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A MO STUDY OF THE CATALYZED (1,3) SIGMATROPIC TRANSPOSITION IN PROPYLENE

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Summary

CNDO/2 and ab initio calculations have been carried out on the (1,3) hydrogen sigmatropic transposition in propylene. It reveals that the non-catalyzed reaction has a concerted, symmetry forbidden mechanism, and that the reaction catalyzed by $HCo(CO)_3$ is facilitated by the occupation of a previously unoccupied bonding orbital.

Introduction

Three possible mechanisms can be considered for the (1,3) sigmatropic transposition (ST) of hydrogen in propylene [1]: (i) a concerted symmetry-allowed process, (ii) a concerted symmetry-forbidden process, and (iii) a route involving a diradical intermediate.

This reaction should involve an antarafacial transition state (symmetry-allowed process), but according to several authors [2,3] the energy of the suprafacial transition state is lower, and no antarafacial transposition has been reported. This reaction was studied by Mango and Schachtschneider [2], who used a very crude model along with the EHMO method to examine the influence of a catalyst on the reaction. In this paper, we examine mechanisms (i) + (ii) above with two aims in mind: (a) verification that the more favourable process is symmetry-forbidden for the uncatalyzed reaction, (b) consideration of the extent to which a transition metal can remove the orbital symmetry restrictions.

Computational details

The LCAO MO SCF CNDO/2 method used, extended to transition elements [4] with a single zeta basis set of Slater orbitals, has already been tested for metallic complexes [5,6]. Results are given without deorthogonalization of the basis set.

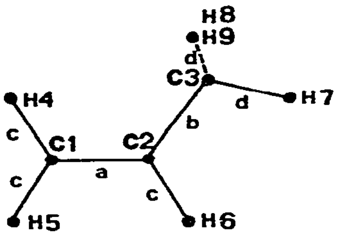


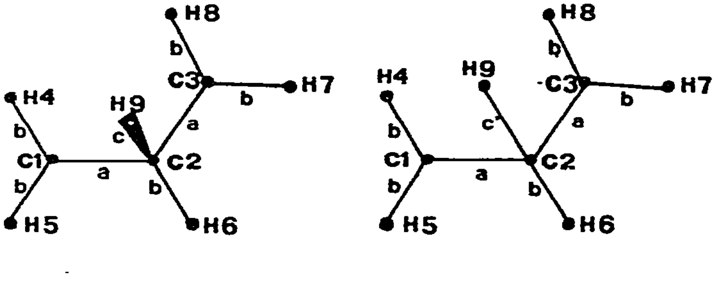
Fig. 1. Schematic representation of the eclipsed form of propylene $a = 1.330$ Å; $b = 1.465$ Å; $c = 1.105$ Å; $d = 1.125$ Å; angles: C(1)—C(2)—C(3) = 124.5°; H(4)—C(1)—C(2) = H(5)—C(2)—C(1) = H(4)—C(1)—H(5) = 120°; C(1)—C(2)—H(6) = C(3)—C(2)—H(6) = 117.75°; other angles equal 109.5°.

Some additional calculations, in particular for the uncatalyzed reaction, were performed by an ab initio method, using a modified version of the Polyatom program [7]. The basis set of Gaussian orbitals [8] of the form (7*s*, 3*p*) [9], for the first row elements, was contracted in (2*s*, 1*p*), and for the hydrogen the (3*s*) basis set was reduced to (1*s*) [10].

Uncatalyzed transposition

Two processes were considered for this reaction: an antarafacial shift in which the hydrogen atom passes through the plane of the molecule (symmetry-allowed), and a suprafacial one in which the hydrogen atom moves in the upper semi-space (symmetry-forbidden). The eclipsed form of propylene [11] is used in the initial state, and results of the geometry optimization are given in Fig. 1.

The most favourable transition state (2A), Fig. 2) corresponds to the suprafacial process, the activation energy being equal to 126 kcal mol^{-1}. That obtained by ab initio methods is 130 kcal mol^{-1} (without geometry optimization). Previous calculations (MINDO) gave an activation energy of 49.2 kcal mol^{-1} [3].



