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INFRARED SPECTRA AND THE STRUCTURE OF AROMATIC CARBONIUM IONS

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Aromatic carbonium ions are formed as a result of the addition of a proton to the molecule of an aromatic hydrocarbon. The formation of such ions as an intermediate stage is involved in numerous and very important reactions of organic chemistry (see, for example, ([1,2])), in connection with which the question of the structure of these compounds is of considerable interest. At present the most widespread and well-supported view is that of the σ-complex structure of aromatic carbonium ions ([3,4]), according to which the proton is attached to one of the carbon atoms of the aromatic nucleus by means of a σ bond, analogous to an ordinary aliphatic C—H bond and formed by two electrons from the aromatic sextet localized on the hybrid sp^3-orbital of the carbon atom (structure I)

$$\left[\text{ benzene ring } \mathrm{C}_1\!\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right]^{+} \qquad \text{(I)}$$

In the limiting case both hydrogen atoms at C_1 are equivalent and are arranged symmetrically with respect to the plane of the ring. (Such a structure is usually assumed.) Aromatic carbonium ions in high concentrations (up to 100%) can be obtained by dissolving the corresponding hydrocarbons in strong acids; the systems most suitable for the study of infrared spectra are σ-complexes with aluminum halides, formed by the interaction of equimolar amounts of ArH, HHal, and $\mathrm{Al_2Hal_6}$. According to data from very detailed physicochemical studies ([3]), these complexes have an ionic structure

$$\mathrm{ArH_2^+ \cdot Al_2Hal_7^-}.$$

Layers of the complexes for spectral investigation were obtained by reacting a thin layer of aluminum bromide, sublimed in a vacuum cuvette onto a KBr substrate (or $\mathrm{CaF_2}$ in control experiments, which confirmed the inertness of KBr toward the complexes under the experimental conditions), in the presence of an

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excess of hydrogen bromide. The complex-formation reaction was carried out at temperatures from $-40°$–$-20°$ (benzene) to $+20°$ (anthracene). The spectra were recorded at a sample temperature of about $-100°$.

Some of the spectra obtained are presented in Figs. 1 and 2. Complex formation leads to a considerable change in the spectra of the hydrocarbons in the region 1600–600 cm^{-1}, which is quite natural in view of the strong perturbation of the π-electron system, which to a significant degree determines the features of the force field and the values of the electro-optical parameters of the molecules considered. However, what first attracts attention is the great similarity between the spectrum of the σ-complex of benzene and the spectra of monosubstituted benzenes, for example toluene (see Fig. 1). Comparison with the data of A. M. Bogomolov (^{5}) shows that in the spectrum of the σ-complex of benzene all the absorption bands characteristic of monosubstituted benzenes are observed, with the exception of the band at 1070 cm^{-1}, and characteristic only in frequency. The result obtained may be explained on the assump-

that the π-electron system of benzene in the σ-complex is perturbed to a considerably lesser extent than is represented in structure I, and the benzenium ion has a structure of type II,

$$\left[\text{benzene ring} - \overset{\overset{\text{H}}{|}}{\text{C}_1} - \text{H}\right]^{+}, \tag{II}$$

in which the added proton is held by a σ-bond formed by electrons located in the p-orbital of the C_1 atom. Perturbations of the π-electron

Fig. 1. IR spectra of aromatic hydrocarbons and their σ-complexes (at $-100°$): 1—benzene, 2—σ-complex of benzene, 3—toluene, 4—σ-complex of toluene

system in this case are analogous to those occurring upon introduction of an electronegative substituent into position I. Such a structure may be called a “localized π-complex,” in contrast to ordinary π-complexes.

(according to Brown and Brady (^{3})), in which the proton (or another acceptor) is assumed to interact equally with all the π-electrons of the aromatic sextet. This conclusion cannot be argued with the same completeness in the case of the σ-complexes of the other hydrocarbons studied, since there are no data on the characteristic frequencies of the corresponding molecules (for example, 4-substituted toluenes or substituted mesitylene).

