60. Studies on Radical Cations, II. Principles Involved in their Electrocyclic Reactions[1])

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Summary

Electrocyclic reactions connecting radical cations are compared with those of the parent neutrals. Principles governing over-all reactivity and stereoselectivity of the open-shell processes are discussed.

Introduction. - The theory of electrocyclic reactions of closed shell systems **M** is highly developed and finds support in numerous experimental observations. The same cannot be said for similar processes of the open shell parent ions $\mathbf{M}^{\pm\cdot}$, of which relatively little is known, both experimentally and theoretically. Since such systems are becoming increasingly important as intermediates in all branches of chemistry, predictive models for their reactions are highly desirable, requiring of course, reliable experimental foundations.

The questions pertinent to electrocyclic reactions are most conveniently stated in a comparative manner: given the usual dual choice of reaction pathways for **M**, one may ask for $\mathbf{M}^{\pm\cdot}$:

1) The 'stereoselectivity' question: is the sequence of barrier heights for the different reaction pathways preserved or not?

2) The 'reactivity' question: is the barrier for a given pathway higher or lower, and (if possible) by what approximate amount?

Results and Discussion. - *General considerations.* For closed shell reactants **M/N**, interconverting along a concerted electrocyclic path, the ground configurations Γ(**M**) and Γ(**N**) either mutually correlate (*O*rbital-symmetry *A*llowed (*OA*) reaction) or correlate with doubly excited configurations Ψ^{**}(**N**) and Ψ^{**}(**M**), respectively (*O*rbital-symmetry *F*orbidden (*OF*) reaction). With respect to orbital correlation diagrams, for species interconverted in an *OA*-reaction only occupied MO's (OMO's) are important. Alternatively, for *OF*-processes also unoccupied MO's (UMO's) play a role [2]. For closed shell *OA*-reactions it does in fact not matter whether the HOMO's correlate directly or with some subjacent orbitals, as

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the qualitative conclusions remain the same. This is, however, not the case in reactions of open-shell $M^{\pm\cdot}/N^{\pm\cdot}$, as discussed further below.

Introduction of electron correlation through configuration interaction (CI.) removes line crossings in the configuration correlation diagrams. As the ground states of M and N are always totally symmetric, both *OA*- and *OF*-processes are *S*tate-symmetry *A*llowed (*SA*) and may proceed in an adiabatic manner.

The situation is more complex for the open shell species $M^{\pm\cdot}$ and $N^{\pm\cdot}$ as noted in [3-5] since now three types of orbital correlation patterns are to be distinguished. *Figure 1* displays these types for radical cation species M^{+}/N^{+} (extension of the discussion to the corresponding radical anions $M^{-\cdot}/N^{-\cdot}$ is straightforward and therefore not done here).

A) The two sets of OMO's on one hand and the two sets of UMO's on the other hand contain an equal amount of orbitals of a given symmetry species[3]) in M^{+} and N^{+}, respectively. Hence, no OMO-UMO correlations appear.

Furthermore, the (singly occupied) HOMO's of M^{+} and N^{+} are of *equal* symmetry[3]) and therefore correlate. As a result the process is of *OA*- and *SA*-type as for the corresponding closed shell reaction. Inspection of various isomer couples involved in pericyclic reactions shows, however, that this case is only seldom realized [3].

B) The condition stated in the first paragraph of A) still holds, but the HOMO's of M^{+} and N^{+} are of *different* symmetry. Therefore, each now correlates with some subjacent occupied MO of N^{+} and M^{+}, respectively. Note, that contrary to the closed shell case the reactants now differ in electronic ground state symmetry and that, therefore, their interconversion is *S*tate-symmetry *F*orbidden (*SF*), obviously also *OF*, and non-adiabatic.

