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Environmental influence on the mechanical strength of chemical bonds in solids–*ab initio* quantum calculations

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To elucidate the mechanism of the adsorption-induced strength decrease in solids with chemical bonds, the quantum-mechanics calculations have been performed of force and energy parameters of single and double carbon–carbon bonds during mechanical deformation, and the influence of hydrogen cations on this process has been studied. The Hartry–Fock–Roothaan method (HONDO program) and 5-31G basis set have been used. In both systems the proton decreases mechanical strength of the C–C bond (i.e. the force required to break the bond) and this influence is very sensitive to the geometry of the carbo-cation formed. The results obtained show the possibility of strength reduction of polymers by strong acids and confirm the relation between the Rehbinder effect and catalysis.

1. Introduction

Among various surface phenomena which are able to cause the strength reduction of solids under the influence of an active medium (Rehbinder effect [1, 2]), the most obvious and "direct" one is the decrease in the force required to break interatomic bonds in a solid when in contact with such an environment. Our first results of the quantum calculations of the mechanical strength of the interatomic bond and medium influence are presented here. We discuss here only the ence are presented here. We discuss here the energy and force parameters. The main feature of our study comparing various quantum calculations is the force of bond rupture and its changes after chemical interaction of the solid with an active medium.

Single and double carbon–carbon bonds in hydrocarbon molecules have been chosen as objects of our investigation as a model of chain polymers because their simple nature allows one to perform *ab initio* calculations and to avoid various assumptions that may cause unpredictable influence. The role of neighbours and chain length may be elucidated by variation of the number of carbon atoms.

If the strength of a solid is determined by chemical bonds, the microaspect of fracture is very similar to (and may be treated as) a chemical reaction. Respectively, facilitation of fracture may be caused by the same substances that are able to accelerate the corresponding chemical process – by the catalysts. This is a new aspect of the earlier proposed [3, 4] relation between catalysis and the Rehbinder effect.

Chemical rupture of carbon–carbon bonds (hydrocarbon cracking) is catalysed by acid catalysts and the process includes a stage of carbo-cation formation. Therefore, we may expect acidic agents to facilitate mechanical rupture of these bonds. In another words, we suppose that acidic agents (such as superacids) in contact with the polymer will produce carbo-cations in the surface layer and cause a decrease in mechanical strength. Therefore calculations for neutral molecules and carbo-cations were performed.

For these calculations we used the Hartree–Fock–Roothaan method as implemented in the HONDO program [5–7] and 5-31G basis set. Certainly this approach is not suitable for analysis of the top of the potential barrier where the electron correlation is especially important, therefore calculations were done up to essentially smaller deformations – to the maximum force, where this effect is not so significant.

2. Results and discussion

For the first calculation, an ethylene molecule was chosen as the simplest sample (and more reactive than ethane). The force acting on carbon atoms versus C=C bond length is shown in Fig. 1. The bond strength is equal to 0.211 atomic units (a.u.) (1.77×10^{-3} dyn), that is 0.978×10^{12} dyn cm^{-2} for the theoretical strength of an ideal polymer structure with 5.38 chain nm^{-2} [8] and with double bonds.

In the absence of deformation, the carbo-cation, $C_2H_5^+$, may exist in two different configurations [9], with a symmetrical location of the additional proton (π-complex) and with the most usual CH_3 group. Our results for free cations show, in contradiction to other data [10], that the last form is more stable; the difference in total energy is 0.012 a.u., i.e. 7.5 kcal mol^{-1}, Table I.

The deformation of the symmetrical cation was studied assuming C_{2v} symmetry (this allows acceleration of calculations). The results shown in Fig. 1 and

0022–2461

Table I indicate a weakening of the bond. The rupture of the asymmetrical cation is much easier (see Fig. 1 and Table I). Reduced strength and critical elongation result in lower energy of bond rupture: 0.04 a.u. instead of 0.10 a.u. for the first configuration and 0.14 a.u. for ethylene molecule.

