# Applications of the Mapping Analysis of Concerted Reactions

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**Abstract:** Several illustrations of the mapping analysis of concerted reactions are given, using well-understood systems for the most part. The interconversion of several $C_4H_6$ species is examined; bicyclobutane, cyclobutene, and butadiene are interconverted according to well-defined stereochemical paths according to the analysis. Coplanar addition reactions of ethylene with ethylene, formaldehyde, cumulene, and ketene are discussed, and the stereospecific thermal opening of 4-methylcyclobutene is briefly examined. The parameters central to the mapping analysis are the overlaps of corresponding orbitals in the mapped ground-state functions, $\sigma_i$, and the state overlap, $\sigma = \Pi_i\sigma_i$. Inspection of the $\sigma_i$ and the orbitals allows the interpretation of reactions in terms of rearrangements within and among bonds.

In the preceding report[2] the formal basis for a new analysis of concerted reactions was presented. The new analysis is based on the assumed requirement that the nuclear motions in concerted reactions will be inhibited from producing new nodes in the molecular orbital wave function by a substantial energy barrier. Thus the distortions which transform the wave functions of reactants into the wave functions of products may be viewed as a mapping which must be a topological identity. An approximate mapping operator which is capable of reflecting the effects of bond bending and twisting has been constructed. This report is concerned with the application of the mapping analysis to some chemically interesting systems.

The first section of this discussion is devoted to the thermal interconversions of the $C_4H_6$ species bicyclobutane, cyclobutene, and butadiene. Additional reactions of carbonyl compounds which seem to violate the Woodward–Hoffmann generalizations are considered in section II. Finally, the mapping analysis is employed to support an explanation of the anchimeric interference of an -OH group on a formally allowed disrotatory 1,4 addition.

## I. Application of Mapping Analyses to Thermal Interconversion of Bicyclobutane, Cyclobutene, and Butadiene

The closure of butadiene to cyclobutene is predicted[2] by symmetry arguments to proceed by a conrotatory motion of the terminal methylenes, in accord with experiment. The mapping analysis is consistent with the group theoretic results (Table I).

The structure of the roots is particularly simple; 9 of the 11 are very close to unity, while the remaining 2 equal 0.63 to a fair approximation. We are free to transform the orbitals within each of these "degenerate" sets to obtain a more direct intuitive picture of the charge distributions they represent. The argument that the orbitals corresponding to the unit roots would depict bonds, etc., which are merely reoriented during the reactions, would suggest that the nine unit roots would be associated with the $\sigma$ bonds of butadiene. Mapped orbitals and the corresponding independently determined orbitals associated with these roots were localized according to the formalism developed above;[2] inspection of the results makes clear that the orbitals do describe the indicated $\sigma$ bonds. Owing to the bulk of the tables of coefficients of the localized orbitals, only the local bond indices will be reproduced here (Table II). The closeness of the bond indices to unity testifies to success of the localization. It is interesting to note that these $\sigma$ orbitals are also recovered in virtually identical form from the results of the mapping by the forbidden disrotatory route. This result indicates that the $\sigma$ framework has little effect on the stereochemical route of the interconversion of butadiene and cyclobutene.

Since the remaining two orbitals have virtually identical roots, combinations of the two may be formed which satisfy the localization criterion. However, since the $\pi$ orbitals associated with these roots are substantially rearranged during the reaction in ways not allowed for by the mapping operator, the results are not very enlightening. The calculations make clear nonetheless that the source of the stereospecificity is the $\pi$ orbitals. The results of this application are far from surprising, and serve only as a rather elaborate corroboration of the conclusions of Hoffmann and Woodward.[3] The advantages of the mapping analysis are more clearly illustrated by the discussion of a more complicated problem.

The Hoffmann–Woodward analysis of the modes of rearrangement of bicyclobutane is not self-evident; a preliminary account based on symmetry arguments was misleading,[4a] and was corrected by a brute-force construction of the necessary correlation diagrams.[4b] As we shall see, mapping analyses treat both interconversions with equal ease, with no particular demand on the intuition of the analyst.

