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# An approach to quantum chemical consideration of "hydride" transfer reactions

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*Abstract*: An approach to the quantum chemical study of "hydride ion" transfer has been proposed, according to which the sequences of changes in ionization potentials, enthalpies and free energies of the affinities to the hydride ion, to the hydrogen atom and to the proton of substrates molecules and their derivatives (cations, radicals, anions), are compared with the experimentally substantiated series of "hydride" mobility. It has been established that the experimental series of "hydride" mobility for six chalcogenopyrans based on "semicyclic" 1,5-diketones is in conformity with the computed ionization potentials of the molecules, and with the affinity of the corresponding radicals to the hydrogen atom involved in the transfer. The direct splitting-out of the hydride ion and the primary deprotonation of the substrates followed by the withdrawal of two electrons was elucidated to be unlikely. Feasible are the mechanisms of "hydride" mobility, the first step of which consists of electron or hydrogen atom transfer from the chalcogenopyrans molecules.

*Keywords*: "hydride" transfer, reaction mechanisms, theory – experiment correlation, quantum chemical consideration, chalcogenopyrans.

## INTRODUCTION

Of great importance in chemistry are reactions involving a step that may be conceived formally as hydride ion transfer.[1] Transformations of 1,5-dicarbonyl compounds and chalcogenopyrans into mixtures of chalcogenopyrilium salts and chalcogenocyclohexanes or chalcogenopyrilium salts and other reduced products serve as examples.[2]

For a wide range of chemical compounds, the following mechanisms of "hydride" transfer are discussed.[1]

1. Direct splitting-out of a hydride ion ($-H^-$).

2. Consequent withdrawing of an electron, a proton and yet another electron ($- e^- - H^+ - e^-$).

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3. Extraction of an electron and a hydrogen atom ($– e^– – H^•$).
4. Transfer of a hydrogen atom and an electron ($– H^• – e^–$).
5. Deprotonation followed by a transfer of two electrons ($– H^+ – e^– – e^–$).

The mechanism of the "minus electron minus electron minus proton" ($–e^– – e^– – H^+$) type is not realizable, since there is little likelihood of the formation of dication radical.

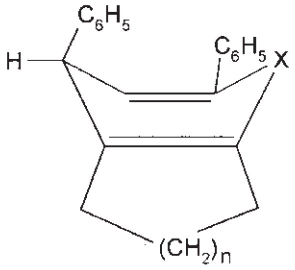
Outside the domain of this paper, one more mechanism probably exists which involves primary protonation of a heteroring and a final step involving the liberation of $H_2$[3] or another electroneutral molecule.[4] The feasibility of heterocycle protonation at a chalcogen atom has been unambiguously proved in the works by Lambert *et al.*[5]

A sophisticated treatment of "hydride" transfer mechanisms is complicated, even when using modern-day experimental methods, for instance, NMR in pulse variant. This is related to the corresponding reaction steps proceeding very fast. Future experimental investigations could become more effective by means of quantum chemical predictions based on known experimental data.

The reactivity of pyrans, thio- and selenopyrans is determined to a considerable extent by the capability of the molecules to split out a "hydride ion".[2] The latter term is put in quotes because the transfer of a hydride ion as such is a rarity in organic chemistry.

Chalcogenopyrans **I–VI** (Table I) synthesized on the basis of "semicyclic" 1,5-diketones are interesting as potential biologically active compounds.[2,6]

TABLE I. Compounds under study: chalcogenopyrans based on "semicyclic" 1,5-diketones



| X | n | Compound |
|---|---|---|
| O | 1 | **I** |
| S | 1 | **II** |
| Se | 1 | **III** |
| O | 2 | **IV** |
| S | 2 | **V** |
| Se | 2 | **VI** |

The aim of the present work consists in developing a strategy for a quantum chemical study of "hydride" mobility in molecules, and evaluating the above approach using "hydride ion" abstraction from the molecules **I–VI** as examples.

## COMPUTATIONAL METHODS

The computations were performed by means of the PM3 method[7,8] using software from the *MOPAC* package[9,10] with complete geometry optimization (Broyden – Fletcher – Goldfarb – Shanno function minimizer[11] involving Thiel's fast minimization algorithm.[12] The preliminary optimization was realized by the molecular mechanics method (the MMX procedure)[13] with software of the *PCMODEL* complex.[13] In the quantum chemical computations, the condition of the gradient norm not exceding 0.084 kJ/(mol·Å) was preset. In some cases, a sufficient decrease in the gradient norm was achieved by abandoning the Thiel's fast minimization routine (the keyword NOTHIEL of the *MOPAC* package was applied), or by optimization using the Davidon – Fletcher – Powell method (keyword DFP),[11] or using a combined aproach involving the keywords NOTHIEL and DFP.

