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Abstract

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ON THE NATURE OF THE INTERACTION OF A BENZENE MOLECULE WITH A HYDROXYL GROUP

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The adsorption of aromatic and unsaturated hydrocarbons and of nitrogen is highly sensitive to the degree of hydration of the adsorbent. The heat of adsorption of benzene on graphite ([1]) and MgO ([2]), in accordance with the results of a calculation ([2]) of the energy of electrokinetic interaction, is less than the heat of adsorption of n-hexane. Likewise, the heat of adsorption of olefins on graphite is less than that of paraffins ([3]). On the surface of magnesium ([4]) and silicon ([5,6]) hydroxides, however, the heat of adsorption of benzene ([4,5]) and propene ([6]) is greater than the heats of adsorption of n-hexane and propane. Correspondingly, upon adsorption of benzene on silicon hydroxide, the absorption bands of the surface hydroxyl groups in the infrared spectrum are shifted considerably more than upon adsorption of n-hexane ([7,8]). This shift is greater upon adsorption of nitrogen than upon adsorption of argon ([9]), whereas on graphite the heats of adsorption of these substances are close ([10]). Dehydration of the silica-gel surface lowers the heat of adsorption of benzene to values smaller than the heat of adsorption of n-hexane ([5]).

The first attempt to investigate the nature of the strengthening of the interaction of benzene with the surface of hydroxides was made by D. P. Poshkus and one of the authors ([11]), on the basis of an approximate estimate of the distribution of the π-electron charge in the benzene molecule and of the Coulomb interaction of this charge and the residual charges of the carbon skeleton with the point charges of the hydroxyl group. It is of interest to take fuller account of the distribution of electron density both in the adsorbate molecules and at the adsorbent surface. In the present work a second step has been taken—the interaction of the benzene molecule with a dipole has been considered by means of a rough model, in which the dipole is still regarded as a pair of point charges, while in the benzene molecule not only the π- but also the σ-bonds are taken into account; for their description the molecular-orbital method is used.*

Geometry of the system. The C—C distance in the benzene molecule was taken as 1.39 Å, and the C—H distance as 1.04 and 1.12 Å (the limiting values of the value reported in the literature, 1.08 ± 0.04 Å). The following values were adopted for the distances of the effective charges of the OH dipole, lying on a straight line perpendicular to the plane of the benzene ring and passing through its center, from this plane: 1) 2.15 Å (H atom) and 3.12 Å (O atom); 2) 3.12 Å (H atom) and 4.09 Å (O atom). The first pair of values was taken for the closest possible approach of the dipole to the molecule ([11]); the second was chosen to facilitate the calculation, so that the center of the H atom in the second variant coincided with the center of the O atom in the first. This pair of values is close to the sum of the van der Waals semithickness of the benzene molecule and the van der Waals radius of the H atom. The effective charges of the poles of the dipole were taken equal to $q_o = q_H = 1.6 \cdot 10^{10}$ abs. units ([11]).

Model of the benzene molecule. The wave function of the bonding electrons of the molecule was taken in the form of a Slater determinant. It is assumed—

localization of the σ-bonds and delocalization of the π-bonds were assumed. Their interaction was neglected. The molecular orbitals entering into the determinant were separated as follows:

1) Molecular orbitals localized on the bonds between carbon atoms C_i and C_{i+1} were taken in the form

$$^1\psi_{i,i+1} = \frac{1}{\sqrt{2(1+S_{\mathrm{C-C}})}}(\chi_{i,i+1} + \chi_{i+1,i}), \tag{1}$$

where $\chi_{i,i+1}$ represents the sp^2 orbital of atom i, directed toward atom $i+1$, and $S_{\mathrm{C-C}}$ is the overlap integral.

2) Molecular orbitals forming the bond between atoms C_i and the neighboring H atom were taken in the form:

$$^2\psi_i = \frac{1}{\sqrt{1+2aS_{\mathrm{C-H}}+a^2}}(\chi_{i\mathrm{H}} + a\eta_i), \tag{2}$$

where $\chi_{i\mathrm{H}}$ represents the sp^2 orbital of atom C_i, directed toward the neighboring H atom, η_i is the $1s$ orbital of this H atom, and S is the overlap integral. Since the exact value of the coefficient a, connected with the polarity of the C—H bond, is unknown, the values 1.2, 1.0, 0.8, 0.6 were used; since the H atom is more electropositive, values between 0.8 and 1.0 are more probable. For estimating a, the dipole of the C—H bond is not decisive.

3) Molecular orbitals of delocalized π-bonds are expressed as follows:

$$^3\psi_1 = \frac{1}{\sqrt{6(1+2S)}}\sum_{j=1}^{6}(p_z)_j; \qquad ^3\psi_{2,3} = \frac{1}{\sqrt{6(1+S)}}\sum_{j=1}^{6}e^{\pm 2\pi ij/6}(p_z)_j, \tag{3}$$

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* A detailed account of the calculation is given in ([12]).

where S is the overlap integral of the p_z orbitals of neighboring C atoms.