It is convenient to use Wiberg's classification[4b] of the modes of opening of bicyclobutane to *cis* butadienes. Here (+) means that the methylene is rotated toward a CC bond to be broken and (−) means that the rotation is away from the breaking bond. Deuterium labels will make the course of the rearrangements more clear (see Figure 1). Orbital overlaps and state overlaps were determined for the three modes; the results are given in Table I. The state overlaps are 0.187 for both the − − and + + modes, and 0.442 for the + − mode.

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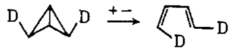
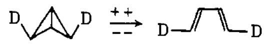
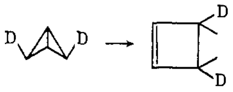
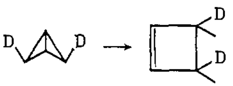
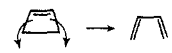
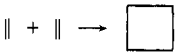
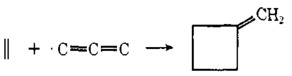
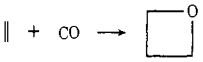
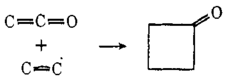
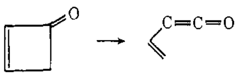
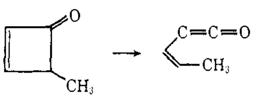
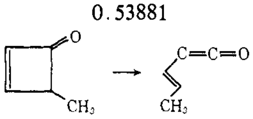
[2] C. Trindle, *J. Amer. Chem. Soc.*, **92**, 3251 (1970).

[3] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395, 2511 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046, 4389 (1965).

[4] (a) K. B. Wiberg and J. Lavanish, *ibid.*, **88**, 5272 (1966); (b) K. B. Wiberg, *Tetrahedron*, **24**, 1983 (1968).

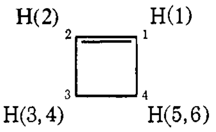
**Table I.** State Overlaps ("Permissibilities") and Squares of Overlaps of Individual Corresponding Orbitals for Several Thermal Interconversions

