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^{13}C NMR STUDY OF THE 1-ISOPROPYL-INDANYL-ION IN METHYLENE CHLORIDE SOLUTION

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Abstract—^{13}C NMR study of the reaction between 3-isopropyl indene and trifluoromethane sulfonic acid in methylene chloride solution at −70° shows the presence of 1-isopropyl indanyl cation. Proposed assignments of the chemical shifts show charge delocalisation due to the aromatic ring.

Study of the reaction of 3-alkyl-substituted indenes with Lewis or Brönsted acids is of interest as these monomers are highly reactive in cationic polymerisation, as shown by Marechal.[1] This author also showed that the 3 - alkyl - substituted - indenes do copolymerise with indene, but do not homopolymerise because of steric hindrance of the double bond. Consequently in reaction with Lewis or Brönsted acids they can be used as model compounds for cationic polymerisation initiation studies. When the dielectric constant of the reaction medium is high, it has been shown that some of the Lewis acids of general use in cationic polymerisation seem to react directly with monomer molecules to give active centres, and this initiation reaction does not seem to need any cocatalytic help.[2–5] The need of cocatalysis for cationic polymerisation initiation has been controversial for many years. The products of the reaction of 3-alkyl indenes with titanium tetrachloride was observed bo be carbocations.[6]

In order to make a comparison we have studied the reaction of 3-isopropyl indene with trifluoromethane sulfonic acid. This acid is strong, but neither oxidizing nor sulfonating. It has been shown to give very clean reactions and has already been used in our laboratory.[16]

Since the work of Olah's group, NMR has proven to be very useful in determining the structure of carbocations.[7–9] A study of a species, stable in methylene chloride at low temperature, is reported using ^{13}C pulse NMR spectroscopy.

1. EXPERIMENTAL

Preparation of reactants. 3-Isopropyl indene was prepared according to Marechal.[10] This monomer was handled under vacuum and purified over sodium films as described.[2] It was then stored under vacuum in sealed phials. The final product was pure 3-isopropyl-indene. This was shown by the ^{13}C NMR spectrum, which is discussed in further detail below. Trifluoromethane sulfonic acid (Schuchardt) was distilled at reduced pressure under N_2 (E 3.8 Torr = 81°) in order to achieve a separation from monohydrate H_3O^+, $CF_3\ SO_3^-$. After the head fraction had been discarded the next fractions were collected in phials equipped with break seals. These phials were sealed under vacuum, the acid content being frozen using liquid N_2. The acid obtained by this method was colourless and has been used without further treatment.

The solvent used was a mixture of protonated and deuteriated CH_2Cl_2 in order to introduce, into the reaction medium, a concentration of deuterium high enough to allow the use of the internal lock of the NMR apparatus. These solvents were handled under vacuum and purified over P_2O_5 films lying on the walls of the storage vessels, as described.[2]

NMR *analysis.* The apparatus was a Jeol PS 100 F.T. working at 25.15 MHz using an EC 100-20 K computer. The sampling tube was filled by condensation under vacuum beginning with the less volatile compound: monomer first, then methylene chloride and trifluoromethane sulfonic acid last. When complete freezing was achieved the sampling tube was sealed off. The temp. of the NMR tube was then allowed to increase to −78° in a dry ice bath in which the tube was shaken in order to promote mixing. It was then transferred to the NMR apparatus cell at −70°. This temp. was kept constant during spectral scanning.

UV *spectra recording.* The mixture was made under vacuum with very carefully purified reactants in all sealed apparatus bearing a UV cell, as described.[20] However in the case of H_2SO_4 the mixture was made in an open cell through a rubber cap introducing a soln of 3-isopropylindene in CCl_4 into a soln of H_2SO_4 in the same solvent. Titanium tetrachloride, purified as reported,[4] and trifluoromethane sulfonic acid were used as in the case of NMR experiments. The concentration of reactants was lower because of the high extinction coefficient of the absorbing species. The spectra were recorded at −70°.

