Physical Chemistry

Quantum-chemical calculation of a spillover model on a graphite support

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The simplest quantum-chemical models of hydrogen spillover over a graphite-like surface as a proton or radical have been considered. The condensed planar $C_{24}H_{12}$ molecule was used as a model surface. The *ab initio* calculations of the interaction of hydrogen with the model surface were carried out by the restricted Hartree—Fock (HF) method in the STO-3G and 6-31G* basis sets. The radical hydrogen can not bind to such a surface, whereas the proton binds to it with an energy release of 186 kcal mol^{-1}. The activation energy of the transfer of the proton between two neighboring carbon atoms (10 kcal mol^{-1}) has been determined. The simplest model of the hydrogen migration as a proton over the model surface can be used for describing the spillover of hydrogen over the graphite surface.

Key words: *ab initio*, quantum-chemical calculation, activation energy, hydrogen spillover.

Hydrogen activated on metals of the platinum group can migrate to inorganic supporters and enter into hydrogenation reactions.[1—4] Such a transfer of the activated hydrogen received the name the hydrogen spillover (HS).[1] Processes based on the use of HS have long been known (see, for instance, Refs. 2—4); however, the chemical nature of migrating particles has not been established unambiguously up to the present. There exist several hypotheses according to which that particle is a solvated proton,[5] a proton-electron pair[6] or atomized hydrogen[7].

The possibility of independent transfer of the proton and pertinent electron over the carbon surface was established in the experimental studies of the HS.[6] An important feature of carbon is that the adsorbed amount of hydrogen thereon is several orders of magnitude higher than that of the aliminum and silicon oxides supports.[8,9] The reason for such a significant difference in the behavior of the spillover-hydrogen on the carbon and oxide surfaces has not been discussed. No theoretical studies based on the quantum-chemical simulation of HS over the graphite surface have been carried out.

In this work the simplest models of hydrogen spillover (as a proton or a radical) over a model graphite-like surface represented by a planar condensed molecule $C_{24}H_{12}$ are considered. The calculations of the model systems were carried out by the restricted Hartree—Fock (HF) method[10] in the STO-3G and 6-31G* basis sets on CRAY C-90 and CRAY XMP-UNICOS supercomputers at the Supercomputer Center (Livermore, USA) using the GAUSSIAN-94 program. The model surface was assumed to have a planar structure. Optimization of the geometric parameters of the systems under study was performed with allowance for this restriction. The ge-

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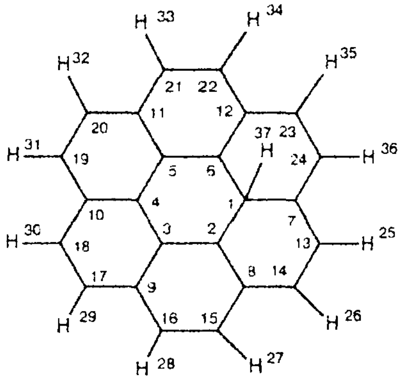
ometry obtained by the HF/STO-3G method was used in the calculations in the 6-31G* basis set.

The model system describing the HS over the graphite surface and the numbering of the atoms are shown below. The results of the calculations of the geometry for both the free model $C_{24}H_{12}$ surface and that coordinated to the H(37) proton are listed in Table 1.



The proton located on the model graphite-like surface in the bound state (II) is above one of the surface atoms. In the transition state (III), the distances between the proton and adjacent carbon atoms are equal, and the proton lies on the line perpendicular to the molecular plane and passing nearly through the middle of the C(1)—C(6) bond. In the case of migration of the proton from the C(1) to the C(2), from the C(2) to the C(3), from the C(3) to the C(4), from the C(4) to the C(5), and from the C(5) to the C(6) atoms the transition states have an analogous structure.

The effective charges (according to Mulliken) on the atoms in structures I—III obtained by the HF/6-31 G* method are listed in Table 2. It can be seen from the data in this table how the redistribution of the electron density proceeds when the proton moves from one carbon atom of the model surface to the other. The proton induces an appreciable polarization of the two-dimensional lattice. Thus, the charge on the C(1) atom bonded to the proton is −0.514 in structure II, whereas the charges on the C(1) and C(6) atoms are approximately 50% smaller (−0.240) in the transition state III. A characteristic feature of the systems in question is that the effective charge on the hydrogen atom migrating over the model graphite-like surface is 0.347 in structure II and 0.375 in the transition state, *i.e.*, this atom has an essential positive charge.