For molecules with closed electronic shells, the restricted Hartree – Fock (RHF) formalism was used. Computations of cation radicals and radicals were conducted by the unrestricted Hartree – Fock (UHF) method.[10]

## RESULTS AND DISCUSSION

The molecular systems studied in this paper are rather large. For this reason semiempirical computations are more appropriate than sophisticated *ab initio* or DFT (*Density Functional Theory*) ones. In support for such a statement, let it be stated that for series of organic and inorganic compounds belonging to different classes and possessing various functional groups, a correctness of the reproduction by the MNDO (*Modified Neglect of Differential Overlap*), AM1 (*Austin Model 1*) and PM3 (*Parametric Method 3*) methods of the most important thermodynamic and molecular characteristics,[14–35] as well as of electronegativity, inductive and mesomeric parameters of atomic groups[36,37] has been established. Furthermore, the relativization principle is valid:[38] quite appropriate is the comparison of quantum chemical indices within a series of compounds with similar structure. Therewith the PM3 scheme[7,8] is the only among the mentioned ones which involves a set of parameters for selenium.[8] These are the reasons for selecting the PM3 method for the purposes of this work.

A characteristic of proton-acceptor ability of substances is known as proton affinity:[39–42] $PA = E(\mathrm{B}^-) + E(\mathrm{H}^+) - E(\mathrm{BH})$, which represents the enthalpy of proton detachment in the gaseous phase ($E = \Delta\Delta H_\mathrm{f}$): $\mathrm{BH} \rightarrow \mathrm{B}^- + \mathrm{H}^+$.

By analogy, the following quantities may be introduced: hydrogen atom affinity: $HAA = E(\mathrm{B}^\bullet) + E(\mathrm{H}^\bullet) - E(\mathrm{BH})$ and hydride ion affinity: $HIA = E(\mathrm{B}^+) + E(\mathrm{H}^-) - E(\mathrm{BH})$.

If the mechanisms are considered in steps it could be shown what are the reactivity indices of what molecular systems, (participants of the individual steps of the reactions) have to be analyzed (Table II, *IP* - Koopmans[43] ionization potential). Therewith the affinity quantities (*PA*, *HAA*, *HIA*) are to be presented in terms of enthalpies and free energies of the corresponding processes ($E = \Delta\Delta H_\mathrm{f}$, $\Delta\Delta G_\mathrm{f}$).

For instance, when the experimental values (thermodynamic, kinetic, *etc.*) characterizing a "hydride" mobility over a series of similarly constructed compounds (*e.g.*, heterocycles differing in the heteroatom) correlate to the ionization potentials of the initial compounds BH, so mechanisms 2 and 3 are feasible provided that the first step is the limiting one. If the experimental values are in agreement with the hydrogen atom affinity of the substrate BH, mechanism 4 occurs; if they are in agreement with the proton affinity of BH, then mechanism 5 occurs (in both cases the first step being limiting). When the experimental data correlate to the hydride ion affinity of BH, then mechanism 1 is probable.

TABLE II. Correspondence between steps of "hydride" transfer and reactivity indices describing the above steps

| Mechanism | Steps of transfer | To be analyzed | |
|---|---|---|---|
| | | Index | For molecular system |
| 1 | $BH \rightarrow B^{+} + H^{-}$ | *HIA* | $B^{+}$ |
| 2 | $BH \rightarrow BH^{\bullet+} + e^{-}$ | *IP* | BH |
| | $BH^{\bullet+} \rightarrow B^{\bullet} + H^{+}$ | *PA* | $B^{\bullet}$ |
| | $B^{\bullet} \rightarrow B^{+} + e^{-}$ | *IP* | $B^{\bullet}$ |
| 3 | $BH \rightarrow BH^{\bullet+} + e^{-}$ | *IP* | BH |
| | $BH^{\bullet+} \rightarrow B^{+} + H^{\bullet}$ | *HAA* | $B^{+}$ |
| 4 | $BH \rightarrow B^{\bullet} + H^{\bullet}$ | *HAA* | $B^{\bullet}$ |
| | $B^{\bullet} \rightarrow B^{+} + e^{-}$ | *IP* | $B^{\bullet}$ |
| 5 | $BH \rightarrow B^{-} + H^{+}$ | *PA* | $B^{-}$ |
| | $B^{-} \rightarrow B^{\bullet} + e^{-}$ | *IP* | $B^{-}$ |
| | $B^{\bullet} \rightarrow B^{+} + e^{-}$ | *IP* | $B^{\bullet}$ |

As a result of studies[44,45] concerned with the equilibrium of heteroaromatic cation – chalcogenopyran, and the determination[46] of a comparative reactivity series, it was established that thiopyrans are more capable or removing a "hydride ion" than the oxygen and selenium analogs.