2A

2B

Fig. 2. Schematic representation of the suprafacial (2A) and antarafacial (2B) transition states for propylene. $a = 1.40$ Å; $b = 1.11$ Å; $c = 1.15$ Å; $c' = 1.28$ Å; angles for 2A: C(1)—C(2)—C(3) = 123°; H(4)—C(1)—C(2) = H(5)—C(1)—C(2) = H(7)—C(3)—C(2) = H(8)—C(3)—C(2) = 120°; the plane C(2)—H(6)—H(9) is bisector of the C(1)—C(2)—C(3) angle; the angle C(2)—H(9)—molecule plane equals 55°. The 2B form is planar.

TABLE 1

ATOMIC POPULATIONS OF $HCo(CO)_3C_3H_6$, INITIAL STATE

Values for propylene alone are shown in parenthesis.

	Co	C	O	H(17)	C(1)	C(2)	C(3)	H(4)	H(5)	H(6)	H(7)	H(8)	H(9)
4s/2s/1s	0.48	1.22	1.75	1.18	0.94 (1.05)	0.90 (1.01)	1.01 (1.02)	0.96 (0.99)	0.96 (0.99)	0.98 (1.00)	0.97 (1.00)	1.00 (0.94)	1.02 (0.99)
$4p_\pi/2p_x$	0.98 }	1.98 }	2.96		1.00 (1.01)	1.00 (1.02)	0.99 (0.99)						
$2p_y$					0.93 (0.94)	0.96 (0.97)	1.01 (1.02)						
$4p_z/2p_z$	0.48	0.70	1.52		1.20 (1.05)	1.17 (0.97)	0.92 (0.97)						
$3d_{z^2}$	1.06												
$3d_{xz} + 3d_{yz}$	2.93												
$3d_{x^2-y^2} + 3d_{xy}$	2.55												
Charges	+0.52	+0.10	−0.24	−0.18	−0.06 (−0.06)	−0.02 (+0.03)	+0.06 (0.0)	+0.04 (+0.01)	+0.04 (+0.01)	+0.02 (0.0)	+0.03 (0.0)	+0.0 (+0.06)	−0.02 (+0.01)

TABLE 2

ATOMIC POPULATIONS OF $HCo(CO)_3C_3H_6$ TRANSITION STATE

Values for propylene alone (2A) are shown in parentheses

	Co	C	O	H(17)	C(1)C(3)	C(2)	H(4)H(8)	H(5)H(7)	H(6)	H(9)
$4s/2s/1s$	0.48	1.20	1.74	1.11	1.01 (1.03)	0.82 (0.99)	0.96 (0.99)	0.95 (0.98)	1.13 (0.98)	1.26 (0.64)
$4p/2p_x$	0.98	1.88	2.95		0.96 (0.92)	0.95 (1.10)				
$2p_y$					0.95 (0.93)	0.94 (1.00)				
$4p_z/2p_z$	0.48	0.80	1.51		1.24 (1.40)	0.98 (0.79)				
$3d_{z^2}$	1.12									
$3d_{xz} + 3d_{yz}$	2.75									
$3d_{x^2-y^2} + 3d_{xy}$	2.61									
Charges	+0.58	+0.12	−0.20	−0.11	−0.16 (−0.27)	+0.31 (+0.12)	+0.04 (+0.01)	+0.05 (+0.02)	−0.13 (+0.02)	−0.26 (+0.36)

The intermediate obtained in the antarafacial process (2B, Fig. 2) is planar (C_{2v} symmetry, C(2)—H(9) bond length = 1.28 Å), and is about 40 kcal mol^{-1} higher in energy than 2A. The difference found by the ab initio method is lower (5 kcal mol^{-1}), but the geometries were not optimized in this case.

The passage from the initial to the transition state 2A corresponds to increasing charges (Tables 1 and 2). For the transition state 2B, the resulting atomic charges are $-0.37e$ for C(1) and C(3), $+0.10e$ for C(2) and $+0.55e$ for H(9). The atomic charges given by ab initio (for 2A) are higher; The carbon atoms are electronegative ($-0.47e$, $-0.38e$ and $-0.47e$ for C(1), C(2) and C(3)) and the hydrogen atoms electropositive, especially H(9) ($+0.42e$) and H(6) ($+0.25e$).