| State overlap | Roots | | | | |
|---|---|---|---|---|---|
| 1. Bicyclobutane-*exo*-$d_2$ to *cis*-butadiene-1,4-*cis,trans*-$d_2$<br>0.44179<br> | | 1.000 | 0.948 | 0.999 | 0.558 |
| | | 1.000 | 0.999 | 0.984 | 0.980 |
| | | 0.992 | 0.403 | 0.960 | |
| 2. Bicyclobutane-*exo*-$d_2$ to *cis*-butadiene-1,4-*trans,trans*-$d_2$<br>0.18699<br> | | 1.000 | 0.994 | 0.918 | 0.988 |
| | | 0.999 | 1.000 | 0.971 | 0.885 |
| | | 0.965 | *0.048* | 0.978 | |
| 3. Bicyclobutane-*exo*-$d_2$ to cyclobutene-2,3-*trans*-$d_2$<br>0.28929<br> | | 1.000 | 1.000 | 0.477 | 0.243 |
| | | 0.741 | 0.995 | 0.987 | 1.000 |
| | | 0.992 | 0.992 | 1.000 | |
| 4. Bicyclobutane-*exo*-$d_2$ to cyclobutene-2,3-*cis*-$d_2$<br>0.09786<br> | | 0.999 | 0.725 | 0.996 | 1.000 |
| | | 0.044 | 0.990 | 1.000 | 0.973 |
| | | 0.994 | 0.343 | 0.915 | |
| 5. Cyclobutene to butadiene (conrotatory)<br>0.59626<br> | | 0.998 | 0.999 | 1.000 | 0.960 |
| | | 0.997 | 0.987 | 0.619 | 0.970 |
| | | 0.989 | 1.000 | 0.635 | |
| 6. Cyclobutene to butadiene (disrotatory)<br>0.00000<br> | | 0.983 | 0.987 | 0.984 | 0.940 |
| | | 0.970 | 0.915 | 0.997 | 0.000 |
| | | 0.942 | 0.954 | 0.052 | |
| 7. Two ethylenes to cyclobutane<br>0.001<br> | | 0.885 | 1.000 | 0.994 | 0.998 |
| | | 0.949 | 0.099 | 0.990 | 0.995 |
| | | 0.997 | 0.975 | 0.989 | 0.000 |
| 8. Ethylene and cumulene to methylenecyclobutane<br>0.021<br> | 0.992 | 1.000 | 0.985 | 0.995 | 0.997 |
| | 0.866 | 0.999 | 0.847 | 1.000 | 0.999 |
| | 0.001 | 0.987 | 0.712 | 0.724 | |
| 9. Ethylene and formaldehyde to oxacyclobutane<br>0.086<br> | | 0.999 | 1.000 | 0.993 | 0.997 |
| | | 1.000 | 0.981 | 0.994 | 1.000 |
| | | 0.987 | 0.080 | 0.999 | 0.742 |
| 10. Ethylene and ketene to cyclobutanone<br>0.244<br> | 0.079 | 1.000 | 0.995 | 0.997 | 0.998 |
| | 0.996 | 0.932 | 0.980 | 1.000 | 1.000 |
| | 0.800 | 0.570 | 0.995 | 0.468 | |
| 11. Cyclobutenone to ethylenylketene<br>0.01555<br> | 0.998 | 0.995 | 0.927 | 0.001 | 0.990 |
| | 0.999 | 0.998 | 1.000 | 0.960 | 0.981 |
| | 0.528 | 0.761 | 1.000 | | |
| 12. 4-Methylcyclobutenone to *cis*-methylketylethylene<br>0.1185<br> | 1.000 | 0.999 | 0.947 | 0.645 | 0.987 |
| | 0.991 | 1.000 | 0.999 | 0.056 | 1.000 |
| | 0.809 | 0.796 | 0.993 | 0.995 | 0.685 |
| | 0.970 | | | | |
| 13. 4-Methylcyclobutenone to *trans*-methylketylethylene<br>0.53881<br> | 0.532 | 0.892 | 0.952 | 1.000 | 1.000 |
| | 0.997 | 0.997 | 0.985 | 1.000 | 1.000 |
| | 1.000 | 0.991 | 0.996 | 0.998 | 0.688 |
| | 0.989 | | | | |

According to the interpretation of the overlaps suggested in ref 2, state overlaps that large mean that the charge distribution is unaffected by the reaction, we would predict that the + − mode would be favored, since it requires less reorganization of the molecular charge distribution. This prediction is in accord with Wiberg's extensive exploration of the system's potential surface, from which he concludes, noting a discontinuity in the bond index of the 1–2 CC bond as + + or − − twisting of the methylenes in bicyclobutane is performed, that these processes are forbidden. No discontinuity is observed in the + − twisting.

**Table II.** Mapping of Butadiene into Cyclobutene[a]

| Roots | Local bond indices | Bond label |
|---|---|---|
| 0.998 | 0.944 | $C_1C_2\sigma$ |
| 0.999 | 0.998 | $C_4H_6$ |
| 1.000 | 0.999 | $C_4H_5$ |
| 0.960 | 0.996 | $C_3H_4$ |
| 0.997 | 0.996 | $C_2H_3$ |
| 0.987 | 1.000 | $C_2H_2$ |
| 0.970 | 0.995 | $C_1H_1$ |
| 0.989 | 0.963 | $C_1C_4$ |
| 1.000 | 0.962 | $C_2C_3$ |



[a] The nine identical roots produced in the mapping of butadiene into cyclobutene by the conrotatory route are associated with a localizable subunit of the charge distribution. Localization of the corresponding subset of orbitals produced a description of the bonds identified at the right. The extent of localization is indicated by the local bond indices which approach unity for complete localization.

