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Valency changes in chemical reactions

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An analysis of valence changes in selected organic gas phase reactions, calculated on SINDO1 potential surfaces, is performed. It is shown that transition states and intermediates have diradical character if singlet and triplets states are nearly degenerate. As a consequence, normal valencies are expected in Woodward-Hoffman allowed reactions and reduced valencies in forbidden reactions. The formalism is also applied to cationic reactions, but the effects of valency changes are less pronounced.

Key words: Valency changes — Woodward-Hoffmann reactions

1. Introduction

The concept of chemical valence was recently revived [1] and generalized to configuration interaction calculations [2]. After earlier applications of the so-called bond index by Wiberg [3] in the work of Armstrong et al. [4] and Semyonov [5], the formalism was now derived from first principles. Atomic valency finally appeared as expectation value of diatomic portions of the density operator [2]. It was possible to express the atomic valency as a sum of contributions from occupied molecular orbitals.

A comparison of the actual atomic valency due to bonding in a molecule with the standard atomic valency, e.g. 4 for carbon, 3 for nitrogen, 2 for oxygen etc., allows one to determine subvalent and hypervalent atoms in molecules [1, 2].

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This concept directly leads to the possibility of recognizing radical, diradical and zwitterionic situations of molecular states [6]. A radical is characterized by a valence reduction of 1, a diradical by 2. By valence reduction we mean the difference of the sum of all normal atomic valencies and the sum of all actual atomic valencies. The triplet state of CH_2 is a diradical in this sense, because the total normal valency of its atoms is 6 compared to 3.91 in a SINDO1 calculation [7]. The valence reduction is 2.09.

It is the goal of this article to illuminate chemical reactions by the study of valence changes during the reaction.

2. Method of calculation

Structures of ground states, intermediates and transition states were determined by the semiempirical method SINDO1 [7]. This method was extensively tested for ground states [8] and its accuracy for geometry and energy documented. The method was then extended to thermal reactions of configuration interaction potential surfaces. Only those configurations were included in the calculation which were relevant for the reaction. This means that no configuration interaction was used for reactant and product to avoid double counting of correlation effects implicitly included through parametrization.

To simplify the procedure we have taken the wave functions of reactions studied in earlier work [9–13]. These wave functions were analyzed at transition states and intermediates on the potential surfaces in terms of atomic valence numbers. These numbers are a measure of the covalent bonding in which each atom is engaged in a molecule. The sharing of two electrons in a molecular orbital is a maximum in terms of valence numbers if polarization effects in the molecule are negligible. We call valence reduction ΔV the difference between normal and actual valence numbers

$$\Delta V = \sum_{A}^{\text{atoms}} (V_A^{\text{normal}} - V_A^{\text{actual}}). \tag{2.1}$$

In the subsequent section we present changes of valence numbers in some simple organic reactions.

3. Valence numbers in reactions

3.1. Concerted thermal reactions

Woodward and Hoffmann [14] have classified some concerted reactions as allowed or forbidden depending on the orbital correlation of occupied and virtual orbital. We calculated the wave functions for three reactions: cyclobutene – butadiene and cyclopropyl cation – allyl cation on SINDO1 potential surfaces [13]. Each reaction was followed along a conrotatory and disrotatory pathway. The valence numbers for reactant, transition states and products are presented in Table 1. The first transition state is along the allowed pathway, the second along the forbidden pathway.

Table 1. Valence changes in rearrangement reactions

Reaction	State	Energy (kcal/mol)	Atomic valence numbers C_1	C_2	C_3	C_4	Reduced valency
Cyclobutene	R	13.1	3.98	3.96	3.96	3.98	0.12
→ butadiene	TS_{con}	61.2	3.97	3.98	3.98	3.97	0.10
	TS_{dis}	69.6	3.10	3.89	3.88	3.10	2.03
	P	0	3.98	3.89	3.98	3.98	0.08
Cyclopropylcation	R	9.7	3.92	3.27	3.92		0.89
→ allyl cation	TS_{dis}	19.1	3.81	3.81	3.79		0.59
	TS_{con}	65.4	3.76	3.61	3.54		1.09
	P	0	3.62	3.91	3.62		0.85

For the neutral molecule reaction cyclobutene - butadiene the forbidden disrotatory pathway is connected with an orbital crossing of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). There is a quasidegeneracy of HOMO and LUMO at the transition state which means a diradical situation. This is reflected in the reduced total valency which is lower by 2.03 than the sum of normal atomic valencies. Total valency of the transition state of the allowed reaction is close to the standard of 16. This is also true for the values of reactant and product as we naturally expected.

