

MO 이론에 의한 반응성의 결정 (XI).
N-아세틸피롤리돈의 친핵성 치환반응

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Determination of Reactivities by MO Theory (XI).
Nucleophilic Substitution Reactions
of N-Acetylpyrrolidone

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요 약. N-아세틸피롤리돈의 산-촉매 친핵성 치환반응을 궤도함수 혼합법을 적용 분석하였다. MO 계산 결과로 전하-조절 반응에서는 카르보닐 탄소원자의 양전하의 증가가, 그리고 궤도함수 조절 반응에서는 LUMO AO 계수의 증가가 프로톤화된 카르보닐 탄소의 반응성을 크게 증가시킴을 밝혔다.

ABSTRACT. The orbital mixing analysis was applied to the acid-catalyzed nucleophilic substitution reaction of N-acetylpyrrolidone. It was found that the reactivity of protonated carbonyl carbon is greatly enhanced due to increase in positive charge (for charge controlled reaction) and also increase in LUMO AO coefficient (for orbital controlled reaction) of the carbonyl carbon atom.

INTRODUCTION

During the last two decades MO theory has been used increasingly to describe and elucidate organic reaction mechanisms. For analysis of the origin of molecular interactions, two basic approaches are now in use employing perturbational molecular orbital formalism. One is to

partition the mutual perturbation energies of the reacting systems into various contributing interaction modes such as coulomb, exchange repulsion, induction and charge-transfer energies.¹⁻⁴

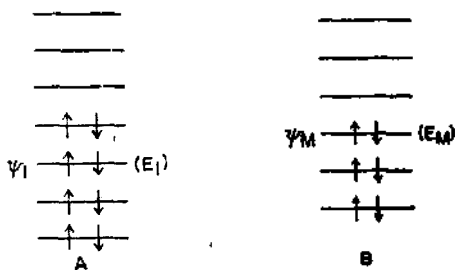
The other is to analyze mixing of orbitals of interacting systems. The concept of orbital mixing has been useful in elucidating different chemical phenomena⁵⁻¹¹. For example Libit and

Hoffmann,⁷ and Whangbo *et al.*⁸, employed the orbital mixing concept in the analysis of substituent and conformational effects. The idea of orbital mixing have been recently applied usefully to the analysis of chemical reactions by Lowe,⁵ Zimmerman,⁶ Fujimoto and Hoffmann,⁹ Imamura and Hirano,¹⁰ and Fukui and Coworkers.¹¹

The purpose of this paper is to apply the orbital mixing analysis to nucleophilic substitution reaction of N-acetyl pyrrolidone and to gain some insight into characteristics of the acid catalyzed reactions of the compound.

THEORY

Let us consider that a molecule A is subjected to the effect of an outer field due to an approaching molecule B. The characteristic set of orbitals of these two molecules will interact as a result of this mutual perturbations.



The new perturbed wave function Ψ_I' of level I in A can be given generally by (1).

$$\Psi_I' = \Psi_I + \sum_{J \neq I} C_{JI} \Psi_J \quad (1)$$

Here the coefficient C_{JI} of the second term measures how much orbital J mixes into orbital I . Obviously the subscript J can be factored into subsets of orbitals on A and B, representing intra- and inter-molecular orbital mixings.

$$\Psi_I' = \Psi_I + \sum_{J \neq I}^A C_{JI} \Psi_J + \sum_M^B C_{MI} \Psi_M \quad (2)$$

Now let the energies of MO's Ψ_I and Ψ_M be E_I and E_M respectively, the one-electron

Hamiltonian of the total system be H , and the change of the one-electron Hamiltonian of molecule A due to the perturbation by the molecule B be H_A' .

By adopting one-electron formalism, the application of perturbation theory becomes particularly simple and we can directly speak of the mixing of orbitals neglecting the attendant interaction of electrons.

Application of the perturbational formalism^{11,12} leads to the following expressions for the mixing coefficients to second order.