Cyclobutene may also be obtained directly from bicyclobutane, though Wiberg suggests that the formation of butadiene is favored energetically. Mapping calculations summarized in Table I indicate that *trans*-deuterated cyclobutene would be formed in preference to *cis*-deuterated cyclobutene. This is also in accord with Wiberg's results. It may be cautiously inferred that formation of the allowed butadiene may be preferred to the formation of the allowed cyclobutene; however, a clear definition of the quantitative significance of the state overlap is necessary before detailed interpretation can be permitted. The localization analysis (Table III) indicates that the charge reorganization in the opening of bicyclobutane to the allowed butadiene is substantial. As in the cyclobutene–butadiene rearrangement, 9 of the 11 roots are near unity. However, it becomes clear from an inspection of the local orbitals and the local bond indices that the assumption that the nine orbitals with roots near unity are merely reoriented during the reaction is not so well borne out as in the butadiene–cyclobutene interconversion. The local bond indices are not satisfactory, since they depart from one noticeably. However, as a basis for rough interpretation, the local orbitals show that CH bonds and the bridge bond are not involved in the rearrangement.

## II. Mapping Analysis of Some Reactions of Carbonyl Compounds

The uncatalyzed concerted dimerization of ethylene to cyclobutane is forbidden, according to symmetry arguments, if the two molecules approach in the same plane. The state overlap is 0.00 according to mapping calculations. But a similar addition in a system with a like number of $\pi$ electrons, ethylene–formaldehyde, which would be predicted again by application of the Woodward–Hoffmann rules to be forbidden, is in fact experimentally observed.[5] The state overlap for the formation of oxacyclobutane from ethylene and formaldehyde is small, 0.083, but indicates that a possibility exists for the addition. A simple account of this anomalous addition can be given by recourse to a special representation of the formaldehyde–ethylene system in terms of an expansion in configurations constructed from orbitals of the ethylene–ethylene system, for which a symmetry analysis may be done. The critical feature here is the polarized CO $\pi$ bond; this bond may be represented by a contribution from the ground ethylene–ethylene configuration, plus a contribution from the ethylene–ethylene configuration having an antibonding $\pi$ orbital in the appropriate position. This antibonding $\pi$ orbital shifts charge in the CO $\pi$ bond, polarizing it. The interesting feature of the latter configuration is that it allows the four-center addition, although the ground configuration forbids it. Thus the admixture of an excited configuration makes the addition partly allowed, which accounts for the observation of addition. A simple calculation accounts for the order of magnitude of the state overlap. Represent the polarized $\pi$ bond by a superposition of bonding and antibonding functions, $(P_C + P_O)/\sqrt{2} + G(P_C - P_O)\sqrt{2}$. The coefficient $G$ can be determined from the $\pi$ charge on the carbon and oxygen of the carbonyl. $G \simeq 0.14$ in this case, which is of the same order of magnitude as the state overlap. A similar situation arises in the reactions of cumulene and ketene with ethylene. Ethylene does not add thermally to cumulene if the two molecules approach in the same plane. The reaction cannot be analyzed easily by symmetry, but mapping leads to a state overlap of *ca.* 0.021. In contrast ethylene will add to ketene;[6] the permissibility is 0.244. In this case the polarity of the carbonyl and the carbonyl $\pi$ system is not critical to the addition. Rather the delocalization of the lone pairs of the oxygen into the CC $\pi$ system of the ketene is the source of the loophole which allows coplanar addition. This assertion is supported by a similar analysis of the ketene–ethylene wave function into a series of configurations built from cumulene–ethylene orbitals. The delocalization of the lone pairs in ketene–ethylene is reflected in a configuration of cumulene–ethylene for which the state overlap for addition is substantial.

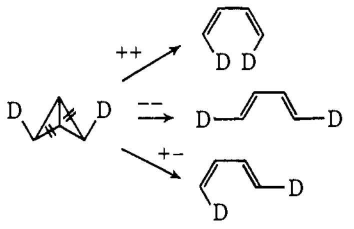


Figure 1.

