THEORETICAL STUDY OF PHYSICAL PROPERTIES
OF ACTIVATED COMPLEXES AND METASTABLE INTERMEDIATES

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Ionization potentials, electron affinities, charges, dipole moments and electronic spectra were calculated semiempirically for the activated complexes and metastable intermediates on the formaldehyde-hydroxycarbene reaction path. It is believed that such data help to prove the existence of activated complexes and metastable states experimentally, particularly spectroscopically. The results conform to the Fukui–Fujimoto principle of the inter-frontier energy gap narrowing.

The question of applicability and justifiability of the theory of absolute reaction rates has been tempting for decades. In spite of some inherent weak points it seems that it is the best theory which is available when a long-lived activated complex is formed. It can be assumed that in such cases it is permissible to consider the activated complex as an ordinary chemical species. It would be ideal if it were possible to prove the existence of activated complexes experimentally, in particular spectroscopically. Enormous development in the field of spectroscopy could perhaps make such direct evidence accessible in the near future. It would certainly be most beneficial to have *a priori* — as a guide — at our disposal at least rough estimates of various physical characteristics for the potential candidates for such a study. This concerns both, activated complexes and possible metastable intermediates.

As there is no real chance to prepare these species in higher concentrations and as they cannot be separated from relatively very high concentrations of reactants and products we have to be interested in such characteristics which are significantly different for reactants and products on the one hand and for transient species on the other hand. It seems that various types of electronic spectroscopy could be particularly useful for this purpose. Therefore, it is the aim of this paper to calculate electronic spectral·characteristics, ionization potentials, electron affinities, electron densities and dipole moments for systems under study. There is, moreover, another reason for getting information on excited states of activated complexes, namely, whether they contribute significantly to the total partition function.

Selection of the System

We have studied the components of the reaction system which consists of formaldehyde (*I*), *cis*-hydroxycarbene (*II*) and *trans*-hydroxycarbene (*III*). The energy

hypersurface of H_2CO was studied thoroughly in our Laboratory[1]. Altogether three real minima, three activated complexes *IV*, *VI*, *VII* and one metastable intermediate (*V*) were found. The reaction scheme is presented in Fig. 1. All seven systems which were studied possess a singlet ground state. No crossing of energy hypersurfaces was observed, therefore the use of the adiabatic approximation is correct.

Calculations

We made use of the INDO/S method with limited configuration interaction which proved useful not only with closed shell systems but also with radicals and radical ions[2]. This procedure is to a certain extent superior to the CNDO/S method[3] and permits reasonable interpretation of not only electronic spectra but also of ionization potentials and electron affinities.

The calculations were performed for stationary points obtained by an automatic energy optimization with respect to all coordinates[1,4]. All geometries presented satisfy the condition $|\mathbf{grad}\ E| = 0$, where E stands for the potential energy of the systems.
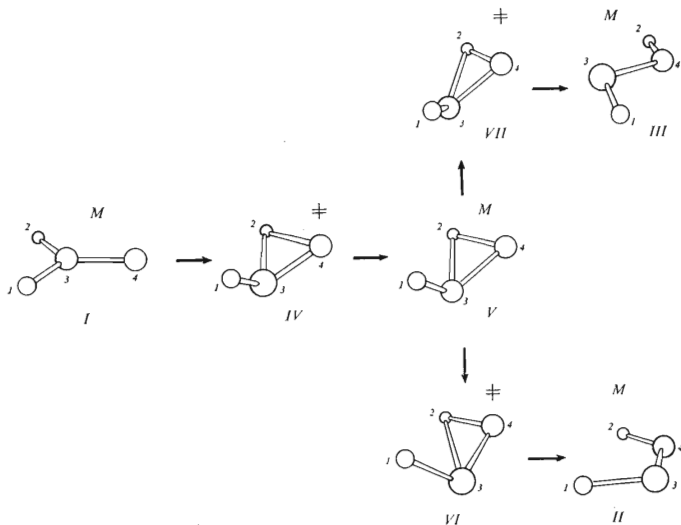

FIG. 1
Perspective Plots of Systems Under Study[1]