The electronic control of the reaction was studied by considering four specific MO's, designated as ψ_1, ψ_2, ψ_3 and ψ_4 (see Fig. 3). In previous work [2], Mango and Schachtschneider obtained the relative order $\psi_1 < \psi_2 < \psi_3^* < \psi_4^*$ and concluded that the reaction is mainly described by the subjacent orbitals ψ_1 and the HOMO ψ_2. These results correspond to the model previously given for concerted symmetry forbidden reactions [12].

The complete MO description shows that the three lowest MO's are responsible for the σ skeleton of the molecule. During the reaction, an increasing interaction appears between s orbitals of C(2) and H(9) (in MO 1) (see Fig. 4),

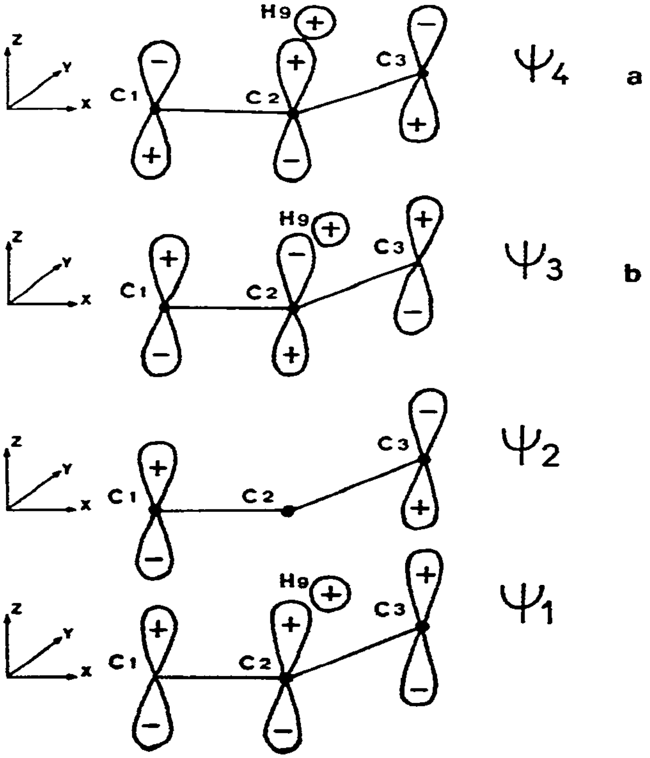


Fig. 3. MO levels controlling the (1,3) hydrogen sigmatropic transposition for propylene (catalyzed and non catalyzed) (a) this level is occupied only in the catalyzed reaction, (b) unoccupied.