One of the referees has pointed out the feasibility of addition of ethylene to ethylene by perpendicular approach of the two molecules. This idea gives a convenient explanation of the observed addition of ethylene to ketene as well. Experimental study of a system in which perpendicular approach is ruled out on steric grounds would be of considerable interest in distinguishing the relative ease of the two modes of addition of ethylene to ketene. Such a system would seem to be

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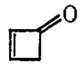
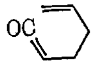
(5) This addition is a borderline case. The addition is routinely done by photoexcitation, but perfluorocyclobutene adds thermally to alkenes.

(6) H. Staudinger and E. Suter, *Chem. Ber.*, **53**, 1092 (1920).

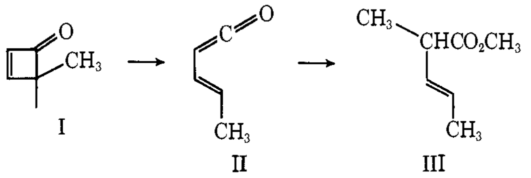
in which the closure to cannot occur by perpendicular approach of the ethylene fragment to the ketene fragment. Unfortunately it is clear from inspection of the localized orbitals of this system that the coupling between the ethylene and the ketene fragments is considerable. A system for which the assumption of independent fragments is less outrageous would be





However, in this system near-perpendicular approach of the fragments is possible.

A final example of a reaction of a carbonyl compound for which the Woodward–Hoffmann rules are not helpful is the thermal opening of cyclobutenones. It appears that the *trans* ketene II is formed initially, though under the conditions of reaction only an adduct to the ketene, III, is isolated.[7] The theoretical difficulty here is the definition of disrotatory and conrotatory motion for the featureless carbonyl group. A mapping analysis of unsubstituted cyclobutenone shows that the opening is substantially forbidden by any twist of the carbonyl and the carbon in the 4 position. However, a substituent with p orbitals in the 4 position (experimentally, chlorine or the methyl group) allowed the opening to a *trans* ketene. Unfortunately, a complete understanding of this influence cannot be claimed. A participation of the 4 substituent may be assumed; the source of the stereospecificity seems to be the establishment of the correct sign of the hyperconjugative interaction of the methyl with the remainder of the π system in the ketene. If this is so, an interesting experimental indication of the extent of hyperconjugation of a substituent could be gained from a study of 4,4-disubstituted cyclobutenones. The results of a localization analysis (Table IV) indicate that the orbitals mapped into the π system of the ketene and the π interaction with the methyl carbon are both substantially reorganized during the opening. The σ system and the carbonyl group seem to have little influence on the course of the reaction, being simply reoriented or rehybridized.



Clearly a more complete account of the influence of the 4 substituent is necessary. It is our hope that a quantitative refinement of the mapping analysis, now in progress, will yield a sufficiently complete description of the intermediate stages of reactions to provide a more detailed explanation.

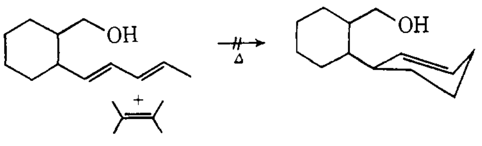
**Table III.** Mapping of Bicyclobutane into Butadiene[a]

| Roots | Local bond indices | Bond label |
|---|---|---|
| 1.000 | 0.917 | $C_1C_2$ |
| 0.948 | 0.903 | $C_2C_3$ |
| 0.999 | 0.909 | $C_1C_4$ |
| 1.000 | 0.971 | $C_1H_1$ |
| 0.999 | 0.991 | $C_2H_2$ |
| 0.984 | 0.958 | $C_3H_3$ |
| 0.980 | 0.960 | $C_3H_4$ |
| 0.992 | 0.964 | $C_4H_5$ |
| 0.960 | 0.957 | $C_4H_6$ |

[a] The rearrangement of bicyclobutane to butadiene causes more profound reorganization of the charge. As in the butadiene the predominant effect is on the "π" orbitals, cyclobutene interconversion though the low local bond indices imply that the "σ" orbitals are definitely influenced by the rearrangement.