Such different properties of stressed cations pose a question about stability of the symmetrical cation under deformation. A series of calculations was carried out with an almost symmetrical initial state but without assuming symmetry. For the small elongations, geometry optimization results in a symmetrical cation, i.e. there is an energy minimum at this geometry. But above some elongation this minimum disappears, the second (asymmetrical) configuration becomes the only stable one and optimization leads to CH_3 group formation. So, the symmetrical cation, metastable in the absence of deformation, becomes labile under influence of an external force.

Because the object of this study was the strength of solid polymers, it was necessary to elucidate the role of chain length. This was done by similar calculations with the butylene molecule, *trans*-butylene-2. In this series again, the length of double bond was varied and the positions of all other atoms were optimized for each deformation. The results (dashed curves in Fig. 1, and Table I) show that the increase in chain length has only a slight influence on the mechanical properties of the double bond. Changes in strength do not exceed 10% and the critical deformation also changes slightly.

Summarizing the results of calculations for olefins, we may conclude that strong proton acids or superacids are able to cause a sharp decrease in the mechanical strength and critical elongation at rupture of double bond due to carbo-cation formation.

Certainly, the most interesting object here is the single carbon–carbon bond, that determines the strength of polymers, diamond and some other carbon materials. Therefore, similar calculations for ethane and the carbo-cation $C_2H_7^+$ were carried out. Our results for equilibrium ethane molecule and the carbo-cation $C_2H_7^+$ (Table I) are in good agreement with literature data [6, 9–11].

The deformation of the molecule shows that a single C–C bond has sufficiently lower mechanical strength than a double one (0.088 a.u.) which corresponds to a theoretical strength of 0.41×10^{12} dyn cm^{-2} (Fig. 2 and Table I) in good agreement with experiment and various calculations [12].

Interaction of ethane with protons results in the formation of either $C_2H_7^+$ carbo-cation or $C_2H_5^+$ and H_2 molecule [10]. In our calculations, both carbo-cations were obtained depending on the initial position of the additional proton and the total energy of $C_2H_7^+$ is 0.012 a.u. lower than $C_2H_5^+ + H_2$ in accordance with previous data [19]. The geometry of $C_2H_7^+$ (H-nucleus on the C–C line) and analysis of the

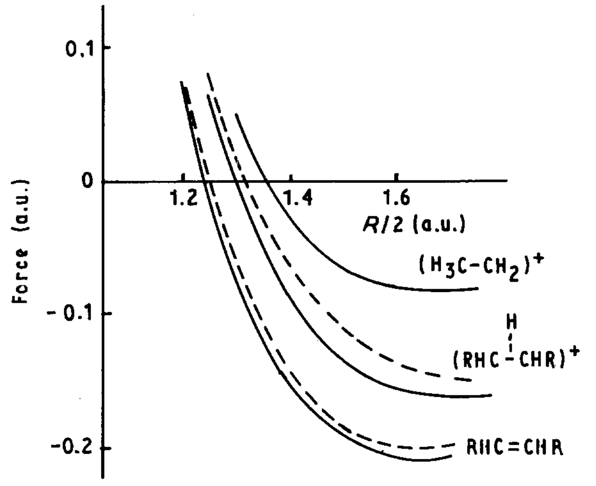

Figure 1 Dependence of the force caused by deformation of the double carbon–carbon bond on the distance between carbon atoms. (——) Ethylene molecule and the $C_2H_5^+$ cation in symmetrical and asymmetrical forms (R = H). (– – –) Trans-butylene-2 molecule and the symmetric $C_4H_9^+$ cation (R = CH_3).