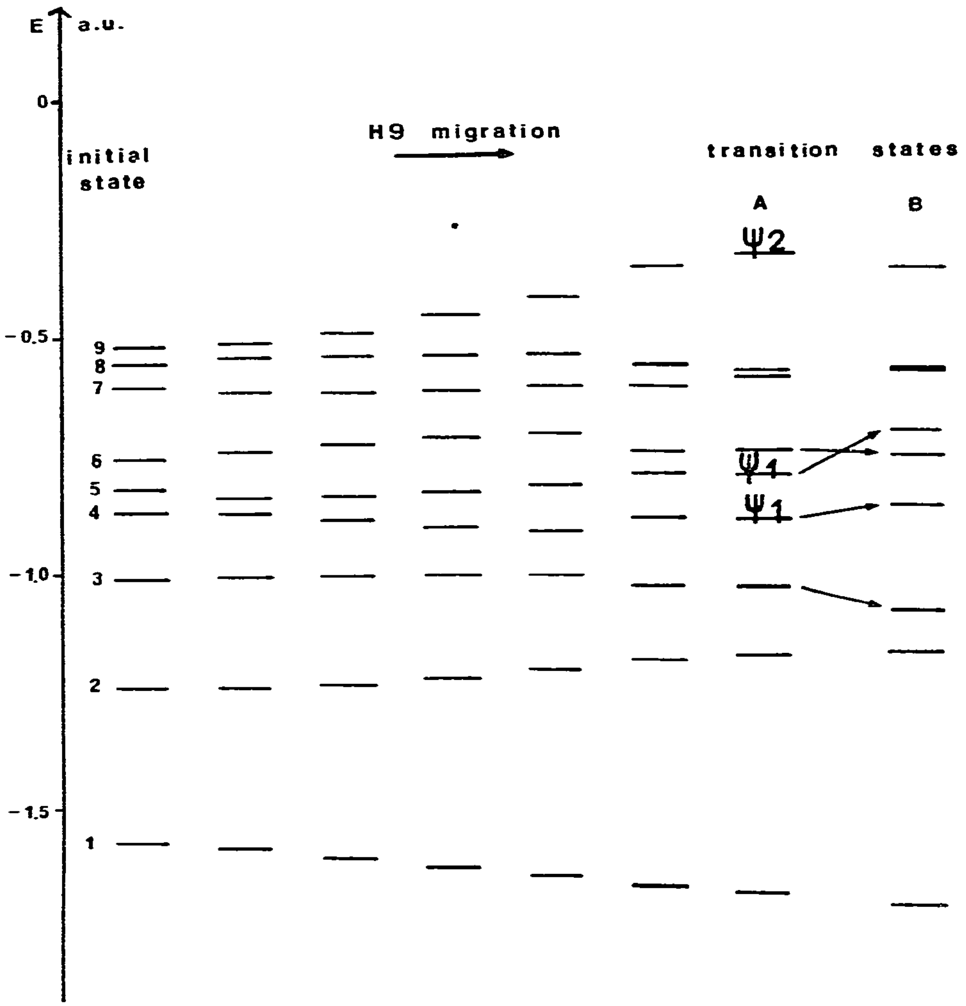


Fig. 4. Variation of the energies of the valence molecular orbitals. A: Symmetry forbidden, suprafacial transition state. B: symmetry allowed, antrafacial transition state.

and H(9) does not participate in MO 2 in the transition state. The MO 3, which contains mainly p_x and p_y orbitals, is obviously favoured in the planar transition state. The next two MO's, of the ψ_1 type, mainly define the π electronic cloud in which the hydrogen moves, and their energy is therefore lower in the suprafacial transition state. The electron densities in MO 4, in the initial and transition states, are shown in Fig. 5. It is seen that in the transition state a high density peak appears near C(2), corresponding to the bonding interaction C(2)—H(9). The MO's 6,7,8 do not involve any bond with H(9) and are not relevant to the present discussion. The next orbital (MO 9) is the HOMO (ψ_2 type) and, according to the Woodward—Hoffman rules, should control the

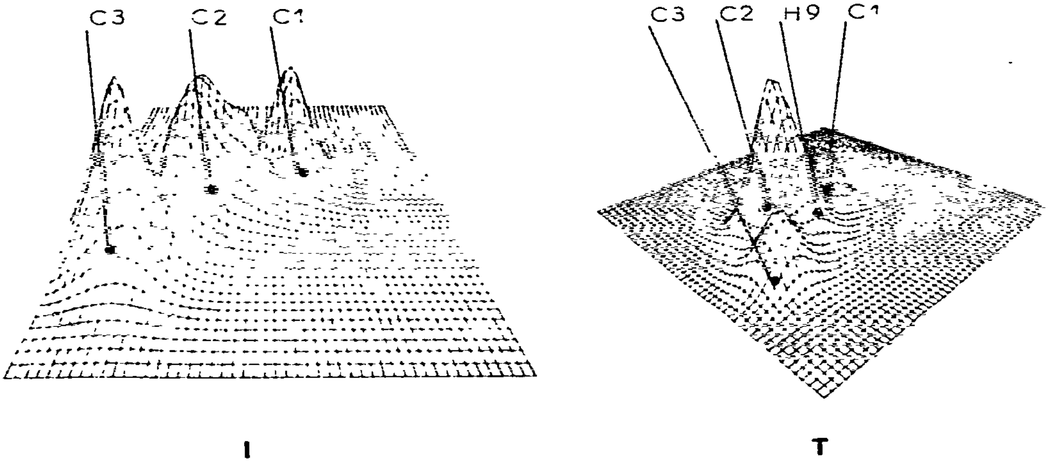


Fig. 5. Sections (at the elevation $z = 1.0$ a.u.) and in a plane parallel to that defined by the carbon atoms, of the electronic density provided by MO 4, of ψ_1 type, in the initial (I) and transition (T) states of propylene. The heights of the dots are proportional to the electronic density.