RESULTS

Before presenting results of calculations a comment is desirable on the reliability of semiempirical calculations in this field. Generally speaking well established semiempirical schemes lead to reasonable results with systems held together by means of strong interactions. This is also the case, if certain premises are satisfied, with systems where medium interactions apply (*e.g.* hydrogen bonds, various solvate–solvent complexes). We feel that numerous activated complexes and metastable species can be assigned to this group. Finally, with complexes held together only by weak forces, semiempirical procedures fail badly[5]. This is easily understandable if one takes into consideration the way in which these methods were parametrized. Useful semiempirical results obtained previously for various radicals and transient species[3,6,7] together with the fact that accurate complete non-empirical calculations of chemicall interesting potential surfaces are beyond present possibilities, make semiempirical approach acceptable.

The results of INDO/S calculations on the systems investigated are presented in Tables I and II. They can be characterized as follows: when one compares the properties of activated complexes and of the metastable intermediate with the properties of reactants and products it is obvious that ionization potentials are smaller, electron affinities higher and excitation energies of the $S_0 \rightarrow S_1$ transitions smaller. Before passing from this qualitative statement to a semiquantitative evaluation of the data it is necessary to stress that this result provides evidence that the Fukui––Fujimoto principle[8] of a narrowing of the inter-frontier energy level separation is valid.

More quantitatively, the properties of the activated complexes and the intermediate with respect to formaldehyde are: *1*) Ionization potentials are lower by 1·2 to 1·5 eV. *2*) Electron affinities are higher by 0·3—0·7 eV. *3*) The $S_0 \rightarrow S_1$ excitation energies are lower by 0·8—1·1 eV. *4*) The $T_1 \rightarrow T_2$ excitation energies increase by 2·7 to 4·4 eV. *5*) The $S_0 \rightarrow T_1$ excitation energies decrease by 1·5—2·0 eV.

Transition from formaldehyde to the metastable species is, moreover, associated with *a*) a decrease of q_O which (except of *IV*) is even deeper when passing to the excited states; *b*) the migrating hydrogen atom behaving as a "proton-like" particle, excitation having no significant effect on the properties studied; *c*) the positive charge on the C atom approaching zero or becoming negative; the negative values are more pronounced (except of *IV*) when passing to the excited states.

The change of dipole moments cannot be simply rationalized. Two conclusions can be drawn from this study: First, the changes in excitation energies ($S_0 \rightarrow S_1$, $S_0 \rightarrow T_1$) are very significant. They are therefore good candidates for potential experimental verification because the transient species theoretically absorb light in the region where both reactant and products are transparent. Second, in spite of large bathochromic shifts of the first bands of the transient species, it is not neces-

sary to include, with the systems under study, the electronic partition function in the total partition function. We feel, however, that numerous transient species exist where such an inclusion would be important.

TABLE I

Results of INDO/S Calculations: Energies (E) and Wavenumbers ($\tilde{\nu}$) of the Electron Transitions, Oscillator Strengths (f), the Main Configurations Contributing to the Excited States and Their Weights

System[a]	Transition	E, eV	$\tilde{\nu}$, cm^{-1}	f	Conf.	Weight, %
I	$S_0 \to S_1$	3·07	24 750	0·0	6—7	100
	$S_0 \to S_2$	7·89	63 650	0·017	4—7	100
	$S_0 \to T_1$	2·52	20 330	0·0	6—7	100
	$T_1 \to T_2$	1·76	14 170	0·0	5—7	100
IV	$S_0 \to S_1$	1·93	15 570	0·009	6—7	98
	$S_0 \to S_2$	6·35	51 240	0·016	5—7	68
	$S_0 \to T_1$	0·73	5 890	0·0	6—7	97
	$T_1 \to T_2$	4·41	35 560	0·037	5—7	71
V	$S_0 \to S_1$	2·30	18 560	0·012	6—7	99
	$S_0 \to S_2$	6·96	56 160	0·017	5—7	78
	$S_0 \to T_1$	0·93	7 500	0·0	6—7	95
	$T_1 \to T_2$	5·00	40 370	0·047	5—7	73
VI	$S_0 \to S_1$	2·14	17 260	0·015	6—7	98
	$S_0 \to S_2$	7·58	61 160	0·021	5—7	93
	$S_0 \to T_1$	0·53	4 280	0·0	6—7	94
	$T_1 \to T_2$	6·09	49 150	0·013	6—8	97
VII	$S_0 \to S_1$	2·20	17 740	0·016	6—7	98
	$S_0 \to S_2$	8·07	65 100	0·131	5—7	59
	$S_0 \to T_1$	0·56	4 520	0·0	6—7	95
	$T_1 \to T_2$	6·20	49 980	0·011	6—8	95
II	$S_0 \to S_1$	2·66	21 480	0·024	6—7	99
	$S_0 \to S_2$	7·97	64 270	0·007	5—7	99
	$S_0 \to T_1$	1·00	8 070	0·0	6—7	96
	$T_1 \to T_2$	5·99	48 290	0·011	6—8	98
III	$S_0 \to S_1$	2·49	20 060	0·017	6—7	99
	$S_0 \to S_2$	8·44	68 050	0·164	6—8	94
	$S_0 \to T_1$	0·86	6 940	0·0	6—7	97
	$T_1 \to T_2$	6·18	49 820	0·009	6—8	97

