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Similarity approach to chemical reactivity. Theoretical justification of the Hammond postulate

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The recently proposed similarity index was applied to the quantitative justification of the empirical Hammond postulate for a series of selected pericyclic reactions. In keeping with the expectations of the postulate the transition states were shown to be reactant-like for exothermic and product-like for endothermic reactions.

1. Introduction

There is probably no other concept that has contributed to the development of chemistry so remarkably as the ill-defined, qualitative concept of similarity [1]. It is not despite but rather because of certain fuzziness that the applications of this concept are extremely broad and touch practically all areas of chemistry [2–5]. An example of the intuitive use of similarity is, e.g., one of the most powerful chemical principles, the principle of analogy which, especially in the early days of chemistry, served as a basis for the classification and systemization of molecules and reactions. To remind us of some fundamental concepts deeply rooted in the principle of analogy notions such as homological series, topicity, functional group, substituent, etc., can be mentioned.

In addition to these applications which are basically of a qualitative nature, the trend also appeared to go beyond the classification of static molecular properties towards the investigation of dynamic systems undergoing structural changes. Although these applications, especially in the early stages, were again only of an intuitive nature, the resulting empirical rules, like the principle of minimal structural change, the least-motion principle or, more recently, the principle of minimal chemical distance still find important applications even in contemporary chemistry [6–15].

Because of the fundamental role which similarity plays in so many different situations it is not surprising that similarity studies have become the focus of intense scientific interest in recent years. The main attention has been devoted to the design of new quantitative measures of molecular alikeness. Among them the so-called similarity indices have found the greatest use [16–21] and a lot of papers have appeared in recent years describing their application in various fields of chemistry [22]. Our aim in this study is to join the recent efforts aimed at the systematic exploration of similarity indices and to apply them to the theoretical justification of one of the most fruitful empirical rules, the so-called Hammond postulate [23]. This postulate was introduced in mid 50s as a simple means of estimating the structure of transition states in chemical reactions. Although clearly understandable qualitatively, the original formulation operating with the concept of reactant- and/or product-like transition state lacks the rigorous theoretical background which would allow us to put the postulate on a safer theoretical footing. This situation, however, has changed in recent years since the advent of various quantitative similarity measures revived the interest in the quantitative reconsideration of the basic principles underlying the validity of this empirical postulate and several papers have recently appeared in which the theoretical justification of the postulate was attempted [24–28]. Into the framework of efforts aimed at the systematic exploration of various quantitative similarity measures it is possible to include also our previous studies in which the applications of the so-called topological similarity index in the field of pericyclic reactivity [29–35] was reported. In this study we apply the topological similarity index to the evaluation of the applicability of Hammond postulate just to this particular class of reactions. The reason for this is that a possibility of anti-Hammond behavior of some of these reactions was proposed some time ago [36] and one of the aims of this study is to check whether or to what extent this proposal is valid.

2. Theoretical

The methodological background of the present study is the so-called topological similarity index [21] resulting from the incorporation of similarity index introduced some time ago by Carbó [17] (eq. (1)) into the framework of the so-called overlap determinant method [34]. Within the framework of this approach, the original Carbó's similarity index r_{AB} characterizing the similarity of two molecules A and B by comparing their electron distributions can be rewritten in form (2).

$$r_{AB} = \int \rho_A(1)\rho_B(1)d\tau_1 \bigg/ \left(\int \rho_A^2(1)d\tau_1\right)^{1/2} \left(\int \rho_B^2(1)d\tau_1\right)^{1/2}, \qquad (1)$$

$$r_{AB} = TrP_A\overline{P_B}/2N\,. \qquad (2)$$

The P_A, P_B are usual charge density bond order matrices and the bar over the matrix P_B denotes the similarity transformation with the matrix T:

$$\overline{P_B} = T^{-1} P_B T\,. \tag{3}$$

This matrix enters into the formalism from the overlap determinant method and its aim is to describe the mutual relation of AO basis sets on molecules A and B, respectively:

$$\chi_\nu^B = \sum_\mu T_{\mu\nu} \chi_\mu^A\,. \tag{4}$$

Although the original introduction of this topological similarity index was restricted only to the level of simple HMO theory, the resulting approach has found many interesting applications especially in the field of pericyclic reactivity [29,33,34]. Despite this extensive use it has become apparent that the limitation to the level of HMO theory has a restricting impact on the applicability of the index.