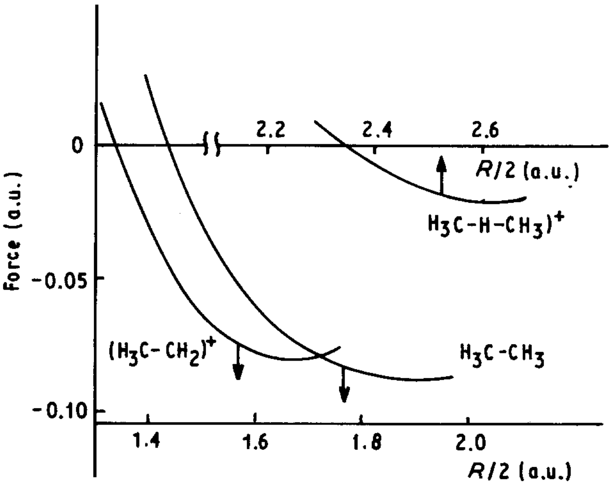

Figure 2 Dependence of the force caused by deformation of the single carbon–carbon bond on the distance between carbon atoms in the ethane molecule and in the $C_2H_7^+$ and asymmetrical $C_2H_5^+$ cations.

TABLE I Results of calculations of the equilibrium distance between carbon atoms, R_e, the total energy at equilibrium, $U(R_e)$, the critical bond length (at force minimum), R_c, the bond elongation at fracture, ΔR, the bond strength (i.e. minus force minimum), $F(R_c)$, and the total energy at R_c, $U(R_c)$. All quantities are in atomic units (a.u.).

Molecule	R_e	$U(R_e)$	R_c	ΔR	$F(R_c)$	$U(R_c)$
C_2H_4	2.495	– 77.9875	3.383	0.888	0.211	– 77.8508
$C_2H_5^+$ sym.	2.602	– 78.2520	3.456	0.854	0.162	– 78.1520
$C_2H_5^+$ asym.	2.715	– 78.2639	3.374	0.659	0.080	– 78.2244
C_4H_8	2.504	– 156.0172	3.243	0.739	0.200	– 155.9115
$C_4H_9^+$ sym.	2.619	– 156.3066	3.437	0.818	0.145	– 156.2208
C_2H_6	2.895	– 79.1808	3.769	0.874	0.088	– 79.1252
$C_2H_7^+$ sym.	4.701	– 79.4071	5.218	0.517	0.022	– 79.4000

electronic structure show that the proton causes the spontaneous C–C bond rupture and C–H–C bridge formation. Thus here we deal with not five-coordinated carbon, but with bivalent hydrogen providing the connection between two fragments of molecule. The energy of this bond is about 17 kcal mol^{-1} (HF/6-31G** and Møller-Plesset approach calculations results in 19.9 and 35.7 kcal mol^{-1}, respectively [10]).

Deformation of $C_2H_5^+$ was described above. It is also shown in Fig. 2 to facilitate comparison with results for C_2H_6 and $C_2H_7^+$. The strength of $C_2H_5^+$ is 10% less than the strength of an ethane molecule. So even its formation results in a reduction of chain strength. The $C_2H_7^+$ cation is much weaker (Fig. 2 and Table I), its strength is four times lower than the strength of C_2H_6; therefore formation of this cation will result in a very sharp strength reduction. Certainly, during the course of deformation and fracture of a macroscopic sample, both cations may appear, and the fracture will go through the weakest link and the strength will be low.

As far as neighbours offer only a slight influence on the properties of the bonds, one may expect similar results for other materials with carbon–carbon bonds (diamond and diamond-like materials). In this case there is no opportunity to split out the hydrogen molecule and interaction with proton leads to hydrogen bridge formation (see above) and a sharp reduction in the strength of the interatomic bond and the whole material.

3. General discussion

Our calculations, in line with other applications of quantum mechanics in materials science and related topics (see, for example, [13–19]), have shown that modern development of methods, techniques and computers allows one to solve rather complex problems of simultaneous action of mechanical stresses and active species on solids, starting from first principles. This opens new opportunities for investigation of mechanisms and trends in the influence of the environment on mechanical properties of materials.