$$C_{II} = 1 - \sum_M \frac{S_{IM}(H_{IM} - E_I S_{IM})}{E_I - E_M} - \frac{1}{2} \sum_M \left(\frac{H_{IM} - E_I S_{IM}}{E_I - E_M} \right)^2 \quad (3)$$

$$C_{JI} = \sum_{M \neq I} \left\{ \frac{H'_{IJ}}{E_I - E_J} + \sum_M \frac{(H_{IM} - E_I S_{IM})(H_{JM} - E_I S_{JM})}{(E_I - E_J)(E_I - E_M)} \right\} \quad (4)$$

$$C_{MI} = \sum_M \frac{H_{IM} - E_I S_{IM}}{E_I - E_M} \quad (5)$$

where

$$H_{IM} = \int \Psi_I H \Psi_M d\tau \quad (6a)$$

$$S_{IM} = \int \Psi_I \Psi_M d\tau \quad (6b)$$

and

$$H'_{IJ} = \int \Psi_I H_A' \Psi_J d\tau \quad (6c)$$

The coefficient C_{II} is the second-order self-correction term arising from a renormalization of the perturbed wave function Ψ_I' . This term is in general qualitatively unimportant. Imamura and Hirano¹⁰ called the first term of (4) "static orbital mixing" and the second term "dynamic orbital mixing". The intermolecular orbital mixing, Eq (5), is a first-order "dynamic orbital mixing".

If we concern ourselves with two orthonormal sets of orbitals with nonzero overlap between orbitals in different set, the mixing coefficients

can be simplified as follows.

$$C_{II} = 1 - \frac{1}{2} \sum_M \left(\frac{H_{IM}}{E_I - E_M} \right)^2 \quad (3a)$$

$$C_{JI} = \sum_{j=I} \left\{ \frac{H_{I'j}}{E_I - E_j} + \sum_M \frac{H_{IM} \cdot H_{jM}}{(E_I - E_j)(E_I - E_M)} \right\} \quad (4a)$$

$$C_{MI} = \sum_M \frac{H_{IM}}{E_I - E_M} \quad (5a)$$

Further simplification was achieved by considering only the frontier orbitals concerned.^{10,11} Eq. (1) now becomes*

$$\Psi'_I = \Psi_I + C^S_{JI} \Psi_J + C^d_{JI} \Psi_J + C^d_{MI} \Psi_M \quad (7)$$

where

$$C^S_{JI} = \frac{H_{IJ'}}{E_I - E_J} \quad (8a)$$

$$C^d_{JI} = \frac{H_{IM} \cdot H_{jM}}{(E_I - E_j)(E_I - E_M)} \quad (8b)$$

and

$$C^d_{MI} = \frac{H_{IM}}{E_I - E_M} \quad (8c)$$

and levels I , J and M are the frontier orbitals, i. e., highest occupied (HO)MO or lowest unoccupied (LU)MO. There are two ways of intra-molecular orbital mixing (eg. J into I).

(a) One is by static orbital mixing which takes place through perturbing electric field of a point charge (Ze) at distance r from an electron. Thus the perturbed Hamiltonian is given by

$$H_A' = -\frac{Ze^2}{r} \quad (9)$$

Substituting this into (6c) and integrating with simplifying assumptions the static orbital mixing coefficient was shown to have a form¹⁶ (10).

$$C^S_{JI} = -Z \left(\frac{a_{Jr} a_{Ir}}{E_I - E_J} \right) \gamma \quad (10)$$

where a_{Jr} and a_{Ir} are the atomic orbital coefficient of atom r which is nearest to the point charge and γ is a positive quantity representing

*Superscripts S (for static) and d (for dynamic) are introduced to distinguish the two modes of orbital mixing.

the electrostatic interaction energy. (b) The second is through dynamic orbital mixing in which the two interacting orbitals of a molecule, e. g., I and J of A , overlap with an orbital of a second molecule, e. g., M of B (Fig. 1).

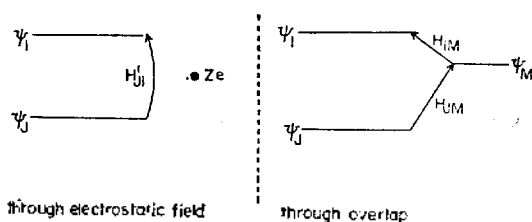


Fig. 1. Schematic representation of intra-molecular orbital mixing: (a) static and (b) dynamic orbital mixings.

These two modes of intra-molecular orbital mixing have been shown to be responsible for the catalytic activity of a point charge and a catalyst orbital¹⁰. Using Eqs. (10) and (8b), Imamura and Hirano¹⁰ were able to arrive at the following general rules of orbital mixing.

(a) Static orbital mixing: Eq. (10) shows that the sign and magnitude of mixing of the orbital J into I are determined by the product $a_{Jr} a_{Ir}$ and the difference $E_I - E_J$ for a given point charge since γ is only dependant on the distance r (Eq. 9) and an AO of the nearest atom to the unit point charge. The sign of C^S_{JI} is given as in the following Table 1.

Table 1. Signs of orbital mixing coefficients.

