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Abstract

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ON THE ELECTRON-ACCEPTOR ABILITY OF METAL HALIDES AND CARBONIUM IONS

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The study of perturbations observed in the vibrational spectra of molecules during intermolecular interaction can provide valuable information on the nature of the interaction, its mechanism, energy, etc. Such methods have found especially broad application in the study of the hydrogen bond; however, a number of works have shown the fruitfulness of this type of investigation also in the case of extremely strong intermolecular interaction—complex formation occurring by a donor–acceptor mechanism. Thus, it has been shown that the magnitudes of the shifts of certain absorption bands of pyridine ([1,2]), the $\nu C = O$ bands of acetophenone and benzophenone ([3]), dimethylpyron ([4]), ethyl acetate ([5]), and others, in complexes with electron-accepting metal halides—aprotic acids—show a correlation with the interaction energies of these acids with standard bases ([5]), with catalytic activity in acid-catalysis reactions ([3]), and, consequently, may serve as a measure of aprotic acidity—the electron-acceptor ability of metal halide molecules.

In the present work, benzonitrile was chosen as the standard base in determining the relative acidity of various electron-acceptor agents; earlier, a number of studies had shown that the frequency of the valence vibration $\nu C \equiv N$ undergoes a considerable increase when an acceptor is attached to the unshared pair of electrons of nitrogen ([6–11]). Table 1 gives the frequencies of the maximum of the $\nu C \equiv N$ absorption band in various complexes of benzonitrile and the magnitudes of the band shifts, measured from its position in the spectrum of liquid nitrile. As is seen from the data in Table 1, the values of $\Delta\nu C \equiv N$ show a correlation with the values of $\Delta\nu C = O$ of ethyl acetate and $\Delta\nu$ of pyridine, which had previously been used to evaluate the relative acceptor ability of metal halides. It should be noted that from data on the perturbation of the frequencies of donor molecules, just as from thermochemical data ([15,16]), it follows that boron and aluminum halides are the strongest acceptors with respect to oxygen- and nitrogen-containing bases, whereas $SbCl_5$ and $FeCl_3$, which in some model reactions proceeding through the stage of formation of the ion $[MetCl_n]^-$ exhibit catalytic activity considerably higher than BF_3 and $AlCl_3$ ([17]), prove to be

comparatively weak acceptors with respect to nitrogen-containing donors.

The use of a nitrile as the standard base gives two substantial advantages: first, owing to the high characteristic nature of the vibration $\nu C \equiv N$ under study, interpretation of the results obtained is considerably facilitated; second, an interesting possibility is presented of comparing, in comparable quantities, the electron-acceptor ability (Lewis acidity) of metal halides and carbonium ions, which must be very strong aprotic acids ([18,19]). This possibility is connected with the fact that cations of nitrilium salts $[R'—C \equiv N—R]^+$, the syntheses of which have been described by Meerwein et al. ([20]) and Klages et al. ([21]), may be regarded as donor-acceptor complexes formed by the base $R'—C \equiv N$: and the acid R^+. (The latter, generally speaking, is true for any ammonium salts; however, the noncharacteristic nature of the vibrations $\nu C—N$ and the strong perturbation of the vibrations

νNH as a result of hydrogen-bond formation do not allow analogous data to be obtained from the spectra of pyridinium and ammonium ions.) Indeed, as is seen from the data presented, the frequency νC ≡ N in nitrilium salts is perturbed still more strongly than upon interaction with boron halides, which should be associated with the higher electron-acceptor ability of carbonium ions. The electron-acceptor ability of carbonium ions—as measured by the magnitude $\Delta\nu$C ≡ N—turns out to depend on the structure of the ion, chiefly on the type of atom accepting the unshared electron pair of nitrogen. The lowest acceptor capacity

Table 1

Frequency νC ≡ N in the spectra of benzonitrile complexes and nitrilium salts* (in cm^{-1})

