.9 for Et_3B, 1.3 for *i*-Pr_3B, and 1.1 for *s*-Bu_3B. Therefore, the constituents of the complex layers are somewhat different from each other.

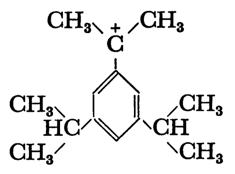
^1H NMR Spectra of Complex Layers. The ^1H NMR spectrum of each complex layer is shown in Fig. 1.

The ring protons of Me_3B and Et_3B exhibited considerably sharp singlet signals at δ 6.0 and 6.4 respectively, but those of *i*-Pr_3B and *s*-Bu_3B were each detected as a set of two broad signals, at about δ 7.5 and 4.6 respectively. The former is a signal of the ring protons, H_3 and H_5, of 2,4,6-trialkylbenzenium ions, while the latter is attributable to the methylene protons, H_1, of 2,4,6-trialkylbenzenium ions, which correspond to those reported by Olah *et al.* in their investigation with superacid. Therefore, the singlets of the ring protons of Me_3B and Et_3B, which unusually shifted to a high field, probably result from the fusions of the ring signals of 1,3,5-trialkylbenzene and the 2,4,6-trialkylbenzenium ion.

In the spectrum of *i*-Pr_3B, a weak singlet signal was observed at δ 3.69; it increased in intensity with the temperature. When this signal was detected somewhat intensely, 1,1-dimethyl-3-methylene-5- or -6-isopropylindan (**1**)[5] was also found in the products. From this fact, and reference to the chemical shifts of the phenyl isopropyl cation, which were shown by Olah *et al.*[6] and Farnum,[7] the singlet signal is assigned to methyl protons of the 3,5-diisopropyl phenyl isopropyl cation (**2**).



(**1**)



(**2**)

^{13}C NMR Spectra of Complex Layers. The ^{13}C NMR spectrum of each complex layer at 30 °C is shown in Fig. 2. In the spectrum of Et_3B, some of the sharp signals obtained at δ 146—125 and 30—16, result from

Table 3. Carbon-13 chemical shifts for 2,4,6-trialkylbenzenium ions

Ion	Carbon-13 chemical shifts[a)]				
	Benzenium-ring carbons				2,4,6-Alkyl-substituent carbons
	C_1	C_2, C_6	C_3, C_5	C_4	Additional
R=Me	b)54.5	193.3	134.8	193.3	$C_{2,6}$–CH_3, 27.3; C_4–CH_3, 29.6
	c)51.9	194.0	133.9	194.3	$C_{2,6}$–CH_3, 25.2; C_4–CH_3, 27.6
R=Et	d)52.9	197.8	128.6	197.8	$C_{2,4,6}$–CH_2, 32.9; $C_{2,4,6}$–CH_3, 14.8
	c)49.8	199.2	130.8	198.3	$C_{2,6}$–CH_2, 32.1; C_4–CH_2, 34.3; $C_{2,4,6}$–CH_3, 12.1
R=*i*-Pr	e)50.3	205.4	130.2	202.8	$C_{2,4,6}$–CH, 39.7; $C_{2,4,6}$–CH_3, 24.1
R=*s*-Bu	e)50.6	204.6	132.0	202.0	C_α–CH, 47.0; C_β–CH_2, 32.1; $C_{\beta'}$–CH_3, 21.4; C_γ–CH_3, 13.5

a) The chemical shifts are in parts per million relative to the external (capillary) TMS. b) Data from Ref. 2; original data converted using $\delta_C^{CS_2}$ 193.7. Counter-ion, $Al_2Cl_7^-$. c) Data from Ref. 1. j) In $HF–SbF_5–SO_2$ at −65 °C. d) This work, at −50 °C. e) This work, at 0 °C.

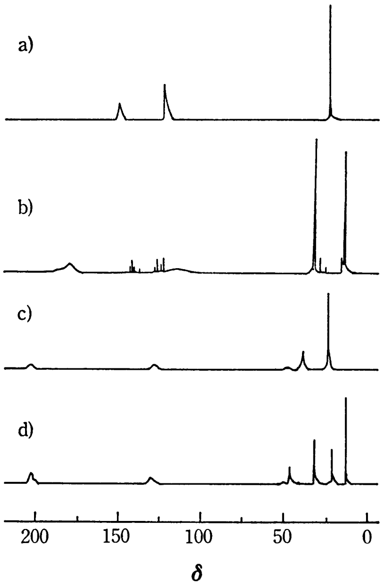
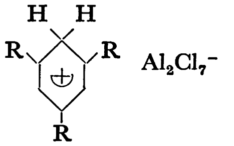


Fig. 2. ^1H decoupled ^{13}C NMR spectra of complex layers of 1,3,5-trialkylbenzenes with aluminum chloride–hydrogen chloride at 30 °C.

a) 1,3,5-Trimethylbenzene. b) 1,3,5-Triethylbenzene. c) 1,3,5-Triisopropylbenzene. d) 1,3,5-Tri-*s*-butylbenzene.

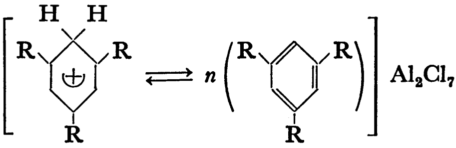
the presence of some other alkylbenzenes produced by disproportionation. The other complex layers were not contaminated by significant disproportionated products. The methylene signals of the 2,4,6-trialkylbenzenium ions were observed at about δ 50 for *i*-Pr_3B and *s*-Bu_3B, but not for Me_3B and Et_3B. The latter complex layers, which were measured at sufficiently low temperatures, apparently gave methylene signals in the spectrum. The chemical shifts of the 2,4,6-trialkylbenzenium ions are shown in Table 3, compared with those cited in the literature.