Z	$a_I a_{Jr}$	$E_I - E_J$	C^S_{JI}
+	+	+	-
	+	-	+
	-	+	+
	-	-	-
-	+	+	+
	+	-	-
	-	+	-
	-	-	+

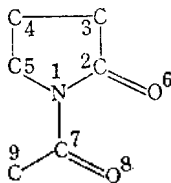
The magnitude of the mixing $|C^S_{JI}|$ is

approximately proportional to the absolute value of the product of the AO coefficients, $a_I a_J$, and inversely proportional to the absolute value of the difference of the two energy levels, $|E_I - E_J|$.

(b) Dynamic orbital mixing: Similarly judged using C^d_{JI} (Eq. 8b). The intermolecular orbital mixing, C^d_{MI} (Eq. 8c), is not important in the proton catalysis and therefore will not be considered here.

CALCULATIONS

CNDO/2 MO's were calculated for both the *trans-trans* and *cis-trans* forms of N-acetylpyrrolidone and for their protonated forms.¹³ The extent to which N-acetylpyrrolidone π -MO's participate in π -MO's of the protonated forms has been calculated by the scalar products between particular MO's of the protonated forms and each of the MO's of N-acetylpyrrolidone⁵ using PDP 11 at the Inha University computing center. Planar conformations have been assumed in the calculation. The numbering scheme for non-hydrogen atoms is given below for the *trans-trans* form.



RESULTS AND DISCUSSION

N-Acetylpyrrolidone is reported to undergo both acyl and ring cleavages at comparable rates in alkaline hydrolysis¹⁴ whereas the ring cleavage proceeds faster in acid hydrolysis.¹⁵ The question of whether the acyl group or the ring will be cleaved is of great interest in synthetic work. Let us now see how this question can reasonably be answered theoretically considering MO's of N-acetylpyrrolidone and

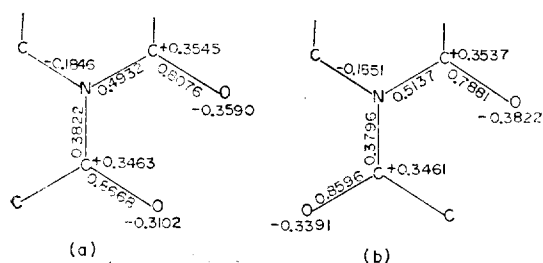


Fig. 2. Atomic charges and π -bond populations for (a) the *trans-trans* and (b) *cis-trans* N-acetylpyrrolidones. (shown for only relevant parts).

its protonated form.

Atomic charges and π -bond populations for the two planar forms of N-acetylpyrrolidone are reproduced for relevant part in Fig. 2.¹³ Among ten π -MOs for the N-acetylpyrrolidone obtained by CNDO/2 calculation, we were able to identify five π -MOs which had large p_z AO coefficients at the five atoms (N₁, C₂, O₆, C₇ and O₈) forming a pseudo-pentadienyl system. These π -MOs are shown in Fig. 3 together with the nodal property of the pentadienyl. Similarity of the nodal characteristics of our pseudo-pentadienyl systems with that of the true pentadienyl is very striking¹³. The two pseudo-pentadienyl systems for the *trans-trans* and *cis-trans* show little difference in energy and have the same nodal properties. In both cases, first three π -orbitals, π_1 , π_2 , and π_3 , are occupied and the rest two unoccupied. The most important orbital in dictating the rate of an orbital controlled nucleophilic substitution reaction is the LUMO, and in this case it is the fourth π -orbital, π_4 . This MO was the lowest unoccupied among all MOs i. e., for σ and π , and also it was the lowest unoccupied among pseudo-pentadienyl π MOs¹⁶. The largest AO coefficient of the LUMO is that of C₇ for both pseudo-pentadienyl systems, indicating that the acyl cleavage will be preferred in an orbital controlled process. However the orbital controlled process will not be very efficient due to very small,