RESULTS AND DISCUSSION

Using UV spectroscopy, we report here the result of a preliminary study of the reaction between 3-isopropyl indene and various Brönsted or Lewis acids. Curve b, Fig. 1, shows that the species produced by reaction with sulfuric acid in carbon tetrachloride at room temperature has a maximum absorption wave length of 318 nm, while curves a and c show that the species produced using respectively trifluoromethane sulfonic acid and titanium tetrachloride at −70° in methylene chloride solvent have the same maximum absorption wave length of 322 nm. The fact that a Brönsted acid seems to give the same absorbing species as a Lewis acid by reaction with a model compound of cationically polymerising monomer rises the problem of the true nature of the reactive species. Direct identification of the species using titanium tetrachloride is very difficult because of the lack of sensitivity of the ^1H or ^{13}C NMR spectroscopy. But in the case of trifluoromethanesulfonic acid the reaction seems to proceed at complete conversion, even at relatively high concentrations. Study of the reaction product between trifluoromethane sulfonic acid and 3-isopropyl indene was also necessary to see whether there is no side reactions in this system (Friedel and Crafts alkylation of the aromatic nucleus for instance).

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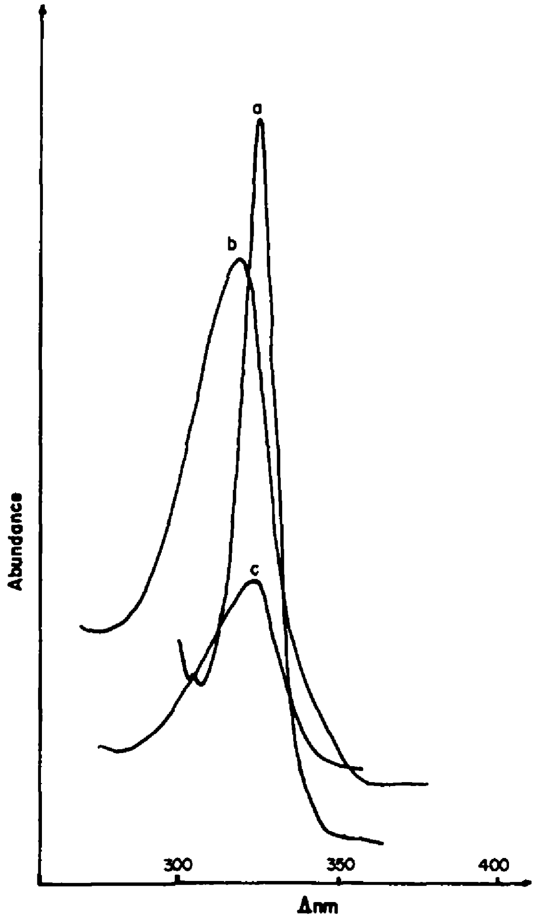
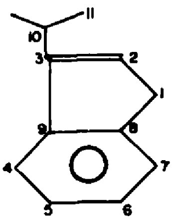


Fig. 1. UV Spectra of various reaction mixtures. (a) 3-Isopropyl indene (2.9×10^{-3} m/l), CF_3SO_3H (0.8×10^{-3} m/l), CH_2Cl_2, −70°. (b) 3-Isopropyl indene (0.6×10^{-3} m/l), $H_2SO_4 + CCl_4$, 20°. (c) 3-Isopropyl indene (0.2×10^{-3} m/l), $TiCl_4$ (2.9×10^{-3} m/l) CH_2Cl_2, −70°.

A ^{13}C NMR spectrum of the monomer model molecule in deuteriated CH_2Cl_2 is shown in Fig. 2. The ten peaks can be assigned to the different carbon nuclei of the 3-isopropyl indene molecule:



The two Me carbons of the isopropyl group being equivalent eleven peaks should be observed. The three peaks in the aliphatic part of the spectrum can be assigned by the off-resonance technique respectively to the C_{11}, C_{10} and C_1 atoms (down field shifts) as in Fig. 2. The first high field peak of the unsaturated carbon region of the spectrum can be assigned to the C_2 carbon atom in the same way. The group of four peaks in this aromatic region are assigned to the C_4, C_5, C_6 and C_7 carbon atoms taking into account the off-resonance spectrum. However, in order to afford a more accurate assignment it is necessary to use the work previously reported on indane {11}. Then the 125.8 ppm peak is assigned to the C_5 resonance, the 125.2 to the C_6 resonance, the 124.4 to the C_4 resonance and the 123.8 to the C_7 carbon atom resonance. Now the resonance of the three atoms C_8, C_9 and C_3 must be found. The 144.9 ppm resonance to the $C_8 + C_9$ carbon atom group and the 151 ppm to the C_3 carbon atom is the most suitable assignment. Another assignment would be C_2C_3 to the 144.9 ppm resonance and C_9 to the 151 ppm one. However there is strong evidence that the former must be considered taking into account that in the indane molecule the C_8 and C_9 resonances appear at the same position (144.1 ppm) very close to the one observed here for indene.