The energy relations and electronic structure of the molecules **I-VI** and the cations, cation radicals, radicals, anions derived therefrom have been computed by means of the PM3 method.

The values of the standard free energy $\Delta G_f$ were calculated from the relationship:

$$\Delta G_f = \Delta H_f - T\Delta S_f,$$

where the standard entropies of formation $\Delta S_f$ were calculated by the formula:

$$\Delta S_f = S - \sum_i S_i,$$

where $S_i$ are the entropies of the elements constituting the molecule in their standard states[47] with regards to hydrogen, oxygen and sulphur being two-atom molecules; $T$ = 298.15 K.

The contributions of the separate degrees of freedom of translational, rotational and vibrational motion to the entropy were computed using the rigid molecule approximation (barriers of rotation and inversion far exceed $kT$) with no allowance for vibrational anharmonicity. The translational contributions were calculated without using quantum chemical computations, and the rotational contributions relied on equilibrium internuclear distances data obtained in the course of quantum chemical treatment. Finally, the contributions of the vibrational components to the entropy were evaluated on the basis of normal vibration frequencies computed by the quantum chemical method. For computing the frequencies after geometric optimization, second-order derivatives of the total energy with natural coordinates (force constants) were preliminarily computed.[48]

In calculating the rotational contributions to the thermodynamic functions, the symmetry number was taken as unity.

The affinity quantities for the hydride ion, hydrogen atom and proton, as well as the ionization potentials of the molecular systems mentioned are presented in Table III.

We have shown that the experimental series of "hydride" mobility S > O ≈ Se[44–46] is not inconsistent with: i) the ionization potentials (*IP*) of the molecules **I-VI**; ii) the hydrogen atom affinities (*HAA*) of the radicals formed by abstraction of the hydrogen atom in position 4 of the heterocycle from the initial systems **I-VI**.

TABLE III. Energies of affinity and ionization

Hydride ion affinity of cations $B^+$:
$HIA = E(B^+) + E(H^-) - E(BH)$, where $E = \Delta\Delta H_f, \Delta\Delta G_f$

| Compound | *HIA*/4.184, kJ/mol | |
|---|---|---|
| | $\Delta\Delta H_f$ | $\Delta\Delta G_f$ |
| **I** | 191.81 | 186.29 |
| **II** | 197.01 | 191.43 |
| **III** | 205.41 | 199.92 |
| **IV** | 192.54 | 187.03 |
| **V** | 198.60 | 192.78 |
| **VI** | 207.98 | 201.62 |

Hydrogen atom affinity of cations $B^+$:
$HAA = E(B^+) + E(H^\bullet) - E(BH^{\bullet+})$, where $E = \Delta\Delta H_f, \Delta\Delta G_f$

| Compound | *HAA*/4.184, kJ/mol | |
|---|---|---|
| | $\Delta\Delta H_f$ | $\Delta\Delta G_f$ |
| **I** | 31.33 | 24.89 |
| **II** | 41.77 | 35.39 |
| **III** | 41.63 | 36.33 |
| **IV** | 32.33 | 25.90 |
| **V** | 43.16 | 36.17 |
| **VI** | 45.09 | 37.80 |

TABLE III. (Continued)

Hydrogen atom affinity of radicals $\mathrm{B}^{\bullet}$:
$HAA = E(\mathrm{B}^{\bullet}) + E(\mathrm{H}^{\bullet}) - E(\mathrm{BH})$, where $E = \Delta\Delta H_\mathrm{f}, \Delta\Delta G_\mathrm{f}$

| Compound | $HAA$/4.184, kJ/mol | |
|---|---|---|
| | $\Delta\Delta H_\mathrm{f}$ | $\Delta\Delta G_\mathrm{f}$ |
| **I** | 52.06 | 43.65 |
| **II** | 51.42 | 42.49 |
| **III** | 54.24 | 45.63 |
| **IV** | 53.54 | 45.00 |
| **V** | 52.24 | 43.34 |
| **VI** | 56.31 | 47.59 |