If the x-axis is placed along the direction of the bond C_i—C_{i+1}, then the orbitals

$$\chi_{i,i+1} = \frac{1}{\sqrt{3}}(2s)_{C_i} + \sqrt{\frac{2}{3}}(2p_x)_{C_i}. \tag{4}$$

The hybridized atomic orbitals $\chi_{i\mathrm{H}}$ are determined analogously, if the x-axis is placed along the direction of the C—H bond.

The atomic orbitals were expressed by hydrogen-like functions

$$(1s)_\mathrm{H} = \sqrt{1/\pi}\, e^{-r}; \qquad (2s)_\mathrm{C} = \varkappa\sqrt{\gamma^5/3\pi}\, re^{-\gamma r} - \omega\sqrt{\beta^3/\pi}\, e^{-\beta r};$$

$$(2p_x)_\mathrm{C} = \sqrt{\varepsilon^5/\pi}\, re^{-\varepsilon r}\sin\vartheta\cos\varphi; \qquad (2p_y)_\mathrm{C} = \sqrt{\varepsilon^5/\pi}\, re^{-\varepsilon r}\sin\vartheta\sin\varphi; \tag{5}$$

$$(2p_z)_\mathrm{C} = \sqrt{\varepsilon^5/\pi}\, re^{-\varepsilon r}\cos\vartheta$$

with parameter values $\varkappa = 1.054$, $\omega = 0.249$, $\gamma = 1.68$, $\beta = 4.52$, $\varepsilon = 1.51$ ([13]) (r, ϑ and φ are spherical coordinates).

Calculation of the interaction energy. Taking into account the large distance between the molecule and the dipole, which makes it possible to neglect deformation of the electron cloud of the molecule, the calculation of the interaction energy was carried out by the perturbation method with allowance for terms of the first order only. The difference was found between the interaction energies of the molecule with both poles of the dipole. The change in the energy of the molecule under the influence of a point charge q, whose position is specified by the vector $\mathbf{R}$, is determined by the equation

$$\frac{\Delta E}{eq} = -2\sum_{i=1}^{N}\int\frac{|\psi_i(\mathbf{r})|^2}{|\mathbf{R}-\mathbf{r}|}\,d^3r + \sum_{k=1}^{M}\frac{z_k}{|\mathbf{R}-\rho_k|}, \tag{6}$$

where N is the number of occupied orbitals in the molecule; M is the number of atoms; z_k and ρ_k are the nuclear charge and radius vector of the k-th atom. Expressing the molecular orbitals ψ_i through atomic φ_j by the formula $\psi_i = \sum_j c_{ij}\varphi_j$, we obtain

$$\int\frac{|\psi_i(\mathbf{r})|^2}{|\mathbf{R}-\mathbf{r}|}\,d^3r = \sum_j |c_{ij}|^2\alpha_j + \sum_{j\neq k} c_{ij}c_{ik}\beta_{jk}, \tag{7}$$

where

$$\alpha_j^* = \int \frac{|\varphi_j(\mathbf{r})|^2}{|\mathbf{R}-\mathbf{r}|}\, d^3r; \qquad \beta_{jk} = \int \frac{\varphi_j(\mathbf{r})\varphi_k(\mathbf{r})}{|\mathbf{R}-\mathbf{r}|}\, d^3r. \tag{8}$$

Equations (6), (7), and (8) have a general character. For the interaction of a benzene molecule with an OH dipole, the change in energy can be reduced to the form

$$\Delta E = \Delta E_{\mathrm{C-C}} + \Delta E_{\mathrm{C-H}} + \Delta E_{\pi}. \tag{9}$$

The separate contributions to the interaction energy are expressed as the sum of "Coulomb" $\Delta E^{(Q)}$ and "exchange" $\Delta E^{(V)}$ terms.* The latter have no classical analogue and depend on the bonding conditions, i.e., on the distribution of atomic orbitals among molecular orbitals.

Calculation of the integrals. In calculating the Coulomb integrals, the hybridized wave functions were expressed by means of (5). The corresponding two-center integrals were calculated according to (14), and it proved sufficient to retain terms expressing only dipole and quadrupole interactions. Therefore the three-center integrals in β_{jk} were calculated in the quadrupole approximation. For the same reason, integrals of all types were calculated in this approximation.