## III. Anchimeric Interference in an Allowed 1,4 Addition

Austin and Pearson[8] have shown that the hydroxy-*trans,trans* diene IV is inert toward maleic anhydride, whereas the analogous molecule without the $-CH_2OH$ group adds quantitatively to the anhydride in the normal Diels–Alder manner. These authors attribute the anomalous inertness of IV toward the nominally allowed addition to the influence of the neighboring hydroxyl group.[9] The perturbation of that group is said to populate an excited π orbital of the diene system, mixing into the wave function a configuration for which the addition is forbidden. The addition is inhibited to the extent that such configurations are required to describe a hydroxyl-perturbed system.


IV

The explanation is appealing and plausible; but it would seem that a numerical validation of the suggestion would be quite tedious to attain, requiring a detailed exploration of the potential surface for a large molecular system. The mapping analysis of concerted reactions can provide a ready semiquantitative account of this and related problems. Recall the assumption that the nearer the permissibility is to unity, the less reorganization (other than of the charge distribution changes in orientation and hybridization) is necessary to effect the reaction. A rough correspondence is assumed between the extent of charge reorganization and the activation energy.

The addition of ethylene with *cis*-butadiene is predicted by mapping calculations to proceed by disrotation of the butadiene methylenes; the permissibility to the disrotation is 0.3369, while the permissibility to the conrotation is 0.000. To obtain analogous numbers for the system perturbed by a neighboring hydroxyl, the following steps were taken.

(1) CNDO–MO wave functions were determined for the model systems V and VI. The hydroxyls were not in the plane determined by the π system due to steric requirements. Coordinates were suggested by space-filling models.

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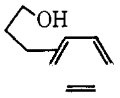
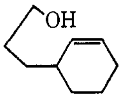
[7] J. E. Baldwin and M. C. McDaniel, *J. Amer. Chem. Soc.*, 90, 6118 (1968).

[8] A. T. Austin and B. Pearson, *Chem. Ind.* (London), 1228 (1966).

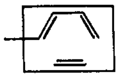
[9] A. T. Austin and B. Pearson, *Nature*, 221, 949 (1969).



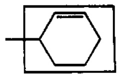
V



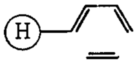
VI



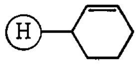
A



B



$C_1$



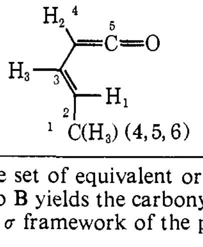
$C_2$

(2) The CNDO–MO wave functions were localized by a steepest ascents population technique.[9] The results are a set of "bond orbitals" which belong to the systems of interest, A and B ($C_6H_9$), or to the perturbing system $C_3H_7O$. One orbital represents the CC bond connecting them. The orbitals describing bonds in the interesting six-carbon system were still expressed in the 56 basis functions of the extended system, so a contraction of the basis set was necessary. Coefficients of basis functions in the perturber system occurring in the local orbitals of the perturbed system were lumped into a single coefficient which was then assigned to a hydrogen 1s orbital on a proton which "sealed off" the perturbed system, shown in C. Thus we recover orbitals describing the six-carbon system as if an *external* static perturbation had been applied by the hydroxyl group.

Given these orbitals, a mapping calculation exactly analogous to that performed for the unperturbed system was executed. The *permissibility* for the nominally allowed disrotatory addition *was reduced* from the unperturbed value of 0.3369 to 0.2555 for the perturbed system. Given the association of low permissibility with high activation energy, this result is consistent with the experimental observation that the hydroxyl interferes with the addition.