[a] The systems are arranged in accordance with the reaction path (Fig. 1).

TABLE II

Results of INDO/S Calculations: Ionization Potentials (I), Electron Affinities (A), Electron Densities (q_i) and Dipole Moments (μ). Hydrogen Atom 1 is Always Attached to the Carbon Atom, the Migrating Hydrogen Atom is Labelled 2, 3 Stands for the Carbon and 4 for Oxygen Atoms

System[a]	State	I, eV	A, eV	q_1	q_2	q_3	q_4	$10^{30}\mu$, Cm
I	S_0	10·37	0·04	0·021	0·021	0·291	−0·334	10·01
	S_1			0·109	0·109	−0·288	0·070	2·63
	S_2			0·049	0·049	−0·189	0·092	1·53
	T_1			0·109	0·109	−0·287	0·069	2·33
	T_2			0·021	0·021	0·026	−0·068	4·70
IV	S_0	8·86	0·35	−0·037	0·241	−0·056	−0·148	7·20
	S_1			0·077	0·196	−0·047	−0·225	7·00
	S_2			−0·046	0·123	−0·190	0·112	4·94
	T_1			0·074	0·193	−0·047	−0·220	6·90
	T_2			−0·038	0·135	−0·208	0·112	5·80
V	S_0	9·03	0·69	−0·033	0·234	−0·026	−0·175	8·07
	S_1			0·085	0·231	−0·216	−0·099	7·17
	S_2			−0·031	0·164	−0·322	0·188	8·27
	T_1			0·081	0·228	−0·221	−0·088	6·84
	T_2			−0·029	0·155	−0·302	0·177	8·54
VI	S_0	9·15	0·51	−0·036	0·206	0·005	−0·175	10·74
	S_1			0·086	0·202	−0·282	−0·006	8·30
	S_2			−0·021	0·187	−0·537	0·370	16·84
	T_1			0·083	0·203	−0·293	0·008	7·17
	T_2			−0·369	0·213	0·085	0·072	9·14
VII	S_0	9·14	0·52	−0·033	0·203	−0·006	−0·165	5·64
	S_1			0·087	0·202	−0·281	−0·009	5·24
	S_2			−0·135	0·193	−0·348	0·290	11·51
	T_1			0·085	0·204	−0·293	0·005	5·40
	T_2			−0·346	0·197	0·087	0·062	14·14
II	S_0	9·44	0·84	−0·038	0·174	−0·044	−0·092	13·01
	S_1			0·089	0·215	−0·176	−0·128	9·00
	S_2			0·014	0·179	−0·637	0·444	20·91
	T_1			0·087	0·214	−0·188	−0·113	7·54
	T_2			−0·369	0·207	0·161	0·000	9·54
III	S_0	9·27	0·77	−0·029	0·173	−0·046	−0·098	6·30
	S_1			0·081	0·193	−0·224	−0·050	5·07
	S_2			−0·378	0·183	0·090	0·105	17·38
	T_1			0·079	0·194	−0·234	−0·039	4·97
	T_2			−0·384	0·181	0·112	0·092	16·78

[a] The systems are arranged in accordance with the reaction path (cf. Fig. 1).

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Translated by the author (R. Z.).