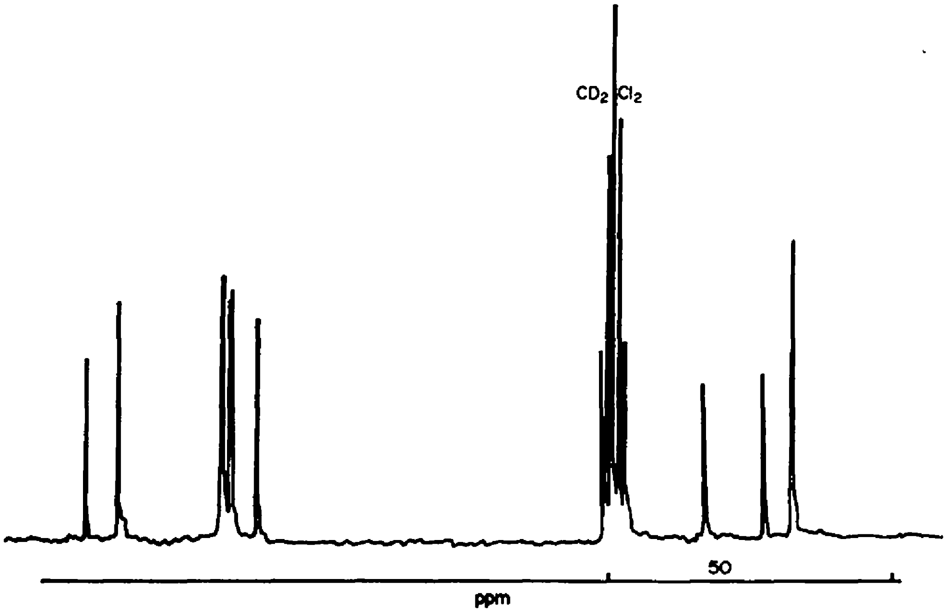


Fig. 2. Noise decoupled ^{13}C NMR spectrum of 3-isopropyl indene, in partly deuteriated methylene chloride, at −70°.

The chemical shifts of the various C atoms of indane, indene, 3-isopropyl indene, and 1-isopropyl-indanyl ion obtained by a reaction between 3-isopropyl indene and trifluoromethane sulfonic acid are given in Table 1.

The ^{13}C NMR spectrum of the mixture of 3-isopropyl indene with trifluoromethane sulfonic acid in methylene chloride is shown in Fig. 3. Eleven peaks can be seen and are assigned to the 1-isopropyl-indanyl ion as shown in Table 1. However, enlarged peaks in the aromatic region are also noticed. They must be assigned to by-products of the protonation reaction since the spectrum of the substituted indene alone does not show the presence of any impurity. Dimers, for instance, can be produced since we have seen that the protonation is not very fast and can be continued in the sampling tube. Polyalkylation can also occur to a limited extent.

The assignment shown in the Table 1 takes into account the fact that the C_2–C_3 double bond must disappear by protonation and, consequently, the C_2 carbon becomes aliphatic.

The assignments listed in Table 1 and the variations of chemical shifts of the C atoms are consistent with the formation of 1-isopropyl-indanyl cation. Indeed there is a variation of chemical shift of 76.1 ppm for the C_2 carbon atom, corresponding to the difference between 119.3 ppm and 43.4 ppm. This value is smaller than the one which could be observed for a transformation from sp^2 to sp^3 hybridization for a C atom. Note for instance the difference of 95 ppm between the corresponding carbon of stylene and ethylbenzene.[13] There is also a difference of 87 ppm for the same type of C atom between α-methylstyrene[12] and isopropylbenzene.[13] Again the difference is 96 ppm for the same carbon between indene and indane.[14] The smaller difference reported here is explained by the positive charge located mainly at the α position of this C atom. We have assigned the resonance at 214.3 ppm to the C_3 carbon atom which bears most of the positive charge. This is strongly supported by the fact that the C_{10} carbon atom shows a low field shift (+7 ppm). If this C atom were at the α position of a double bond which simply transformed into a saturated single bond, a high field shift (−3 ppm) would be observed.