In the cationic cyclopropyl - allyl closed-shell reaction the normal total valence number should be 12 since we refer to the neutral atoms. Here again the total valence number along the forbidden pathway is lower than along the allowed pathway, but the reduction is not as large as in the first case. This could be due to the difficulty in locating the region of quasidegeneracy in this case.

3.2. Nonconcerted thermal reactions

We had previously investigated the unsubstituted and substituted cyclobutane fragmentation [10] and the retro Diels-Alder reaction of cyclohexene - butadiene + ethylene. All these reactions involve intermediates and should not be governed by the Woodward-Hoffman rules. However, the well depth of the intermediates is less than 4 kcal/mol and it would be experimentally difficult to intercept them. We present energies and valence numbers along these reaction pathways in Table 2. In all three cases the intermediates should be called diradicals since their reduced valency, i.e. the difference between the sum of normal atomic valence numbers and sum of actual atomic valence numbers is about 2. The first transition states involve the twisting and breaking of one ring bond. They are also diradicals. The last transition states involve the breaking of the remaining bond. Their diradical character is practically lost. These conclusions are in agreement with the conclusions drawn by the singlet-triplet (S-T) splitting criterion for diradicals by Salem and Rowland [15]. The same conclusions hold for the 1,1-dicyano-2-methoxycyclobutane -1,1-dicyanoethylene + methoxyethylene reaction. They involve diradicals, but not zwitterions as the work of Huisgen [16] on tetracyanoethylene in solution seemed to suggest.

Table 2. Valence changes in fragmentation reactions

Reaction	State	Energy (kcal/mol)	S-T Splitting (kcal/mol)	Atomic valence numbers						Reduced valency
				C_1	C_2	C_3	C_4	C_5	C_6	
Cyclobutane	R	0	—	3.93	3.93	3.93	3.93			0.28
→ 2 ethylene	TS_1	70.1	−0.82	3.13	3.88	3.88	3.13			1.98
	I_1(gauche)	66.2	1.44	3.16	3.89	3.89	3.16			1.90
	TS_2	70.1	1.88	3.18	3.88	3.88	3.18			1.88
	I_2(trans)	68.7	2.38	3.18	3.88	3.88	3.18			1.88
	TS_3	72.8	25.29	3.63	3.87	3.87	3.63			1.00
	TS_4	72.6	27.29	3.63	3.87	3.87	3.63			1.00
	P	37.9	—	3.99	3.99	3.99	3.99			0.04
1,1-Dicyano-2-methoxycyclobutane	R	0	—	3.92	3.99	3.99	3.94			0.16
→ 1,1-dicyanoethylene	TS_1	40.9	−0.38	3.10	3.92	3.94	3.28			1.76
+ methoxyethylene	I_1(gauche)	39.6	−0.25	3.09	3.91	3.95	3.28			1.77
	TS_2	40.8	0.06	3.09	3.91	3.95	3.28			1.76
	I_2(trans)	40.2	−0.00	3.09	3.92	3.94	3.28			1.77
	TS_3	62.4	24.80	3.71	3.91	3.88	3.73			0.77
	TS_4	61.6	25.60	3.70	3.91	3.88	3.73			0.78
	P	16.3	—	3.93	3.96	3.98	3.97			0.16
Cyclohexene	R	0	—	3.98	3.98	3.99	3.99	3.99	3.99	0.08
→ butadiene + ethylene	TS_1	81.6	0.13	3.95	3.98	3.10	3.99	3.98	3.11	1.89
	I	77.8	−0.00	3.95	3.98	3.09	3.97	3.98	3.10	1.93
	TS_2	88.7	30.30	3.70	3.97	3.89	3.85	3.91	3.91	0.77
	P	46.4	—	3.98	3.98	3.98	3.98	3.99	3.99	0.10