In order to remedy this partial limitation and to broaden thus the applicability of the approach, we recently proposed a generalization of the original index [37] to the level of semiempirical MO methods [38]. The basic idea of this generalization is the determination of the form of the transformation matrix T from the condition of the maximization of the similarity index [39]. The result of this optimization is a completely positionally invariant index, which, because of taking into account all valence electrons, can be applied to various real chemically interesting problems. An example of such a problem is the theoretical justification of the Hammon postulate. The basic idea of such a justification is extremely simple and consists of the evaluation of the similarity of the reactant vs. the transition state and the product vs. the transition state and in correlating them with the exo- and/or endothermicity of the process. This requires that we first localize the corresponding key molecular species on the potential energy hypersurface, determine that the transition state is indeed a true saddle point and then calculate the similarity indices $r_{R,TS}$ and $r_{P,TS}$.

The above simple methodology was applied to a series of three selected pericyclic reactions, electrocyclic transformation of 1,3 butadiene and 1,3,5 hexatriene to cyclobutene and 1,3 cyclohexadiene, respectively, and the Diels–Alder reaction of 1,3 butadiene with ethene. For all these reactions only the mechanisms allowed by Woodward–Hoffmann rules were considered. The reason is that the critical structures near the top of the energy barrier on the forbidden reaction path frequently do not correspond to true saddle points (transition states) [40] and so it is not clear whether the Hammond postulate should be applicable to them. The calculations were performed at the level of the AM1 method [41] included into the MOPAC package [42] and the resulting values of heats of formations of all key molecular species (reactants, products and transition states) are summarized in Table 1. These data can be compared with those previously reported for the butadiene to cyclobutene cyclization and the Diels–Alder reaction in [43,44]. Such a comparison indicates the close coincidence of our and literature results. Unfortunately we did not find any data to compare with the cyclization of hexatriene but we believe that

Table 1
AM1 calculated values of δH_f (in kcal/mol) for the reactants, products and transition states of the studied series of reactions.

Reaction	$\delta H_f(R)$	$\delta H_f(P)$	$\delta H_f(TS)$
Butadiene to cyclobutene	30.7	45.7	81.1
Hexatriene to cyclohexadiene	48.0	17.9	73.9
Butadiene and ethene to cyclohexene	47.1	−10.2	70.2

because of the close coincidence in the previous two cases, the structures found here are reliable enough for our comparisons.

3. Results and discussion

Having proved the close coincidence of our and previously reported thermochemical data, it is possible to attempt the comparison of density matrices of individual species via the similarity indices. In keeping with the philosophy of the Hammond postulate the comparison concerns the similarity indices $r_{R,TS}$ vs. $r_{P,TS}$ for each of the studied reactions. The calculated values of similarity indices for all studied reactions are summarized in Table 2.

Let us now attempt to discuss the conclusions suggested by the data, first for the conrotatory cyclization of butadiene to cyclobutene. As can be seen from the Table 1, the reaction written in the direction *butadiene → cyclobutene* can be expected to be endothermic so that the Hammond postulate allows us to expect the transition state to be product-like. This expectation can be directly checked by comparing the similarity indices and, as can be seen from Table 2, the corresponding indices are indeed consistent with the expectations of the Hammond postulate. The same qualitative agreement between the predictions of the Hammond postulate and the theoretical expectations based on similarity indices are also observed for the remaining two reactions, the hexatriene to cyclohexadiene cyclization and the Diels–Alder addition of butadiene to ethylene to yield cyclohexene. As can be seen from the Table 1, both these reactions are predicted to be exothermic so that the reactant-like transition states can be expected. Also, as can be seen from Table 2, this empirical expectation is indeed confirmed. This result is especially interesting

Table 2
Calculated values of similarity indices $r_{R,TS}$ and $r_{P,TS}$ for a series of selected pericyclic reactions.

Reaction	$r_{R,TS}$	$r_{P,TS}$
Butadiene to cyclobutene	0.907	0.975
Hexatriene to cyclohexadiene	0.978	0.966
Butadiene and ethene to cyclohexene	0.979	0.966

for the Diels–Alder reaction where the possibility of anti-Hammond behaviour of potential energy surfaces was proposed some time ago [36]. Here it is interesting to remark that some time ago a similar Hammond-like behavior, even if for different Diels–Alder systems, was reported by Cioslowski et al. [25]. In connection with this result it is, of course, necessary to be aware of the fact that these conclusions are valid only for the particular systems studied but since the above methodology is completely general, the same approach can be applied to any other reaction. The systematic examination of other systems thus provides the possibility of theoretical justification of the Hammond postulate as well as of evaluation of the factors responsible for its eventual failure.

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