Acceptor	νC ≡ N	$\Delta\nu$C ≡ N	$\Delta\nu$ of pyridine**	$\Delta\nu$C = O of ethyl acetate
—	2229			
$BiCl_3$	2244	+15	+14 (2)	−66
$SbCl_5$	2248	+19	+13	
$FeCl_3$	2261	+32	+17 (2)	
$SnCl_4$	2265	+36	+23 (2)	−128 (5)
$TiCl_4$	2265	+36	+21 (2)	−121 (5)
$ZnBr_2$	2270	+41	+21	−111
$ZnCl_3$	2276	+47	+24	−98
$AlCl_3$	2281	+52	+28 (2)	−117 (5)
$AlBr_3$	2285	+56	+28 (2)	−138 (5)
O	2306***	+74	+23 (12)	
BBr_3	2312	+83	+33 (12)	−191 (5)
$C_6H_5^+$	2314	+85		
$C_6H_5—C^+(CH_3)_2$	2321	+92		
$(CH_3)_3C^+$	2323	+94		

Acceptor	$\nu C \equiv N$	$\Delta\nu C \equiv N$	$\Delta\nu$ of pyridine**	$\Delta\nu C = O$ of ethyl acetate
BCl_3	2323	+94	+33 (12); +42 (13)	−176 (5)
BF_3	2327	+98	+33 (14)	−119 (5)
$CH_3{-}CH^+{-}CH_3$	2339	+110		
$CH_2{=}CH{-}CH_2^+$	2345	+116		
$CH_3{-}CH_2^+$	2349	+120		

* The anion in nitrilium salts is $[SbCl_6]^-$.
** Shift of the frequency of the pulsation vibration of the pyridine ring, 992 cm^{-1}.
*** *N*-oxide of 4-chlorobenzonitrile.

is possessed by the aromatic carbon atom; on passing from a tertiary to a secondary and then to a primary carbon atom, the acceptor ability increases, which may be connected with the inductive influence of atoms located in the α-position to the atom—the acceptor. A double bond in the α-position to the atom—the acceptor has an insignificant influence on the acceptor ability.

The very fact of an increase in the frequency $\nu C \equiv N$ upon addition of an acceptor, because of its unusual character, has been discussed repeatedly; moreover, despite the existence of X-ray structural data indicating a shortening of the $C \equiv N$ bond upon complex formation ([22,23]), some authors considered that the increase in frequency is caused by kinematic effects of the interaction of vibrations and does not reflect an increase in the quasi-elastic constant of the $C \equiv N$ bond ([10,11]). Meanwhile, in view of the high characteristic nature of the valence vibrations of the triple bond, the question posed can readily be resolved unambiguously; for this it is sufficient to consider the vibrational problem for the four-atom model C—C N—A. Three possible causes of the increase in frequency upon complex formation and of its different values in complexes with different acceptors should be considered:

1. A change in the mass of the atom—acceptor at unchanged values of the quasi-elastic constants of the C N and N—A bonds. It may be noted that the data given in Table 1 approximately correspond to a linear dependence between $\nu C \equiv N$ and ε_A with

$$\frac{\partial \nu}{\partial \varepsilon_A} = 1000 \text{ cm}^{-1} \qquad \left(\varepsilon_A = \frac{1.088}{m_A}, \text{ where } m_A \text{ is}\right.$$

the mass of atom A in atomic units), although it is not clear whether this dependence is a consequence of the fact that light atoms are stronger acceptors, since they use orbitals with smaller n for acceptance. If this is not so, and the change in acceptor mass directly affects the frequency of the vibration under

consideration, the use of the quantities $\Delta\nu C \equiv N$ to estimate acceptor ability loses its meaning.

2. The change in the frequency $\nu C \equiv N$ in different complexes may reflect a difference in the magnitude of the quasi-elastic constant of the N–A bond; moreover it is natural to expect that, as the strength of the acceptor increases, the value K_{NA} increases. Indeed, from calculation of the spectra of a series of complexes the following values are known: $K_{NSn} = 4.8$[10], $K_{NAl} = 6.5$[24], $K_{NB} = 6.9 \div 7.0$[25,26], $K_{NC^+} = 8.7$[27], which fit a linear dependence of K_{NA} on ε_A with the value

$$\frac{dK_{NA}}{d\varepsilon_A} = 3.5 \cdot 10^6 \text{ cm}^{-2}$$

(here and below, the values of the quasi-elastic constants are given in $1 \cdot 10^6$ cm^{-2}).