The method of Salem and Rowland [15] to determine diradicals by singlet-triplet splitting and also the more general method of Döhnert and Koutecky [17] on the basis of occupation numbers of natural orbitals are *global* methods which relate to the molecule as a whole. In contrast, the valency method is a *local* method since it allows to determine the location of diradical centers in addition to the assignment of the label diradical to the whole molecule. We wish to demonstrate this advantage by the review of isomerization reactions involving the 2,3-dimethylene-1,4-cyclohexadiyl which was studied by us previously [11]. The latter compound is a diradical in the sense of Berson [18] since it is a molecule with an even number of electrons which contains one bond less than the standard rules of valence imply. This diradical was isolated and extensively studied in gas phase and solution reactions by Roth [19]. We present the reaction

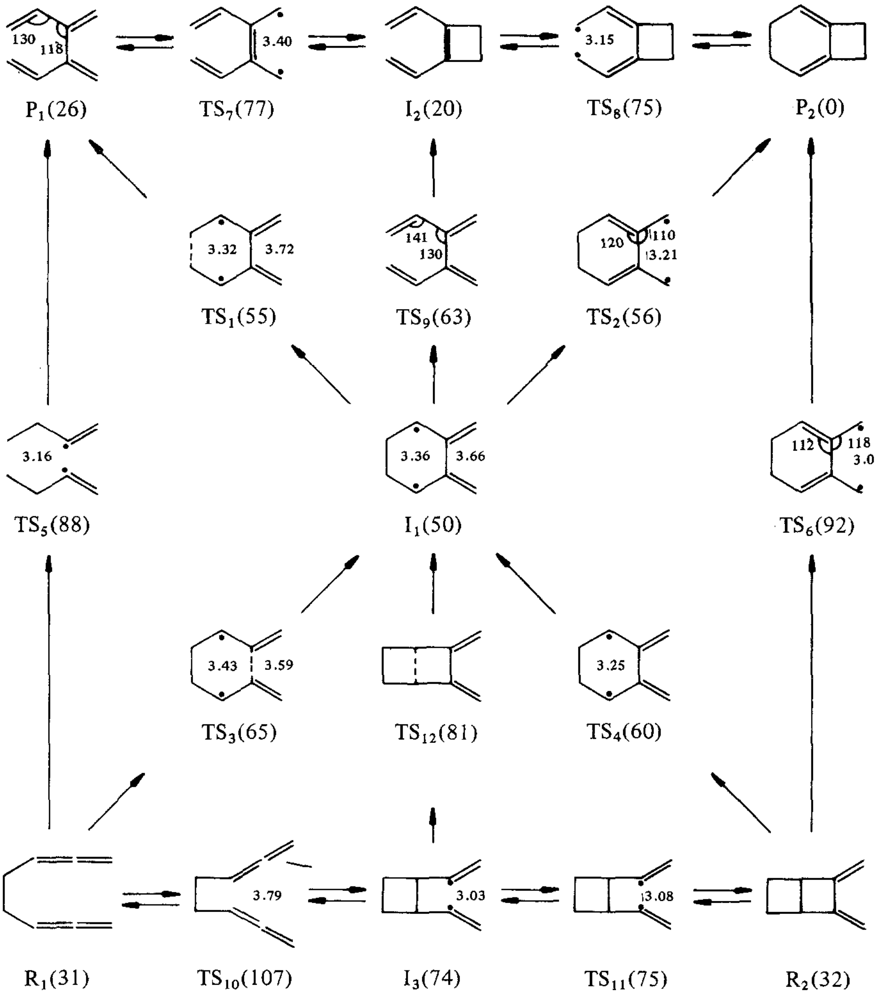

Fig. 1. Energies valence numbers and diradical centers of thermal reaction mechanism involving 2,3-dimethylene-1,4-cyclohexadiyl

mechanism, energies and valence numbers of diradical centers in Fig. 1. From this figure it is apparent that two intermediates (I_1, I_2) and nine transitions states (TS_1-TS_8, T_{11}) could be called diradicals.