C) There is at least one MO in the occupied set of M^{+} (N^{+}) which has no symmetry equivalent counterpart in the OMO-set of N^{+} (M^{+}); hence, correlation lines joining OMO's and UMO's must occur. The process leading from ground

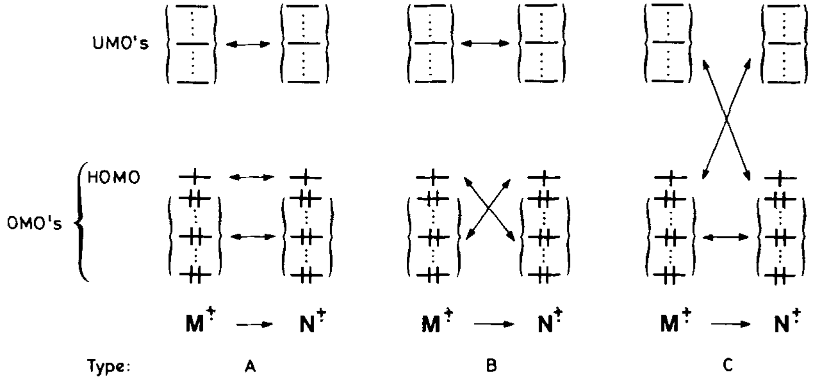

Fig. 1. *Types A, B and C of orbital correlations for electrocyclic reactions of doublet ions*

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[3]) M and N are classified in the point group containing all elements of symmetry conserved during their interconversion.

Table. *Summary of 'selection rules' for reactions of doublet ions involving types A, B and C of orbital correlations*

	Type of electrocyclic process		
	A	B	C
$\mathrm{M} \rightarrow \mathrm{N}$	*OA, SA*	*OA, SA*	*OF, SA*
$\mathrm{M}^{+} \rightarrow \mathrm{N}^{+}$	*OA, SA*	*OF, SF*	*OF, SF*

OA	*O*rbital-symmetry *A*llowed	*SA*	*S*tate-symmetry *A*llowed
OF	*O*rbital-symmetry *F*orbidden	*SF*	*S*tate-symmetry *F*orbidden

state M^{+} to ground state N^{+} is *OF* and *SF* as the reactants again differ in electronic ground state symmetry. The *Table* summarizes the points just discussed.

Qualitative predictions. Does the above scheme provide an answer to the two questions raised in the introduction?

As we know of no example of case A we shall henceforth refer only to cases B and C. Both processes are *OF* and *SF* in $\mathrm{M}^{+}/\mathrm{N}^{+}$. In practice, however, slight perturbations of various kinds [6] will lead to coupling between the crossing states and adiabatic conversion results also on the doublet hypersurface. Nevertheless, we note that the zeroth order crossing points provide a much better approximation to the real barriers for the doublet ions than for the closed shell neutrals, as for the latter the energy of the transition state is considerably lowered relative to the crossing points as a result of CI. We shall limit the discussion again to the case of radical cations since we can avail ourselves profitably of an experimental tool, photoelectron spectroscopy (PES.), giving direct insight into the energies of some of their excited states.

Approaching now the 'stereoselectivity' question we compare the heights of the crossing points in the configuration correlation diagram for B and C *(Fig. 2).*

For case B we note that crossing occurs between lines joining the ground configurations $\Gamma(\mathrm{M}^{+})/\Gamma(\mathrm{N}^{+})$ with excited *'Koopmans'* configurations $\Psi_{K}^{*}(\mathrm{N}^{+})/\Psi_{K}^{*}(\mathrm{M}^{+})$. Excited states dominated by such configurations are observed in PES.; typically, they lie less than 3 eV above the ionic ground states.

The crossing configuration lines for case C lead from $\Gamma(\mathrm{M}^{+})/\Gamma(\mathrm{N}^{+})$ to *'Non-Koopmans'*-excited configurations $\Psi_{NK}^{*}(\mathrm{N}^{+})/\Psi_{NK}^{*}(\mathrm{M}^{+})$. Since states dominated by such configurations cannot be attained by sole ejection of an electron from ground state M/N, PES. unfortunately provides no insight into their energetics. From the electronic spectra of the cations in comparison with the PE. spectra of the parent neutrals these values can in principle be extracted, but only a few experimental efforts have yet been undertaken in this direction [1] [5] [7]. A crude

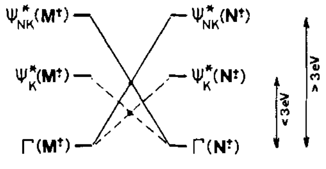

Fig. 2. *Configuration correlation diagram for type B (---) and type C (——) ionic processes* (relative height of crossing points)

estimate for these energies is obtained within a *Hückel*-type orbital approximation. The energy gap between lowest $\Psi^*_{NK}(\mathbf{M}^+)$ and $\Gamma(\mathbf{M}^+)$ is the same as between the first excited singlet state of **M** and its ground state. Since the latter quantities lie typically higher than 3 eV in small organic molecules, $\mathrm{E}(\Psi^*_{NK}(\mathbf{M}^+))$ will in most cases be significantly higher than $\mathrm{E}(\Psi^*_K(\mathbf{M}^+))$. Hence, the barrier of a type C process will most likely be higher than that for the corresponding type B, and $\mathbf{M}^+ \to \mathbf{N}^+$ will therefore exhibit the same stereoselectivity as $\mathbf{M} \to \mathbf{N}$. Although this preference is less pronounced on the doublet manifold and may in fact be overruled by geometrical biases [3], it appears to be supported by the few appropriate experimental observations published yet [3] [8].