reaction. The electron density given by this orbital is represented in Fig. 6. It is seen that it is bonding in the initial state between C(1)—C(2), C(3)—H(8) and C(3)—H(9), and becomes non bonding in the transition state. The orbital energy increases greatly (0.195 a.u.) and is mainly responsible for the high activation energy required (0.200 a.u.). Moreover, the energy of this orbital is almost the same in the allowed and forbidden processes, and differentiation is not possible from this standpoint.

Since the LUMO (ψ_4 type) contains important contributions from the p_z

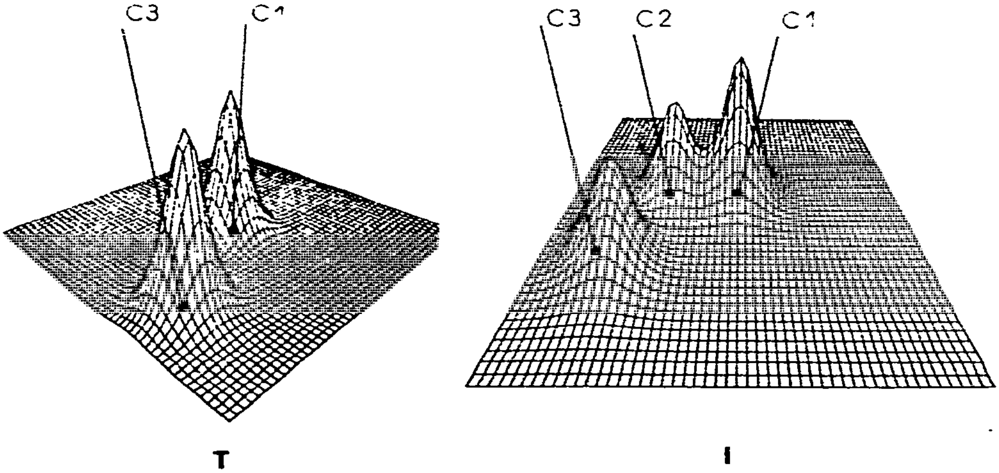


Fig. 6. Sections (at the elevation $z = 1.0$ a.u.) and in a plane parallel to that defined by the carbon atoms, of the electronic density provided by the HOMO, of ψ_2 type, in the initial (I) and transition (T) states of propylene. The heights of the dots are proportional to the electronic density.

orbitals of C(1), C(2), C(3) and from the 1*s* orbital of H(9), it could provide an important additional contribution to the C(2)—H(9) bond if it were occupied. This is also true for the MO 11 (ψ_3 type). The ab initio results are quite similar, except that the MO 5 and 6 are inverted; however, the same general conclusions are valid. Thus it appears that the HOMO does not adequately describe this reaction, and that subjacent orbitals control can be invoked, involving ψ_1 type orbitals [12].

Catalyzed reaction

The non-catalyzed ST goes through a suprafacial transition state. However, the activation energy is high and the HOMO becomes non bonding in the transition state. In an examination of the mechanism of the catalyzed reaction, we performed CNDO/2 calculations on the $HCo(CO)_3C_3H_6$ complex (Fig. 7). This model was used previously [5] within the framework of the olefin hydroformylation, a synthesis which can involve a ST among other possible rearrangements.

In the initial state of the complex (before hydrogen migration), the geometry of the olefin has been kept identical to that of the olefin alone (see Fig. 1). The geometry of the olefin was optimized in the transition state (see Table 3 and Fig. 8). This leads to a suprafacial configuration in which the $HCo(CO)_3$ moiety remains unaltered.