The total energies of structures I—III calculated in the HF/STO-3G and HF/6-31G* approximations are listed in Table 3. Two important values can be determined from these energies: the proton affinity of the model graphite-like surface and the activation energy of the hydrogen migration from one carbon atom to the other. Their values are also given in Table 3. The calculated activation energy of the hydrogen migration is close to that experimentally determined from the temperature dependence of the diffusion coefficient (15.5 kcal mol^{-1} for HS over the carbon surface).[7]

Table 1. Interatomic distances (Å) in structures I—III

R(i—j)	I	II	III	*R*(i—j)	I	II	III
1—2	1.437	1.492	1.460	7—37	—	1.798	2.202
1—6	1.437	1.492	1.485	8—14	1.437	1.449	1.457
1—7	1.395	1.481	1.436	8—15	1.437	1.433	1.427
1—37	—	1.151	1.321	9—16	1.437	1.436	1.431
2—3	1.437	1.420	1.427	9—17	1.437	1.440	1.444
2—8	1.395	1.387	1.388	10—18	1.437	1.443	1.444
2—37	—	1.922	2.222	10—19	1.437	1.443	1.431
3—4	1.437	1.445	1.446	11—20	1.437	1.440	1.427
3—9	1.395	1.399	1.397	11—21	1.437	1.436	1.457
4—5	1.437	1.445	1.427	12—22	1.437	1.433	1.448
4—10	1.395	1.388	1.397	12—23	1.437	1.449	1.400
5—6	1.437	1.420	1.460	13—14	1.349	1.362	1.344
5—11	1.395	1.399	1.388	15—16	1.349	1.354	1.358
6—12	1.395	1.387	1.436	17—18	1.349	1.349	1.346
6—37	—	1.922	1.321	19—20	1.349	1.349	1.358
7—13	1.437	1.427	1.448	21—22	1.349	1.354	1.344
7—24	1.437	1.426	1.400	23—24	1.349	1.362	1.389

Note. Here and thereafter I is the free $C_{24}H_{12}$ molecule (without the H(37) atom); II is the local minimum (the corresponding structure is shown above); III is the transition state in the case of migration of the proton from the C(1) to the C(6) atom. The most characteristic interatomic distances obtained by the HF/STO-3G method are given.

Table 2. Effective charges on the atoms (according to Mulliken)

Atom	Structure			Atom	Structure		
	I	II	III		I	II	III
C(1)	−0.022	−0.514	−0.240	C(14)	−0.200	−0.113	−0.156
C(2)	−0.023	0.083	0.040	C(15)	−0.200	−0.192	−0.206
C(3)	−0.022	−0.031	−0.013	C(16)	−0.201	−0.187	−0.180
C(4)	−0.022	0.021	−0.013	C(17)	−0.200	−0.201	−0.187
C(5)	−0.023	−0.031	0.040	C(18)	−0.200	−0.176	−0.187
C(6)	−0.022	0.083	−0.240	C(19)	−0.200	−0.176	−0.180
C(7)	0.003	0.193	0.103	C(20)	−0.200	−0.201	−0.206
C(8)	0.004	−0.022	0.006	C(21)	−0.200	−0.187	−0.156
C(9)	0.004	0.024	0.003	C(22)	−0.201	−0.192	−0.200
C(10)	0.003	−0.020	0.003	C(23)	−0.200	−0.113	−0.201
C(11)	0.004	0.024	0.006	C(24)	−0.200	−0.242	−0.201
C(12)	0.004	−0.022	0.103	C(37)	—	0.347	0.375
C(13)	−0.200	−0.242	−0.200				

Table 3. Total energies (*E*), the proton affinities (PA), and the activation energies of the proton migration (E_a) calculated for structures I—III

Basis set	*E*/au			PA	E_a
	I	II	III	kcal mol^{-1}	
STO-3G	−904.8227	−905.1731	−905.1485	204.3	15.4
6-31G*	−915.9499	−916.2465	−916.2305	186.0	10.0

A calculation of the interaction between the hydrogen atom and the model surface has been carried out by the restricted HF method in the STO-3G basis set. Only local minima of the structural type II, when the hydrogen atom is between two adjacent carbon atoms (C(1)—C(6), C(1)—C(2), C(2)—C(3), C(3)—C(4), C(4)—C(5), and C(5)—C(6)) were found on the potential energy surface. The total energy of each of these states (−905.2649 a.u.) is higher than the sum of the total energies of compound $C_{24}H_{12}$ and that of atomic hydrogen, *i.e.*, the radical state obtained in the calculation is metastable. On the basis of the calculated total energies of the $C_{24}H_{12}$ and $C_{24}H_{13}$ systems and the free hydrogen atom (−0.5 a.u.) we obtained the value of 36.3 kcal mol^{-1} for the enthalpy of the reaction $C_{24}H_{12} + H = C_{24}H_{13}$. It indicates that, unlike the proton, the bonding between the radical hydrogen and the model graphite-like surface is not favorable.

Thus, as follows from the results of the calculations, the considered simplest quantum-chemical model of migration of the hydrogen as a proton can be used for describing the HS over the graphite surface.

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