We now turn our attention to the 'reactivity' question. For case B the height of the activation barrier as approximated by the crossing point can be estimated if one has information about the energy of the lowest lying state $\Psi^*_K(\mathbf{N}^+)$ which correlates with $\Gamma(\mathbf{M}^+)$, and *vice versa*. Such data are provided by PES. In addition, the relative energy of the ground states of $\mathbf{M}^+$ and $\mathbf{N}^+$ is required and obtained from

$$\Delta H_r(\mathbf{M}^+ \to \mathbf{N}^+) = \Delta H_r(\mathbf{M} \to \mathbf{N}) + I_1^a(\mathbf{N}) - I_1^a(\mathbf{M}). \qquad (1)$$

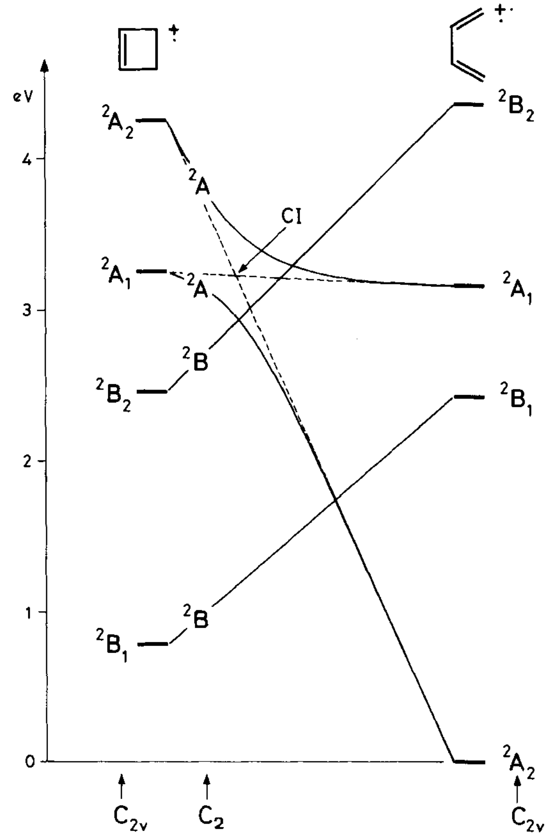

Fig. 3. *State correlation diagram for the disrotatory opening of cyclobutene cation to butadiene cation* (see text)

Inspection of several ionic model reactions of type B suggests that their barriers should usually be less than 1 eV. Consider for example the conrotatory ring opening of cyclobutene (**CB**) cation to butadiene (**BD**) cation. From (1), using $\Delta H_r^0(\mathbf{CB} \rightarrow \mathbf{BD}) = -46.8$ kJ mol$^{-1} \hat{=} -0.49$ eV, $I_1^a(\mathbf{CB}) = 9.43$ eV [9] and $I_1^a(\mathbf{BD}) = 9.03$ eV [9] we obtain $\Delta H_r(\mathbf{CB}^+ \rightarrow \mathbf{BD}^+) \hat{=} -85.4$ kJ mol$^{-1} = -0.89$ eV[4]), the ionic reaction being about twice as exothermic as the neutral one. The states of $\mathbf{CB}^+$ and $\mathbf{BD}^+$[4]) as taken from [9] are displayed in *Figure 3* with reference to ground state $\mathbf{BD}^+$ ($^2A_2$ in C_{2v}). The height of the crossing point of the ^2B- and ^2A-correlation lines (in C_2) suggests a thermal barrier around 0.9 eV. The actual barrier may well lie somewhat below this value due to departure of the reaction from the idealized C_2-coordinate, resulting in avoided crossing of the correlation lines.