Classical molecular dynamics using mainly pair potentials has been successfully applied to systems with molecular forces [20]; it may also be extended to ionic systems and polar-active media. However, rigorous studies of solids with covalent and metallic bonds demand application of quantum mechanics, because chemical interaction of a solid with an active medium and/or alterations of electron density (in the case of liquid metal embrittlement of solid metals may cause drastic changes in the potentials of interaction between atoms in a solid.

Even in the absence of any medium, there is an important problem that has not yet been completely solved – the influence of a surface itself on the interatomic interactions in the surface layer of solid. Because any process of deformation and/or fracture is always associated with the creation of new surface, this effect may play a role in the mechanical behaviour of solids and should be taken into account.

We expect that quantum mechanics calculations, similar to those described above, may be extended to various objects, including modern materials, ceramics, metals, minerals, and so on. They may be used both for prediction of mechanical properties and durability of materials in various media and for searching for new active media that facilitate various types of materials processing, including cutting, boring, grinding, etc. While the carbon–carbon bonds are the main bonds in organic substances, natural and synthetic polymers (and also in diamond and diamond-like materials), in the field of inorganic substances, especially natural ones, the Si–O–Si bond is the most common and widespread. We are now beginning studies of it in the manner described above.

The problem of the influence of the chemical interaction with the medium on mechanical properties of solids belongs to a wide field of such boundary or interdisciplinary physico-chemical problems as stress corrosion, mechanical activation of chemical reactions, etc. First, the above-mentioned relation between adsorption-induced strength reduction and heterogeneous catalysis [3, 4, 21] may be placed here – the mutual influence of solid catalysts and reacting fluid. The chemical reaction may cause a sharp increase in mobility of solid surface atoms, and reconstruction of the surface [22–24]. In exothermic reactions of ammonia synthesis in iron, and benzene hydrogenation in nickel (in both cases there is dissociative adsorption of the hydrogen molecule on metal) we found a four to five order of magnitude increase in the surface diffusion coefficient [25, 26] caused by the formation of metal adatoms on the surface in the catalytic process. It is resonable to relate this effect to hydrogen embrittlement of iron and nickel. Earlier direct studies were carried out of the decrease in strength of catalysts caused by chemical processes at their surface [27, 28]. Thus the evident appearance of the mutual influence of solid and medium takes place: the formation of bonds between their atoms causes weakening of bonds inside both the medium and solid material. If we also take into consideration possible deformations of medium molecules adsorbed on the surface, and mechanical stresses in catalysts (caused by various reasons), the similarity of both components become clearer still: both are exposed to action of a strength reduction caused by "adsorption" (i.e. by interaction between them). (While there should be a decrease in the strength of catalysed molecules (otherwise the solid is not a catalyst), there is, in principle, no compulsory reduction in the strength of solid. If the interaction is caused by electron transfer to a bonding or from an antibonding orbital of a solid, its strength may be increased by this interaction. Similar problems were discussed in [29]. In some cases an increase in strength of catalysts during the reaction was observed, but it was not clear if it was a direct influence of the interaction with the medium, or if it was a secondary effect of strength reduction, due to sintering of the porous solid and/or stress relaxation, both caused by increased mobility of the atoms of the catalyst, i.e. an effect of the facilitation of bond rupture.)

Another aspect of this relation may be formulated as both facilitation of mechanical rupture of the bond by interaction with the medium, and mechanical activation of the catalytic process by an applied force. In both situations we may consider some shared participation of chemical interactions and the mechanical work of an applied force in the process of rupture and reconstruction of interatomic bonds [30].

Association of molecular dynamics, quantum calculations and other methods and approaches, aimed at clarifying the trends in such processes at the level of atoms and molecules, would allow inclusion of them in a general quantitative theory that will be able to predict the optimum combination of mechanical and physico-chemical factors to control properties of materials and technological processes.

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