Results and discussion. The "Coulomb" $F^{(Q)}$, "exchange" $F^{(V)}$, and total $F^{(T)}$ interaction energies of benzene with a dipole whose poles are at distances Z_1 and Z_2 from the center of the benzene ring were calculated from the formula

$$F^{(L)} = \Delta E^{(L)}(Z_1) - \Delta E^{(L)}(Z_2); \qquad L = Q,\ V,\ T, \tag{10}$$

where $\Delta E^{(L)}(Z_1)$ and $\Delta E^{(L)}(Z_2)$ are the interaction energies of pole 1 and pole 2 with the different bonds of the molecule. The largest absolute contributions to the total energy $F^{(T)}$ are made by the interactions of the dipole with the σ-bonds. Thus, for a, the average between 1.0 and 0.8, at $Z_1 = 2.15$ Å, $F^{(T)}_{\mathrm{C-C}} = -13.3$, $F^{(T)}_{\mathrm{C-H}} = +15.7$, and $F^{(T)}_{\pi} = -5.8$, so that $F^{(T)} = -3.4$ kcal/mole (at $Z_1 = 3.12$ Å, $F^{(T)}_{\mathrm{C-C}} = -4.7$, $F^{(T)}_{\mathrm{C-H}} = +6.1$, and $F^{(T)}_{\pi} = -2.9$, so that $F^{(T)} = -1.5$ kcal/mole). The contributions of the C–C and C–H σ-bonds have opposite signs and are partially compensated, so that in this calculation, as in (11), the largest role is played by the contribution of the π-bonds; however, it is comparable in magnitude with the total contribution of the σ-bonds. The interaction energies $F^{(Q)}$ and $F^{(T)}$ for the entire benzene molecule are given in Table 1. They depend little on possible fluctuations in the length of the C–H bond, but strongly on the value of a. For the most probable value $a = 0.8 - 1.0$, they are in agreement with the measured difference in the heats of adsorption of benzene on the surface of silica containing and not containing hydroxyl groups (up to 3 kcal/mole (5)). This agreement, however, should not be overestimated, since the energy is obtained here as the difference of large numbers, which is due to the complexity of the physical nature of the effect. Thus, the contributions to the total energy of integrals of Coulomb type compensate one another to a considerable extent, and the decisive role apparently belongs to exchange terms, which are, however, very sensitive to the choice of model, for example, to the value of a. It is very difficult to estimate how strongly the numerical values of the energy depend on the parameters of the atomic orbitals.

The calculations were carried out only for one position of the molecule with respect to the dipole. The magnitude and sign of the contributions of different groups of the complex molecule are very sensitive to the geometry of the system. The contribution of single bonds depends especially strongly on the orientation of the molecule with respect to the dipole. Therefore an analogous calculation for different relative positions and orientations of the benzene molecule and hydroxyl is of great interest.

* The exchange terms $\Delta E^{(V)}$ are formed from the β_{ik} terms in (7).

Table 1

Computed interaction energies of a benzene molecule with an OH dipole, $F^{<>}$ in kcal/mol, for different distances to the centers of the dipole Z_1 and Z_2 and for different C–H bond lengths

a		C–H 1.04 Å$Z_1 = 2.15$ Å$Z_2 = 3.12$ Å	C–H 1.04 Å$Z_1 = 3.12$ Å$Z_2 = 4.09$ Å	C–H 1.12 Å$Z_1 = 2.15$ Å$Z_2 = 3.12$ Å	C–H 1.12 Å$Z_1 = 3.12$ Å$Z_2 = 4.09$ Å
0.6	$F^{(Q)}$	3.94	1.48	4.19	1.59
0.6	$F^{(T)}$	−6.63	−2.92	−7.47	−3.33
0.8	$F^{(Q)}$	1.38	0.45	1.60	0.54
0.8	$F^{(T)}$	−4.31	−1.82	−4.84	−2.08
1.0	$F^{(Q)}$	−0.49	−0.31	−0.31	−0.24
1.0	$F^{(T)}$	−2.47	−0.98	−2.78	−1.09
1.2	$F^{(Q)}$	−1.90	−0.88	−1.75	−0.82
1.2	$F^{(T)}$	−1.06	−0.27	−1.14	−0.29

It must also be borne in mind that the experimental value of the difference in heats of adsorption on the hydrated and dehydrated surface of silica gel could be affected both by the different geometry and by the different contributions of dispersion forces in these two cases. We therefore consider most interesting not so much the closeness of the calculated value of the interaction energy of a benzene molecule and an OH dipole to the measured changes in the heat of adsorption of benzene upon dehydration of silica gel, as the relation, established by the calculation, of this effect to the quantum-mechanical nature of the model used. As was already noted, the principal contribution to the interaction energy is made by exchange integrals. Therefore the observed difference in the behavior of benzene and hexane on a hydrated surface is rather quantitative than qualitative in character, which is in agreement with changes in the infrared spectrum ([8,9]).

Theoretical and experimental work in this direction should undoubtedly help to clarify the nature of effects that appear predominantly in particular cases. It is of interest to study the adsorption of molecules of different structure with the electronic structure of both the adsorbate and the adsorbent taken into account as fully as possible. The possible role of a purely exchange effect should also be clarified.

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