A. I. Kitova and Ya. M. Varshavskii

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Abstract

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A. I. Kitova and Ya. M. Varshavskii

Electronic Absorption Spectra of Solutions of Aromatic Hydrocarbons in Liquid HCl in the Presence of $AlCl_3$

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In certain conditions, aromatic hydrocarbons in solutions exhibit the ability to add protons from molecules of protonic solvents and to give the corresponding carbonium ions. The suggestion of processes of this kind was first put forward by Hammett (^{1}), according to whom, in solutions of liquid hydrogen fluoride, the corresponding reactions proceed according to the scheme:

$$\mathrm{Ar} + \mathrm{HF} \rightleftarrows \mathrm{ArH}^+ + \mathrm{F}^-.$$

Subsequently this scheme was confirmed experimentally by the example of solutions of certain aromatic hydrocarbons not only in liquid hydrogen fluoride ($^{2-6}$), but also in sulfuric acid (^{7}) and in trifluoroacetic acid (^{8}). A number of authors ($^{8-10}$) carried out a parallel study of the process of formation of carbonium ions of the ArH^+ type and of isotopic exchange of hydrogen with the solvent; it was shown that the exchange rate is the greater, the higher the concentration of ions.

Ionization of aromatic hydrocarbons with the formation of positively charged hydrocarbon ions may also occur by a fundamentally different route, namely as a result of the removal of an electron from the hydrocarbon molecule. Ionization of this kind in solutions of strong acids in the presence of oxidizing agents has recently been studied in detail in the work of Aalbersberg, Mackor, and others (^{11}). If the solvent is a protonic compound and at the same time possesses oxidizing properties (for example, H_2SO_4), or contains an oxidizing agent as an impurity (for example, oxygen from the air), then both processes may proceed simultaneously, and the formation of positively charged ions of both types will take place in the solution. It is also necessary to take into account the possibility of the formation of complexes between hydrocarbons and solvent molecules.

The absorption spectra of the carbonium ions and complexes that are formed must differ sharply from the spectra of neutral molecules. Therefore, one of the most convenient methods for identifying these highly unstable particles, which apparently exist only in solutions, and also for investigating the conditions of their formation, is the spectral method. This method is also convenient because the absorption spectrum of ions does not depend very strongly on the degree of their solvation, nor on whether they are in the free state or are constituents of associated ion pairs. Small differences in the positions of the corresponding

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

absorption bands undoubtedly exist and, in a number of cases, can be recorded; however, they are so small that they cannot in any way compare with the differences between the spectra of ions and molecules. Unlike molecules, ions have characteristic absorption spectra not only in the near ultraviolet but also in the visible region, and therefore possess highly specific and vivid colors.

Anhydrous liquid hydrogen chloride is of great interest as a strong protogenic solvent which, relatively easily (especially in the presence of catalysts), donates a proton to the molecule of an aromatic compound, without at the same time causing secondary and irreversible chemical change of the corresponding substance. There are studies devoted to possible ways of using liquefied HCl in industry[12], as well as to investigation of the properties of solutions in liquid HCl at low temperatures[13,14]. In Ref.[15], hydrogen isotope-exchange reactions in solutions of liquid DCl at room and elevated temperatures were studied with the use of sealed apparatus made of Monel metal.

Fig. 1. Optical transparency of a solution of $AlCl_3$ in liquid HCl at room temperature.
$C_{AlCl_3} \simeq 2 \cdot 10^{-3}$ mol/l, $d = 26$ mm

The experimental difficulties that arise in working with pure liquid HCl at room temperature are due, on the one hand, to the high elasticity of its vapor (46 atm. at 25°C and 78 atm. at 50°), which makes it impossible to use glass and plastic apparatus, and, on the other hand, to the strong corrosive ability of HCl, which hinders the use of base metals.

We have developed apparatus made of Monel metal and platinum that makes it possible to prepare solutions quantitatively in pure HCl at room temperature under pressures up to 100 atm. Along with this, a special cuvette was designed and constructed with sufficiently thin plane-parallel transparent windows of crystalline aluminum oxide (colorless ruby)* and thick-walled windows of quartz glass, which provide good transmission in the near ultraviolet, visible, and also infrared regions of the spectrum and withstand the required pressure. The diameter of the windows is 20 mm; the normal thickness of the solution layer is 26 mm.