**Table IV.** Mapping of 4-Methylcyclobutenone to *cis*-Methylketylethylene[a]

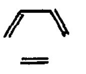
| Roots | Local bond indices | Bond label |
|---|---|---|
| 0.892 | 0.980 | $C_1H_1$ |
| 0.952 | 0.985 | $C_1C_2$ |
| 1.000 | 0.985 | $C_2H_4$ |
| 1.000 | 0.996 | $C_2H_5$ } $CH_3$ |
| 0.997 | 0.996 | $C_2H_6$ |
| 0.997 | 0.990 | $C_1C_3\sigma$ |
| 0.985 | 0.997 | $C_3H_3$ |
| 1.000 | 0.991 | $C_3C_4\sigma$ |
| 1.000 | 1.000 | $C_4H_2$ |
| 1.000 | 0.962 | $C_4H_5\sigma$ |
| 0.991 | 1.000 | $C_5O\pi$ |
| 0.996 | 0.965 | $C_5O\sigma$ |
| 0.998 | 0.980 | Olp |
| 0.989 | 0.998 | Olp |



[a] Localization of the set of equivalent orbitals having unit roots in the mapping of A to B yields the carbonyl group and the methyl group in full, plus the σ framework of the planar ketene B.

With Austin and Pearson's explanation of the inertness of the hydroxyl compound in mind, it would be of interest to determine a series representation of the perturbed six-carbon systems in terms of configurations of the unperturbed systems, to determine the excited configuration responsible for the inhibition of the addition. It becomes clear rapidly that expression of the localized effect of the hydroxyl perturber in terms of delocalized excitations given by the symmetry-adapted virtual orbitals requires a long and uninformative series. The unperturbed virtual orbitals were localized; these local virtual orbitals are fair approximations to "natural" orbitals, which allow maximum convergence of the CI series, so the major terms in the CI series could be obtained easily. Results are summarized in Table V.

**Table V.** Configuration Interaction Representation of Perturbed Butadiene–Ethylene and Cyclohexane in Terms of Configurations of the Unperturbed Systems[a]

|  | | |  | | |
|---|---|---|---|---|---|
| Ground state 0.9464 | | | Ground state 0.888 | | |
| Exciton | Hole | Coefficient | Exciton | Hole | Coefficient |
| $(C_1H)^*$ | $C_1H$ | 0.0154 | $(C_1C_6\pi)^*$ | $C_1C_6\pi$ | 0.1890 |
| $(C_1C_2\sigma)^*$ | $(C_6H_1\pi)$ | 0.0522 | $(C_1C_2\sigma)^*$ | $(C_1C_2\sigma)$ | 0.0711 |
| $(C_1C_2\pi)^*$ | $C_1C_2\pi$ | 0.0860 | $(C_2C_6\sigma)^*$ | $(C_1C_6\sigma)$ | 0.0190 |
| $(C_1C_2\sigma)^*$ | $C_1C_2\sigma$ | 0.0778 | $(C_1H)^*$ | $(C_1H)$ | 0.0142 |
| $(C_1C_2\sigma)^*$ | $C_1C_2$ | 0.0466 | | | |

[a] The localized excitations, the corresponding localized holes, and the associated CI coefficient are given for each system.

The major effect on butadiene–ethylene is excitation of the local π orbital nearest the –OH, as we might expect. However, there is a nonnegligible σ-orbital effect too, which would be missed by a π-only study of this system. The effect of the hydroxyl on the cyclohexene is less pronounced, with several local excitations of comparable import.

The localized virtual orbitals are essentially two-center antibonding orbitals. It is clear that no mapping transform which must avoid altering nodal structure can produce a bonding orbital from an antibonding orbital, so we can assign a permissibility of attaining the ground state from these configurations equal to zero. It is conceivable that an excited configuration of butadiene–ethylene could be mapped into an excited configuration of cyclohexene, but such a contribution to the total permissibility would not exceed 0.01 in this example.

Thus we can account for the reduction of the permissibility by the fact that a "region of lenience" encompassing the population of the ground states of the reactants and products is reduced by factors of 0.888 and 0.946. According to this argument, the permissibility should be reduced from 0.337 to 0.283; the discrepancy between 0.283 and the observed 0.256 is probably due to the fact that not all topologically invariant operations are incorportated into the approximate mapping operator available. (Recall that rehybridization and reorientation are included, but alterations in amplitude within each orbital are not considered.) If the amplitude variation changes its contribution to the deformation of the charge distribution, the computed permissibility would also vary as the perturbation due to the hydroxyl is introduced. However, the qualitative behavior of the system is reproduced.