The results show that the 2,4,6-trialkylbenzenium ion is evidently formed in the complex layer of the $AlCl_3$–HCl system, much as in other superacid systems, and that those ions from *i*-Pr_3B and *s*-Bu_3B are substantially stable even at room temperature. As the molar ratios of *i*-Pr_3B and *s*-Bu_3B to HAl_2Cl_7 are almost 1 (1.3 for *i*-Pr_3B and 1.1 for *s*-Bu_3B), the complex layer may mainly consist of the following product:



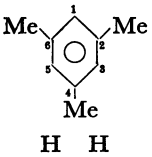
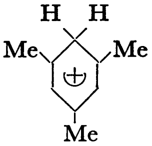
R=*i*-Pr, *s*-Bu

On the other hand, the molar ratios of 1,3,5-trialkylbenzenes to HAl_2Cl_7 in the complex layers of Me_3B and Et_3B are 4.5 and 1.9 respectively. These two complex layers are considered to be formed by both 1,3,5-trialkylbenzene and its protonated product, and to be in a certain equilibrium state by means of proton exchange as follows:



R=Me (*n*=3.5), Et (*n*=0.9)

In these states, the spectra of complex layers may exhibit fused signals between 1,3,5-trialkylbenzene and the 2,4,6-trialkylbenzenium ion. The chemical shift of the fused signal may be estimated by means of the molar ratio of two components. An example of calculation for Me_3B will be given:

	Molar ratio	Unsubstituted carbon		Me substituted carbon	
		C_1	C_3, C_5	C_2, C_6	C_4
	3.5	127.6		137.7	
	1.0	54.5	134.8	193.3	193.3
		108.0		193.3	
Fused signal calcd		123.3		150.1	
Fused signal obsd		123.3		151.6	

The calculated chemical shift of the fused signal agreed fairly well with the observed one. In the case of

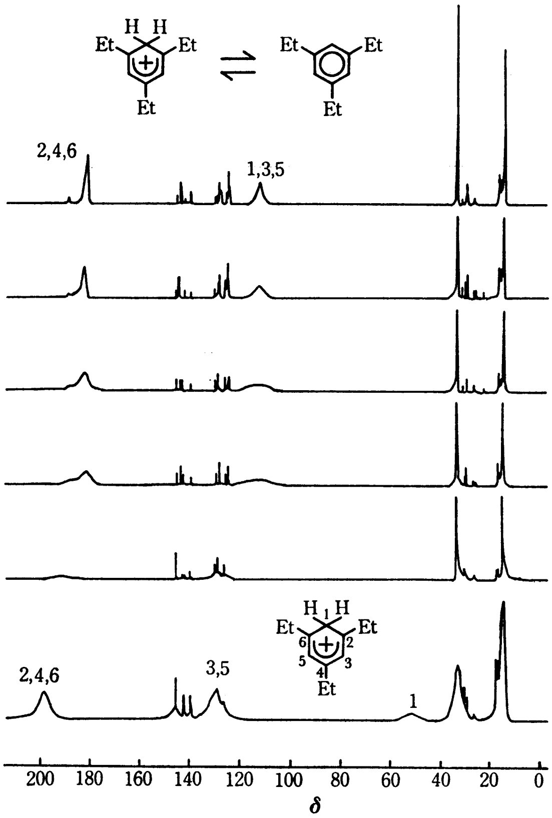


Fig. 3. Temperature-dependent ^{13}C NMR spectra of 1,3,5-triethylbenzene complex layer.

Et_3B, the calculated chemical shift of unsubstituted carbon (δ 113.8) agreed with the observed one (δ 114.0), but that of methyl-substituted carbon (δ 172.6) showed a considerable difference from the observed one (δ 182.5). This difference results from the existence of disproportionated products in the case of Et_3B.

Temperature-dependent ^{13}C *NMR Spectra of the* Et_3B *Complex Layer.* The ^{13}C NMR spectra of the Et_3B complex layer were measured in the temperature range from −50 to 110 °C; the results are shown in Fig. 3. A lot of small sharp signals observed at about δ 140 and 30 are attributable to the formation of disproportionated products. The spectrum obtained at −50 °C apparently exhibited a ring methylene signal, which indicates the presence of the 2,4,6-triethylbenzenium ion. In the spectrum at −25 °C, the weak, broad signals of ring carbons are interpreted as indicating that the life-time of the two components decreases through the critical range in the proton exchange at this temperature. At elevated temperatures the signals tend to coalesce in a singlet and to sharpen with the increase in the temperature.

All these pieces of evidence support the idea that some parts of the 1,3,5-trialkylbenzene in the complex layer are protonated by HAl_2Cl_7 and are in a certain equilibrium state with other parts by means of proton exchange.

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5) In the ^1H NMR spectrum of **1**, the chemical shifts are δ 1.3 (m, CH_3), δ 2.1 (s, CH_2), δ 2.8 (m, CH), δ 5.9 (s, $=CH_2$), and δ 7.1 (m, ring H) in a ratio of 12: 2: 1: 2: 3.

6) G. A. Olah, *J. Am. Chem. Soc.*, **86**, 932 (1964); G. A. Olah and Y. K. Mo, *ibid.*, **95**, 6827 (1973).

7) D. G. Farnum, *J. Am. Chem. Soc.*, **86**, 934 (1964).