Fig. 2. Absorption spectra of solutions of hexamethylbenzene and pyrene in liquid $HCl + AlCl_3$ ($d = 26$ mm).
1 –hexamethylbenzene, $C \simeq 8 \cdot 10^{-3}$ mol/l, $C_{AlCl_3} \simeq 2 \cdot 10^{-3}$ mol/l; 2 –pyrene, $C \simeq 6 \cdot 10^{-5}$ mol/l, $C_{AlCl_3} \simeq 2 \cdot 10^{-3}$ mol/l

Figure 3

Figure 3: Figure 3

Figure 4

Figure 4: Figure 4

The body of the cuvette is made of metal and is lined on the inside with Fluoroplast-4[**]. Some parts of the cuvette that are in direct contact with the solution under study, as well as the test tubes, are made of platinum. With this apparatus, on an SF-4 spectrophotometer with a somewhat modernized cuvette chamber, the absorption spectra of solutions of a number of aromatic hydrocarbons both in pure liquid HCl and in the presence of $AlCl_3$ additives. All the compounds studied form brightly colored solutions in the presence of $AlCl_3$. Thus, hexamethylbenzene gives a yellow solution, naphthalene a ruby-red one, β-methylnaphthalene a reddish-brown one, fluorene a lilac-red one, anthracene a yellow-green one, pyrene a lemon-yellow one, etc.

Figure 1 shows the optical transparency of a solution of $AlCl_3$ in liquid HCl. It is easy to see that this solution, used as the solvent, contained no absorbing contaminants or impurities, and at wavelengths greater than 300 mμ its absorption can practically be disregarded. The absorption spectra of some of the solutions we studied are given in Figs. 2–4. All the spectra shown have characteristic maxima in the visible region. For anthracene and pyrene, along with bands in the visible region of the spectrum, one can observe a system of narrow bands in the near ultraviolet, corresponding to absorption by nonionized molecules of the initial hydrocarbon.

Fig. 3. Absorption spectra of solutions of β-methylnaphthalene and anthracene in liquid HCl + $AlCl_3$ ($d = 26$ mm). 1—β-methylnaphthalene, $C \simeq 2 \cdot 10^{-3}$ mol/l, $C_{AlCl_3} \simeq 2 \cdot 10^{-3}$ mol/l; 2—anthracene, $C \simeq 6 \cdot 10^{-5}$ mol/l, $C_{AlCl_3} \simeq 2 \cdot 10^{-2}$ mol/l.

Fig. 4. Change of spectra with time: 1a—fluorene solution 30 min after preparation ($C = 3.8 \cdot 10^{-4}$ mol/l, $C_{AlCl_3} \simeq 2 \cdot 10^{-3}$ mol/l); 1b—the same solution after 12 h; 2a—phenanthrene solution 30 min after preparation ($C \simeq 1 \cdot 10^{-2}$ mol/l; $C_{AlCl_3} \simeq 2 \cdot 10^{-3}$ mol/l); 2b—the same spectrum after 24 h.

Practically in all cases, the observed spectra change with time. Such a change may be illustrated by the example of a fluorene solution. The three absorption maxima in the spectrum of this solution in the visible region (380, 450, and

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[*] The use of this material for studying spectra in liquid HF is described in Refs.[16,17].

[**] The construction of the cuvette will be described separately.

560 mμ) are responsible for the exceptionally bright color of this solution; its intensity gradually increases after the solution is prepared over the course of a day, after which it remains unchanged. An analogous picture is also observed in the case of other solutions. Figure 4 shows the change with time of the spectra of fluorene and phenanthrene. Such a change is apparently connected with the fact that the processes by which the absorbing species arise under the conditions studied proceed with time. We believe that the spectra we observed (in the absence of oxidizing agents) are due to absorption by carbonium ions formed as a result of the reversible reaction of addition of protons from solvent molecules to hydrocarbon molecules according to the Hammett scheme given above. This assumption is supported, in particular, by comparison of the spectra of some of the compounds studied with the spectra of solutions of these same compounds in liquid HF in the presence of BF_3 (see Table 1). It is easy to see that, in the cases of hexamethylbenzene, phenanthrene, and pyrene, the positions of the absorption bands in both solvents practically coincide. For β-methylnaphthalene, the correspond-

general data in the literature are lacking. As for anthracene, in solution in liquid HF (^{4,11,18}) there is one broad band with a maximum at 400 mμ. The spectrum obtained by us has one narrow band at 440 mμ and one broad band at 680 mμ. The absence of a system of narrow bands of molecular anthracene in HF solution is consistent with the assumption of complete ionization of anthracene in the presence of BF_3, whereas in HCl solution ionization does not proceed to completion even in the presence of $AlCl_3$.

Table 1

Substance	$HF + BF_3$(Reid' s data)(mμ)	$HCl + AlCl_3$(mμ)
Hexamethylbenzene	390	370–400
Phenanthrene	410 and 520	410 and 560
Pyrene	470 and 380	470 and 380

In light of the data obtained, the question of the nature of the carbonium ions formed is of interest. The characteristic spectra in the visible region observed by us arise, in the case of solutions, only for those compounds whose molecules, according to the available data (see, for example, (^{6})), have regions with sharply increased electron density at individual carbon atoms of the aromatic ring. This circumstance permits the supposition that the processes of formation of π-complexes in the systems studied are less probable than the processes of ion formation as a result of proton addition at a double bond, which, apparently, are responsible for the appearance of the coloration and the observed spectra. The investigation of the corresponding systems is continuing.

Physicochemical Institute
named after L. Ya. Karpov

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Note: Figure translations are in progress. See original paper for figures.