A charge transfer of 0.23*e* occurs from the $3d_{z^2}$ AO of Co towards the olefin and this mainly results in a strong negative charge for H(9), which passes from +0.36*e* in the non catalyzed transition state to —0.26*e* in the catalyzed one. C(1) and C(3) remain negatively charged, and the positive C(2) charge increases (see Table 2). This considerable modification of the H(9) charge can account

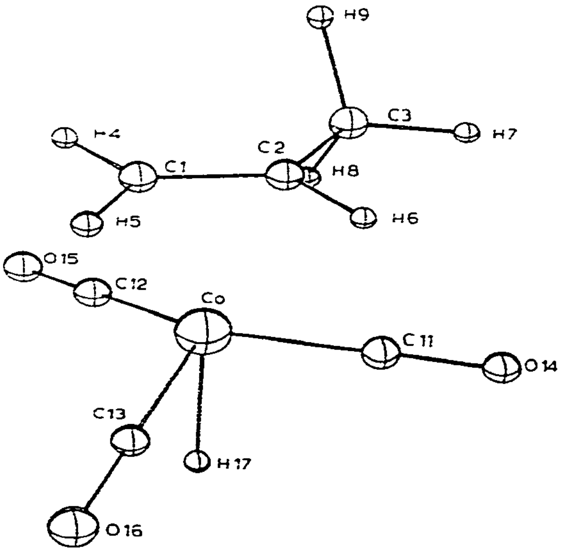


Fig. 7. $HCo(CO)_3C_3H_6$ complex in the initial stage.

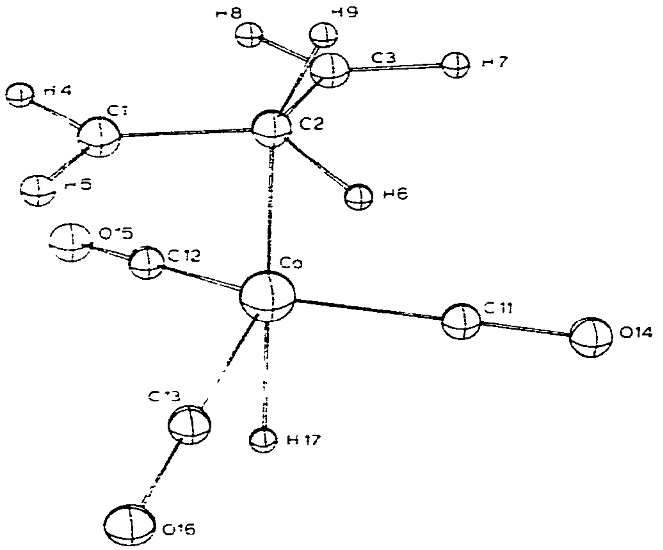


Fig. 8. Optimized geometry of $HCo(CO)_3C_3H_6$ complex in the transition state.

for the fact that this atom takes up a different position in the catalyzed ST (see Fig. 9) in order to reduce the charge interactions.

We now examine the MO scheme, and the corresponding description of the reaction-controlling factors. The ψ_1 type orbitals provide a significant contribution to the bonding between C(1), C(2), C(3) and H(9). The ψ_2 type orbital no longer corresponds to the HOMO and does not change in the catalyzed transition state, The HOMO itself does not in this case include any bonding interaction between H(9) and C(2), and is antibonding between C(1), C(2) and H(9). The ψ_3 type orbital is still unoccupied. The main feature of the electronic structure lies in the ψ_4 type MO, (Fig. 3), which is strongly bonding between C(2) and H(9). This orbital, which was unoccupied in the non catalyzed ST, is now filled by contributions from the $3d_{xz}$ and $3d_{yz}$ AO's of the cobalt atom. In order to have a symmetry allowed reaction, the HOMO should have been of ψ_3 type, as obtained by EHMO. In our case, we found that the HOMO cannot describe the

TABLE 3

CALCULATED GEOMETRY OF $HCo(CO)_3C_3H_6$ IN THE TRANSITION STATE

Interatomic distances (Å)		Angles (°)	
C(1)—C(2) C(2)—C(3)	1.41	C(1)—C(2)—C(3)	120
C—H [a]	1.11	C(2)—H(9)—plane C(1)C(2)C(3)	62
C(2)—H(9)	1.24	C(2)—H(6)—plane C(1)C(2)C(3)	−13
Co—C(2)	1.74	C(1)—C(2)—plane C(2)H(6)H(9)	120
Co—C(11)Co—C(12)Co—C(13)	1.76	C(3)—C(2)—plane C(2)H(6)H(9)	120
C—O	1.23	C(1)—H(4), C(1)—H(5), C(3)—H(7), C(3)—H(8)	120
Co—H(17)	1.62	Co—CO—plane XOY	11

[a] H ≠ H(9).

