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REACTION OF ALKYLBENZENE. A STUDY ON THE COMPLEX LAYER OF ALKYLBENZENE - ALUMINUM CHLORIDE - HYDROGEN CHLORIDE USING NMR AND IR SPECTROSCOPIES

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Recently, several kinds of alkylbenzenium cations formed in strong acids have been studied in frozen states by NMR spectroscopy.1-4) These investigations are very interesting for understanding reaction mechanisms of alkylbenzene. We wish to report here some evidence for the presence of n-propylbenzenium cations in the complex layer of a n-PrPh - $AlCl_3$ - HCl system by means of NMR and IR spectroscopies.

The preparation of the n-PrPh - $AlCl_3$ - HCl system was carried out under the condition of deficient hydrogen chloride. About 3 g of aluminum chloride placed in a long side tube of a reaction vessel, was sublimed and transferred gradually into an almost equal amount of n-propylbenzene in the vessel immersed in an ice bath. During the sublimation, HCl gas5) was firstly evolved and absorbed into n-PrPh, and then the sublimed $AlCl_3$ was dissolved in proportion to the amount of the absorbed HCl. The preparation was carried out under 2 mmHg for 70 min. The mixture was separated into two layers: hydrocarbon as an upper layer and a viscous colored complex as a lower one. The latter complex layer having similar constituents in each run can be held stably for a few weeks at room temperature.

The ^{1}H-decoupled ^{13}C NMR spectrum6) of the complex layer [FIG. 1 (b)] showed signals similar to those of the starting material [FIG. 1 (a)] and in addition some new signals. Among the ring ^{13}C signals, a signal at + 64.3 ppm (from CS_2) probably due to a benzene ring was enhanced. By considering each intensity of the ring ^{13}C signals, we can predict that there are about equimolar amounts of two kinds of n-propylbenzenes in the complex layer: one is ordinary n-propylbenzene and another is a dissociated one, of which n-propyl group is

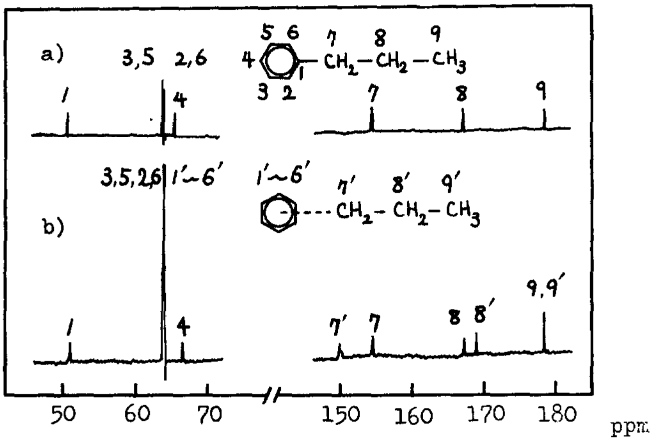
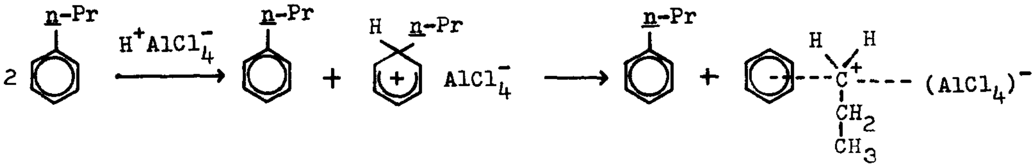


FIG. 1. ^{1}H-decoupled ^{13}C NMR spectra of starting n-propylbenzene (a) and its complex layer (b) at 26 °C.

liberated.

This consideration is also supported by the presence of two sets of ^{13}C signals due to the n-propyl group. One set is the same as that of the starting material and another one [7', 8', and 9' in (b)] is assigned to the dissociated n-propyl group.



(I)

The chemical shift value (150.5 ppm) of the α-CH_2 carbon of the dissociated n-propyl group is much larger than that expected from a trivalent carbenium ion reported by Olah,$^{7)}$ who postulated that carbocation centers in trivalent carbenium ions are highly electron-deficient but those in penta- or tetra-coordinated carbonium ions are less electron-deficient.$^{8)}$ Therefore, the α-CH_2 carbon appears to be cation center of a penta- or tetra-coordinated carbonium ion rather than that of a carbenium ion. Consequently, the n-propyl group liberated from the benzene-like ring [1] is not completely dissociated, and might have some interaction with $AlCl_4^-$.$^{9)}$

Similar findings were obtained.in the ^{1}H NMR spectrum$^{6)}$ of the complex layer (FIG. 2), in which the presence of two kinds of proton signals due to *n*-propylbenzene is ascertained clearly.[10)]

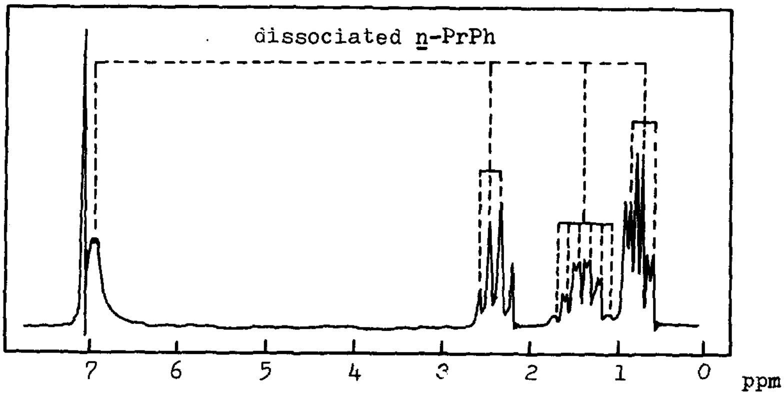


FIG. 2. ^{1}H NMR spectrum of the *n*-propylbenzene complex layer at 22.5 °C (TMS = 0 in δ ppm).