Proton affinity of anions $\mathrm{B}^{-}$:
$PA = E(\mathrm{B}^{-}) + E(\mathrm{H}^{+}) - E(\mathrm{BH})$, where $E = \Delta\Delta H_\mathrm{f}, \Delta\Delta G_\mathrm{f}$

| Compound | $PA$/4.184, kJ/mol | |
|---|---|---|
| | $\Delta\Delta H_\mathrm{f}$ | $\Delta\Delta G_\mathrm{f}$ |
| **I** | 339.95 | 330.77 |
| **II** | 330.28 | 320.95 |
| **III** | 328.85 | 319.56 |
| **IV** | 341.89 | 332.88 |
| **V** | 331.66 | 322.97 |
| **VI** | 331.14 | 322.07 |

Proton affinity of radicals $\mathrm{B}^{\bullet}$:
$PA = E(\mathrm{B}^{\bullet}) + E(\mathrm{H}^{+}) - E(\mathrm{BH}^{\bullet+})$, where $E = \Delta\Delta H_\mathrm{f}, \Delta\Delta G_\mathrm{f}$

| Compound | $PA$/4.184, kJ/mol | |
|---|---|---|
| | $\Delta\Delta H_\mathrm{f}$ | $\Delta\Delta G_\mathrm{f}$ |
| **I** | 187.83 | 179.43 |
| **II** | 192.54 | 183.63 |
| **III** | 186.82 | 179.21 |
| **IV** | 189.69 | 181.06 |
| **V** | 193.16 | 183.91 |
| **VI** | 189.78 | 180.95 |

TABLE III. (Continued)

Ionization potentials of molecular systems (*IP*/4.184, kJ/mol)

| Compound | Molecular system | | |
|---|---|---|---|
| | BH | $B^\bullet$ | $B^-$ |
| **I** | 198.67 | 178.75 | 54.93 |
| **II** | 191.48 | 181.01 | 61.37 |
| **III** | 198.67 | 185.78 | 66.49 |
| **IV** | 198.72 | 178.40 | 56.02 |
| **V** | 192.42 | 181.42 | 62.68 |
| **VI** | 198.90 | 185.76 | 66.99 |

Let us compare that to the data from Table II. The *IP* index describes an electron extraction from the substrate molecule BH – the first step of mechanisms 2 and 3. The ejection of a hydrogen atom from the initial molecule BH (the *HAA* value corresponds just to this process) presents the first step of mechanism 4. Provided that the first step is the rate-determining one, correlation of experimental results with the ionization potentials implies the realization of mechanisms 2 or 3, and agreement with the affinity of the radicals $B^\bullet$ for the hydrogen atom means mechanism 4 is operative.

Hence mechanisms 1 and 5 are to be rejected. Mechanisms 2 to 4 are feasible provided that the first step is the limiting one in every case.

The results obtained allow experimental researchers to focus their attention on the problem of substantiating the actual mechanisms possible for "hydride" transfer in the chemistry of chalcogenopyrans.

The approach developed in the present work seems to be applicable to quantum chemical studies of reactions accompanied by "hydride" transfer with the participation of compounds from different classes.

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## ИЗВОД

## КВАНТНОМЕХАНИЧКИ ПРИСТУП РАЗМАТРАЊУ РЕАКЦИЈЕ ПРЕНОСА "ХИДРИДА"

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Предложен је квантномеханички приступ проучавању преноса "хидридног јона" код којег је извршено поређење израчунатих потенцијала јонизације, енталпије и слободне енергије за афинитет према хидридном јону, водоничном атому и протону у молекулима супстрата

и њихових деривата (катјона, радикала и анјона) са експериментално добијеним низом "хидридне" покретљивости. Утврђено је да су експериментално утврђени низови "хидридне" покретљивости за шест халкогенопирана заснованих на "полуцикличним" 1,5-дикетонима у сагласности са израчунатим потенцијалима јонизације молекула и афинитетом одговарајућих радикала за водонични атом који учествује у трансферу. Директно отцепљење хидридног јона и примарна депротонација супстрата уз накнадно отцепљење два електрона не сматра се вероватним. Прихватљиви су механизми "хидридне" покретљивости код којих је први ступањ пренос електрона или атома водоника са молекула халкогенопирана.

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