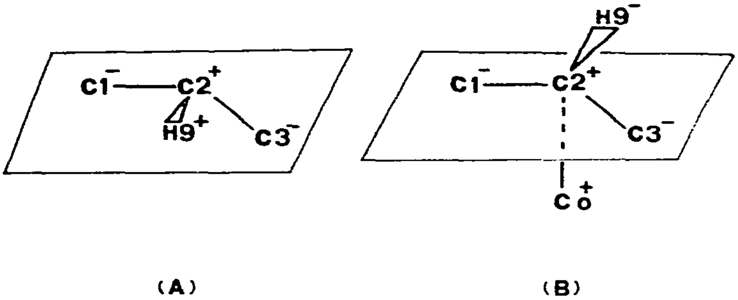


Fig. 9. Charge patterns in the uncatalyzed (A) and catalyzed (B) transition states.

catalyzed ST and that the second HOMO, of ψ_4 type, is antibonding between C(1), H(9) and C(3), and strongly bonding between C(2) and H(9). We thus consider that the presence of a catalyst, in this case, does not make the reaction symmetry allowed. Moreover, simple application of the Woodward—Hoffman rules appears to be difficult in view of the fact that the HOMO symmetry is not conserved between the initial and transition states. We found that the catalyzed reaction is facilitated only because a nonoccupied orbital in the non catalyzed transition state (which described the bond between C(2) and H(9) is now occupied and the C(2)—H(9) bond reinforced.

The CNDO activation energy obtained for the catalyzed is slightly greater than that for the non catalyzed reaction. However, comparison between ab initio and CNDO results for hydroformylation [5] has shown that the CNDO energies are greatly overestimated. For example, in the $\pi \rightarrow \sigma$ rearrangement of a complex between propylene and $HCo(CO)_3$, CNDO results give an energy of ca. 100 kcal; ab initio computations on a similar complex between ethylene and $HCo(CO)_3$ give 20 kcal. We can thus reasonably expect a lower activation energy for the catalyzed isomerization of propylene, than is indicated by the CNDO calculations.

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References

1 Nguyen Trong Anh, Les règles de Woodward—Hoffmann, Ediscience, Paris, 1970.
2 (a) F.D. Mango and J.H. Schachtschneider, Transition metals in homogeneous catalysis, G.N. Schrauzer, 1971, p. 261; (b) F.D. Mango, Adv. Catalysis, 20 (1969) 291.
3 R.C. Bingham and M.J.S. Dewar, J. Amer. Chem. Soc., 94 (1972) 9107.
4 G.L. Allen and D.W. Clack, J. Chem. Soc., A, (1970) 2668.
5 J.P. Grima, F. Choplin and G. Kaufmann, submitted for publication.
6 J.Y. Saillard, D. Grandjean, F. Choplin and G. Kaufmann, J. Mol. Struct., 23 (1974) 363.
7 I.G. Csizmadia, M.C. Harrison, J.W. Moskowitz, S. Seung, B.T. Sutcliffe and M.P. Barnett, Polyatom program set for non empirical molecular calculations, Q.C.P.E. no. 47.
8 S.F. Boys, Proc. Roy. Soc., London, A, 200 (1950) 542.
9 B. Roos and P. Siegbahn, Theor. Chim. Acta, 17 (1970) 209.

10 S. Huzinaga, J. Chem. Phys., 42 (1965) 1293.

11 D.R. Lide Jr. and D. Christensen, J. Chem. Phys., 35 (1961) 1374.

12 (a) J.A. Berson and L. Salem, J. Amer. Chem. Soc., 94 (1972) 8917; (b) J.A. Berson, Accounts Chem. Res., 5 (1972) 406.