It is most interesting that in three cases (I_1, TS_1, TS_3) the nonbonding electrons are not localized at two centers, but are distributed over four centers. In the figure we have only dotted the main centers. In TS_3 the valence numbers 3.43 in the ring and 3.59 at the methylene ends are almost equally large. Generally there is no way to predict the location of the radical centers by looking at the formal structure of reactants, products and intermediate I_1.

3.3. Photochemical reactions

We have recently studied the photoreaction of cyclopentanone [12]. This reaction shows three products: 4-pentenal, cyclobutane + carbon monoxide, and two ethylene + carbon monoxide. We have claimed that all of the pathways involve diradicals. We present now in Fig. 2 the valence numbers of the essential atoms and the diradical centers. Triplet intermediates $^3I_1$ and $^3I_1'$ are diradicals, but not degenerate with the singlet. The criterion of Salem [15] would not predict these. With Koutecky's criterion [17], one could not easily predict the diradical centers. On the other hand, the states $^{1,3}D$ and $^{1,3}D'$ leading to fragmentation would be

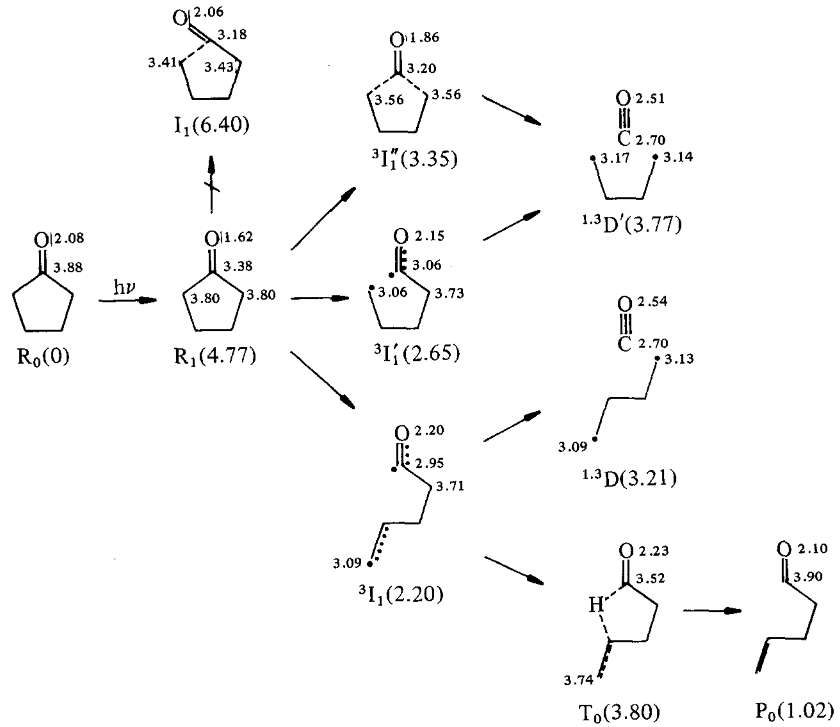

Fig. 2. Energies, valence numbers and diradical centers of photochemical reaction mechanism of cyclopentanone

easily identified as diradicals by all three methods since there is singlet-triplet degeneracy.

4. Conclusion

We have presented a method based on valence numbers which is able to furnish complementary information on chemical reaction along reaction pathways. During reactions the actual valence numbers of atoms in molecules are usually reduced during reactions, compared to the valence numbers of stable reactants and products. The magnitude of this reduction depends on how much configuration interaction is involved in the wavefunction during the process of breaking and forming of bonds. Woodward-Hoffmann allowed reactions with closed-shell neutral molecules suffer little reduction in valence numbers, whereas forbidden reactions involving orbital crossing are accompanied by substantial valence number reductions. The method can equally be applied to nonconcerted and photochemical reactions. In particular it is capable to determine diradicals. For ionic systems the effects seem less pronounced.

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