A more detailed examination of the energy surface for this reaction would be desirable, since a rather small change in the activation energy has major consequences on the course of the reaction. However, it is not clear that an exhaustive exploration of the energy surface by MO calculation is the best way to begin this study; the reaction is probably influenced by variations in energies less than 10 kcal/mol, which may be out of reach of the best MO calculation. An improvement of the mapping operator and an analysis of the quantitative significance of the state overlap is possibly a more fruitful avenue.

## Summary

Applications to the rearrangements of the butadiene–cyclobutene–bicyclobutane system, the addition reactions of alkenes and carbonyl compounds, the opening of cyclobutenones, and the interference of neighboring groups on an allowed cycloaddition illustrate the use of the new mapping analysis of concerted reactions. Predictions on the course of concerted reactions which previously could have been obtained only from large numbers of MO calculations may now be based on the calculation of a single parameter, the "state overlap." A more precise and quantitative expression of the meaning of the state overlap is necessary for a fuller understanding of certain reactions (notably the opening of cyclobutenone). Such an expression is being sought, and will be discussed in a forthcoming report.

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# A New Method for the Estimation of Dissociation Energies and Its Application to the Correlation of Core-Electron Binding Energies Obtained from X-Ray Photoelectron Spectra

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**Abstract:** Dissociation energy is defined here as the energy required to break all the bonds of a species so that the electrons of each bond are divided equally between the atoms of the bond. A method based on electronegativities is devised for estimating the differences in the dissociation energies of pairs of isoelectronic species. Such differences, for appropriately chosen isoelectronic pairs, are closely related to atomic core-electron binding energies obtained from X-ray photoelectron spectra. It is shown that carbon 1s electron binding energies for a variety of carbon compounds correlate reasonably well with the estimated differences in dissociation energies for the carbon compounds and the corresponding isoelectronic nitrogen-containing cations. By an empirical treatment of carbon 1s binding energy data, a set of parameters, $p_i$, are evaluated for atoms so that binding energies can be estimated from the relation $E_B = \sum_i p_i$, where the summation is carried out over the atoms directly bonded to the carbon atom.

It has been shown that, when a core electron is removed from an atom in a molecule or ion, the valence electrons adjust as if the nuclear charge of the atom had increased by one unit.[1] Thus a core-electron binding energy is closely related to the energy difference between the species containing the atom and that of the isoelectronic species containing the atom of one higher atomic number. Unfortunately the energy data required for the correlation of binding energies are not always available. Therefore there is a need for a method for estimating the energy differences for pairs of isoelectronic species. The purpose of this research was to devise such a method and to apply it to the correlation of core-electron binding energies.

Differences in energy between pairs of species can be expressed in various ways, which differ in the arbitrary choice of the energy reference level. For example, both differences in the heats of formation from the elements in their standard states and differences in the energies of dissociation to atoms are acceptable, although different, measures of the energy differences. We have chosen to estimate differences in the dissociation energies of pairs of isostructural isoelectronic species. For simplicity we have restricted ourselves to gaseous species.

## A Method for Estimating Differences in Dissociation Energies

**A Generalized Definition of Dissociation Energy.** We shall be concerned with pairs of isoelectronic species in which one species differs from the other only by having one of its atoms (the "transmutable" atom) possess an atomic number that differs by ± 1 from that of the corresponding transmutable atom of the other species. (Examples of such pairs are $NO_2^-/O_3$ and $CH_4/NH_4^+$.) In such pairs of isoelectronic species, at least one species must be an ion. This fact immediately poses a problem that apparently has not previously been resolved, *i.e.*, how do we define the dissociation energy of an ion? When we break the bonds of an ionic species, there is ambiguity in the choice of prod-

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[1] W. L. Jolly and D. N. Hendrickson, *J. Amer. Chem. Soc.*, 92, 1863 (1970).