Assignment of the observed resonance at 178.3 ppm to the C_8 carbon atom is supported as follows: there must be a strong correlation between the phenomenon that we observe here and those observed on cations derived from cumene:[15]

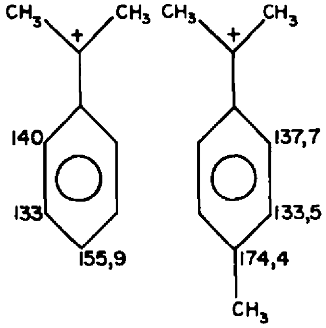


Table 1. ^{13}C magnetic resonance data for indane, indene, 3-isopropyl indene and isopropyl-indanyl ion

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
Indane	33.6	25.6	33.6	125	126.4	126.4	125.0	144.1	144.1	—	—
Indene	38.8	120.9	132.0	123.5 +	124.5 +	126.2 +	133.8	144.8	132.5	—	—
3-Isopropyl indene	37.5	119.3	151.1	124.4	125.8	125.2	123.8	144.9	144.9	27.1	22
1-Isopropyl-indanyl ion†	37.7	43.4	214.3	142.4	131.2	152.5	128.4	178.3	132.7	34.1	21.5

†Chemical shifts in ppm measured against CH_2Cl_2 and converted from TMS using the conversion factor: $\delta CH_2Cl_2/TMS = 53.8$ ppm.

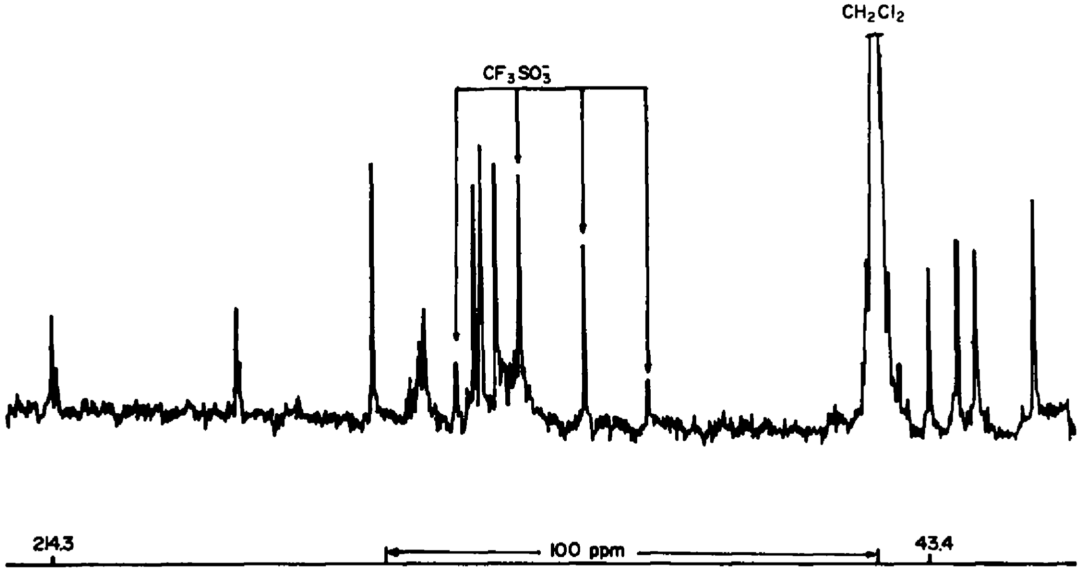


Fig. 3. Noise decoupled ^{13}C NMR spectrum of 1-isopropyl-indanyl ion, in partly deuteriated methylene chloride, at −70°.

For these species it is noticed that the Me substituted C atom in the ring is strongly deshielded. In other words, the donating effect of the Me group induces a more important localisation of the positive charge on the C atom which bears the Me group. The same effect is probably operating in this cationic species.

At present it is not possible to derive an unambiguous assignment for the resonance of the C_5, C_7 and C_9 carbon atoms corresponding to the resonances observed at 132.7–131.2 and 128.4 ppm. C_9 is a C atom of an aromatic ring and is located at the α position of the cation.[19] The corresponding chemical shift must change only slightly, as in the case of the cumyl ion.[18] Then it may be assumed to absorb at 132.7. The assignment of C_5 and C_7 resonance follows the order observed in the indane molecule. The assignment of C_4 and C_6 is proposed according to the observations made on cumyl ion. Whatever the assignment, the normal behaviour for an aryl substituted cation is seen clearly.

CONCLUSION

This work has attempted to show the almost quantitative creation of the 1-isopropyl-indanyl cation through protonation of 3-isopropyl indene by trifluoromethane sulfonic acid in methylene chloride solvent at −70°.

This also allows a clear assignment of the UV spectrum observed with the same system. This identification is very important for the interpretation of the mechanism of the initiation reaction of cationic polymerisation.[17]

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