Fig. 2. IR spectra of mesitylene σ-complexes (at –100°): 1 –mesitylene; 2 –σ-complex of mesitylene, 3 –σ-complex of mesitylene + excess mesitylene, 4 –σ-complex of mesitylene + excess benzene

Figure 2: Fig. 2. IR spectra of mesitylene σ-complexes (at –100°): 1 –mesitylene; 2 –σ-complex of mesitylene, 3 –σ-complex of mesitylene + excess mesitylene, 4 –σ-complex of mesitylene + excess benzene

Fig. 3. Dependence between the position of the maximum of the νCH band and the ionization potential of the hydrocarbon molecule: 1—benzene, 2—toluene, 3—mesitylene, 4—naphthalene, 5—hexamethylbenzene, 6—anthracene

Figure 3: Fig. 3. Dependence between the position of the maximum of the νCH band and the ionization potential of the hydrocarbon molecule: 1—benzene, 2—toluene, 3—mesitylene, 4—naphthalene, 5—hexamethylbenzene, 6—anthracene

Fig. 2. IR spectra of mesitylene σ-complexes (at –100°): 1 –mesitylene; 2 –σ-complex of mesitylene, 3 –σ-complex of mesitylene + excess mesitylene, 4 –σ-complex of mesitylene + excess benzene.

Generally speaking, it may be assumed that, in going from the benzene ion to the ions of polymethylbenzenes and condensed hydrocarbons, there is a gradual transition from structure II to structure I (since in this series the strength of the σ-complexes increases); however, the retention in the spectra of the complexes of a number of bands very characteristic of aromatic systems and belonging to vibrations that are, to a considerable extent, skeletal vibrations of the aromatic ring (for example, the band at 1620 cm^{-1}) makes it possible to extend the conclusion regarding the existence of carbonium ions in

in the form of localized π-complexes for all the systems studied with methylbenzenes.

In the region 2740-2850 cm^{-1}, intense absorption bands were found in the spectra of σ-complexes in a number of cases. Judging by the magnitude of the isotope shift observed when bromohydrogen is replaced by bromodeuterium (deuteration of aromatic hydrocarbons proceeds readily in the systems studied), these bands should be assigned to CH stretching vibrations ($\nu_H/\nu_D = 1.347 \pm 0.007$).

Fig. 3. Dependence between the position of the maximum of the νCH band and the ionization potential of the hydrocarbon molecule: 1—benzene, 2—toluene, 3 —mesitylene, 4—naphthalene, 5—hexamethylbenzene, 6—anthracene

However, the bands at 2740-2850 differ substantially from ordinary bands both in position and in the type of contour—they are very broad, sometimes asymmetric; they resemble the bands of OH and NH groups that have formed hydrogen bonds. The positions of the absorption maxima in these bands exhibit a clear correlation (a linear dependence) with the value of the ionization potential of the hydrocarbon forming the σ-complex (Fig. 3). Special experiments showed that these bands become stronger when an excess of hydrocarbon over the molar amount of hydrogen halide or aluminum halide is ensured (see curves 3 and 4 in Fig. 2). It is known ([3]) that in systems containing an excess of hydrocarbon, carbonium ions are solvated by hydrocarbon molecules, and therefore it is natural to associate the appearance of the bands under discussion with the formation of a solvation shell.*

Frequencies of absorption bands in the spectra of σ-complexes (in cm^{-1}):

1. Benzene complex: 3094, 3073, 3040, 2805, 2760, 2715 . . . 1600, 1503, 1475, 1444, 1409, 1322, 1270, 1204, 1175, 1034, 1010, 981, 953, 900, 865, 815, 783, 767, 693, 641, 581.
2. Toluene complex: 3095, 3058, 3048, 2965, 2925, 2890, 2780 . . . 1612, 1485, 1463, 1343, 1303, 1242, 1220, 1185, 1142, 1018, 1012, 965, 897, 853, 805, 740, 712, 700, 596.
3. Mesitylene complex: 3000, 2960, 2925, 2850, 2790 . . . 1623, 1505, 1470, 1441, 1373, 1362, 1277, 1260, 1250, 1156, 1115, 1033, 1018, 900, 888, 870, 856, 798, 773, 690.
4. Hexamethylbenzene complex: 3000, 2950, 2905, 2800 . . . 1600, 1535, 1472, 1455, 1426, 1375, 1350, 1333, 1265, 1180, 1075, 1062, 1046, 1018, 990, 975, 920, 794, 766, 690.

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* Similar bands have been observed in the spectra of organolithium compounds, and their origin has still not received a satisfactory explanation (^{6}).

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

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