In FIG. 3, the IR spectrum of the complex layer is shown in comparison with that of a benzene complex layer.[11)] The spectrum (a') showed two new strong bands at 1610 and 1476 cm^{-1}, besides all of the absorption bands of the spectrum (a). These two bands may correspond to those of a benzenium ion (b')[12)] at 1595 and 1478 cm^{-1}. Further, almost all of the absorption bands of the benzene complex layer (b') were observed in the spectrum (a'). These facts also provide evidence for the existence of the benzene-like ring.

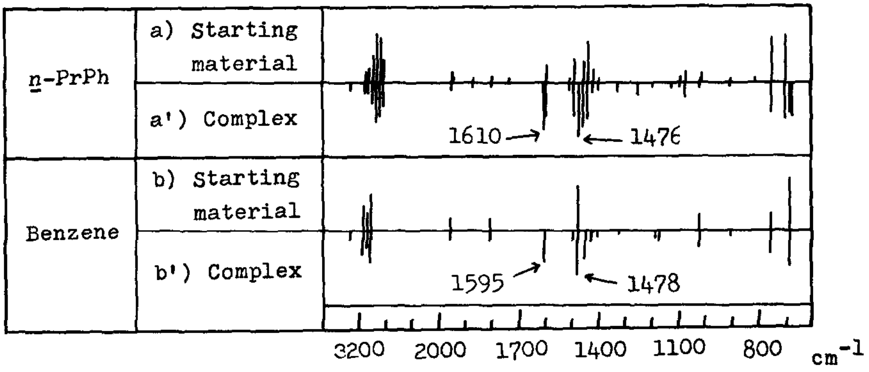


FIG. 3. Schematic IR spectra of *n*-propylbenzene and benzene, and of their complex layers at room temperature.

Similar results were obtained in the NMR and IR spectra of *n*-butylbenzene complex layer; ^{13}C NMR (1C : 50.1, 2,3,5,6,$1'\sim6'$C : 64.3, 4C : 66.1, 7'C : 152.6, 7C : 156.8, 8C : 158.6, 8'C : 160.9, 9C : 169.5, 9'C : 169.9, 10C : 178.4, 10'C : 178.8 ppm) ; IR (new strong bands : 1609 and 1475 cm^{-1}).

From all of the present results, it is concluded that the complex layer mainly consists of two kinds of *n*-RPh: the dissociated alkylbenzene and the ordinary one. However, mutual relation of two kinds of alkylbenzenes in the complex layer is not clear at the present investigation.

References

1) C. MacLean and E. L. Makor, *Discuss. Faraday Soc.* 165 (1962).
2) D. G. Farunum, *J. Amer. Chem. Soc.* **89**, 2970 (1967).
3) V. A. Koptyug, A. I. Rezvukhine, E. T. Lippma and T. Pehk, *Tetrahedron Lett.* 4009 (1968).
4) R. Nakane, *Nippon Kagaku Zasshi* **90**, 17 (1969).
5) HCl gas was generated by the reaction of $AlCl_3$ with moisture which was adsorbed on the catalyst.
6) The ^{1}H-decoupled ^{13}C NMR spectra were recorded on a JEOL C-60HL spectrometer with a 15.09 MHz RF unit. The chemical shifts were measured relative to CS_2. The ^{1}H NMR spectrum was obtained on a JEOL JNM-3H-60 spectrometer with TMS as an external standard in the neat liquid.
7) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.* **91**, 5801 (1969).
8) G. A. Olah, *ibid.* **94**, 808 (1972); G. A. Olah and A. M. White, *ibid.* **91**, 3954, 6883 (1969).
9) The contents of Al and Cl in the complex layer were 5.9 ± 1.0 and 27.0 ± 2.0 wt%, respectively.
10) The signals of the dissociated *n*-propyl group were assigned by referring to the shifts of ^{13}C signals.
11) Since $AlCl_3$ hardly dissolved in benzene under the presence of HCl, the complex layer of benzene was prepared with $AlBr_3$ and HBr. The contents of Al and Br in the complex layer were 5.1 ± 1.0 and 51.2 ± 2.0 wt%, respectively.
12) The ^{13}C and ^{1}H NMR spectra of the benzene complex layer did not show two kinds of signals but a single one. Therefore, the proton exchange probably proceeds between benzene and its benzenium ion intermolecularly as well as intramolecularly (Ref. 1, and also see G. A. Olah, et al, *J. Amer. Chem. Soc.* **94**, 2034 (1972)). Then, benzene in the benzene complex layer seems to behave like a single species of benzenium ion.