Unfortunately, the correlation diagrams for the corresponding closed shell reactions $\mathbf{M} \rightarrow \mathbf{N}$ do not provide any similar clue to the associated barriers, and a comparison with the ions is therefore impossible on this simple basis. For each case, however, the estimated upper bound for the barrier of the ions may be compared with the experimental one for the neutrals. For our example $\mathbf{CB} \rightarrow \mathbf{BD}$, $E_a = 1.41$ eV [10], indicating the ionic process $\mathbf{CB}^+ \rightarrow \mathbf{BD}^+$ to be more efficient[5]).

Even though PES. does not yield the energies of Ψ_{NK}^*, the comparison between $\mathbf{M} \rightarrow \mathbf{N}$ and $\mathbf{M}^+ \rightarrow \mathbf{N}^+$ is more straightforward for case C. Here, the following points will generally apply if the working hypothesis of a concerted synchronous interconversion is maintained:

(i) From a *Hückel*-type orbital model it is evident that the excited configurations used in the correlation diagram lie only half as high in energy for $\mathbf{M}^+ \rightarrow \mathbf{N}^+$ than for $\mathbf{M} \rightarrow \mathbf{N}$: for both processes the same orbitals are involved, but in the former only

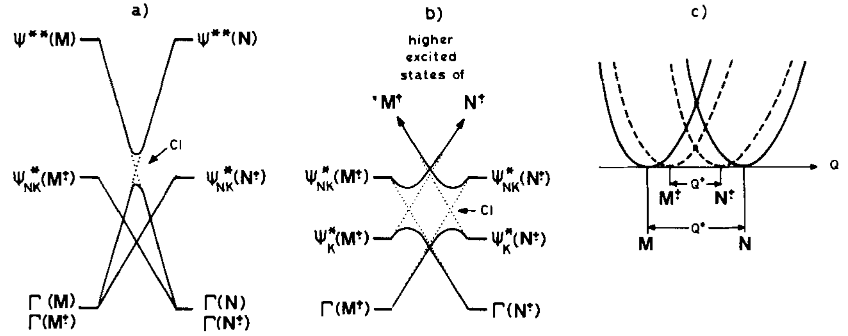

Fig. 4. a) *Configuration correlation diagram for a type C ionic process in comparison with that for the corresponding neutrals*

b) *Effect of CI. on barrier height for an ionic type C process*

c) *Energetic consequence of the shortening of the reaction coordinate for the ionic type C process*

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[4]) We assume for our crude estimate the experimental values obtained for *trans*-**BD** to be applicable also to *cis*-**BD**.

[5]) Experimental results dealing with the thermal and the photo-chemistry of the matrix-isolated system $\mathbf{CB}^+/\mathbf{BD}^+$ will be published in the near future in this journal [11].

one electron is raised to a virtual level *(Fig. 4a).* For straight correlation lines this relation applies also to the crossing points. It is unlikely that CI. for the neutrals will invert this sequence. Note that the pertinent correlation line $\Gamma(\mathrm{M}^+)$-$\Psi^*_{NK}(\mathrm{N}^+)$ is likely to cross symmetry equivalent ones connecting low lying $\Psi^*_K(\mathrm{N}^+)$ with higher lying $\Psi^*(\mathrm{M}^+)$, and *vice versa,* and CI. comes into play also for the ions. But unlike for the neutrals *(Fig. 4a),* the crossing point is not directly affected through this CI. effect although it might ultimately be depressed somewhat *(Fig. 4b).*

(ii) Inspection of several valence isomer couples rearranging according to type C reveals that their HOMO's have positive partial bond orders for the bonds being deleted and negative ones for the bonds being formed in the reaction. The reverse is true for the virtual orbitals involved. Ejection of an electron from the HOMO's of M/N generating $\mathrm{M}^+/\mathrm{N}^+$, thus leads for one reactant to a structural relaxation directed towards the geometry of the other. This results in a shortening $\Delta\mathrm{Q} = \mathrm{Q}^+ - \mathrm{Q}^0 < 0$ of the reaction coordinate for the ions, hence in a lowering of the crossing points of the potentials curves, if similar force constants are assumed for M/N and for $\mathrm{M}^+/\mathrm{N}^+$ *(Fig. 4c).*

These points suggest that type C processes are more favorable for the ionic species. The following paper gives experimental and detailed theoretical support to this conclusion for the system quadricyclane/norbornadiene [12].

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