3. If the causes indicated above cannot explain the experimentally observed changes in the frequency $\nu C \equiv N$ upon complex formation and in complexes with different acceptors, it should be assumed that the frequency shift is caused by a change in the force field of the nitrile molecule itself.

In the calculation, a potential function of the form

$$2U = K_{CC}q_{CC}^2 + K_{CN}q_{CN}^2 + K_{NA}q_{NA}^2 + Hq_{CC}q_{CN} + H'q_{CN}q_{NA}.$$

The derivatives of $\nu C \equiv N$ were calculated by Mayants' method [28], with variation of the force constants within the limits $K_{CC} = 8.0 \div 8.5$; $K_{CN} = 22.0 \div 31.5$; $K_{NA} = 4.0 \div 8.7$; $H = -2.0 \div +2.0$; $H' = -2.0 \div +2.0$ (the frequency $\nu C \equiv N$ during variations of the force constants was kept equal to 2270 ± 10 cm^{-1}).

It was obtained that

$$\frac{\partial\nu}{\partial K_{CN}} = 35 \cdot 10^{-6} \text{ cm}, \qquad \frac{\partial\nu}{\partial K_{NA}} = 6 - 11 \cdot 10^{-6} \text{ cm}, \qquad \frac{\partial\nu}{\partial\varepsilon_A} = 15 \div 100 \text{ cm}^{-1}.$$

As is easily seen, the value obtained from the calculation, $\partial\nu/\partial\varepsilon_A$, is at least an order of magnitude smaller than the value that must be assumed in order to attribute the observed frequency changes to the effect of the change in acceptor mass. The combined influence of the change in the mass of the acceptor atom and of the change in the quasi-elastic constant K_{NA} can conveniently be estimated by calculating

$$\frac{d\nu}{d\varepsilon_A} = \frac{\partial\nu}{\partial\varepsilon_A} + \frac{\partial\nu}{\partial K_{NA}} \cdot \frac{dK_{NA}}{d\varepsilon_A} = 35 \div 140 \text{ cm}^{-1}.$$

This value also proves to be considerably less than 1000 cm^{-1}, which permits the change in the quasi-elastic constant of the C N bond to be regarded as the principal cause of the change in the frequency $\nu C \equiv N$ upon complex formation. Generally speaking, the frequency $\nu C \equiv N$ is quite sensitive to a change in the off-diagonal force coefficients H and H′:

$$\frac{\partial \nu}{\partial H} = -47 \cdot 10^{-6} \text{ cm} \quad \text{and} \quad \frac{\partial \nu}{\partial H'} = -33 \cdot 10^{-6} \text{ cm},$$

however, in view of the fact that the indicated constants always have a small magnitude, usually less than 10^6 cm^{-2}, the same change in the frequency $\nu C \equiv N$ requires a 20-50 times greater relative change of the constants H and H′ in comparison with the necessary magnitude of the relative change of K_{CN}.

In order to decide whether the observed dependence of the frequency $\nu C \equiv N$ on the structure of the molecule–acceptor at one and the same

atom–the acceptor (boron halide complexes, various nitrile salts), the kinematic consequence of the change in the mass of the atoms situated in the α-position to the atom–the acceptor was evaluated by calculating the quantity $\frac{\partial \nu}{\partial \varepsilon_\alpha}$ (where ε_α is the reciprocal mass of the atoms in the α-position to the atom–the acceptor), which, as was to be expected, owing to the high characteristic nature of the $\nu C \equiv N$ vibration, proved to be very small, +0.2 cm^{-1}; hence it follows that the entire difference in the frequencies $\nu C \equiv N$ is caused in these cases by the dependence of the electron-acceptor ability of the acceptor molecule on its structure.

Experimental part. The IR spectra in the region of absorption $\nu C \equiv N$ were recorded on an IKS-11 instrument with a LiF prism. Because of the high hygroscopicity of the complexes of benzonitrile with metal halides, a cell of special design was used in the work ([6]), making it possible to obtain spectra of complexes prepared in vacuum without exposing them to air. The complexes were obtained by contacting benzonitrile vapor with a layer of metal halide sublimed onto a NaCl substrate. The nitrile salts were prepared by the methods described in the literature ([20,21]), and were recorded in the form of a paste in vaseline oil. The preparation of samples for recording spectra was carried out in an atmosphere of dry air.

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