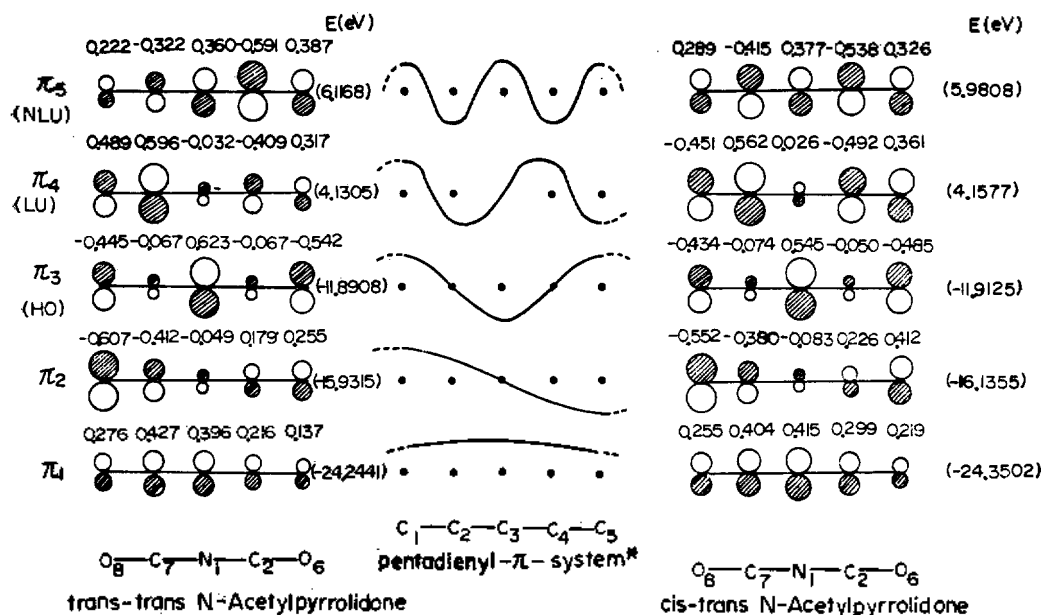


Fig. 3. Nodal properties of pentadienyl- π -system and CNDO/2 π -MOs of pseudo-pentadienyl systems of *trans-trans* and *cis-trans* N-acetylpyrrolidones. (AO coefficients and energies are shown for N-acetylpyrrolidone- π -systems)

*A. Streitwieser Jr., "MO Theory for Organic Chemists", John Wiley, New York, 1961.

almost negligible, AO coefficient of the N atom giving very small *anti*-bonding character to the C₇-N₁ bond. On the other hand, Fig. 2 shows that the ring cleavage is preferred in a charge controlled process since positive charge is greater at the ring carbonyl carbon, C₂. Again this preference will not be an overwhelming one, since π -bond order of the N₁-C₂ bond which must be broken at the initial stage of the nucleophilic attack is larger, and hence it is more difficult to break, than that of N₁-C₇ bond which must be broken in the acyl cleavage. It may be possible that the ring cleavage is slightly faster since the nucleophiles in the neutral and alkaline hydrolysis are hydroxyl anion and water molecules, hard bases,¹⁷ and the reaction will be charge controlled.¹⁶ But it is more likely that in a neutral or alkaline hydrolysis no one mode of cleavage prevails over another and the two

processes proceed at comparable rates.

The situation becomes very different and the preference in the mode of cleavage becomes more definite for the protonated form. Table 2 shows the formal atomic charges of the two carbonyl carbon atoms and the AO coefficients of LUMOs for various protonated forms of the pseudo-pentadienyl systems. In the previous report, we have shown that the protonation should occur on oxygen atoms, the ring carbonyl oxygen being a little preferred. For the protonated forms, the formal positive charge is larger at the protonated carbonyl carbon atom; thus for the ring carbonyl oxygen protonated, TTR and CTR, C₂ has the larger positive charge whereas for the acyl oxygen protonated, TTA and CTA, C₇ is more positive. This means that ring cleavage will occur for TTR and CTR while acyl cleavage prevails for TTA and CTA in the

Table 2. The formal atomic charges (positive) of carbonyl carbons and the AO coefficients of LUMO₃(π) for the various protonated and unprotonated forms of N-acetylpyrrolidone (shown for the pseudo-pentadienyls only).

	Formal atomic charges(+)		AO coeff. of LUMO (π)				
	C ₂	C ₇	O ₈	C ₇	N ₁	C ₂	O ₆
TTR1	0.406	0.346	-0.346	0.357	0.276	-0.711	0.314
TTR2	0.408	0.332	-0.307	0.263	0.353	-0.702	0.078
TTR3	0.401	0.334	-0.328	0.306	0.317	-0.729	0.311
TTR4	0.459	0.341	-0.334	0.326	0.295	-0.719	0.326
TTA1	0.339	0.436	-0.354	0.759	-0.278	-0.223	0.257
TTA2	0.336	0.452	-0.120	0.734	-0.310	-0.203	0.260
TTA3	0.350	0.442	-0.364	0.756	-0.248	-0.254	0.257
TTA4	0.343	0.492	-0.374	0.754	-0.261	-0.232	0.254
CTR1	0.403	0.341	-0.382	0.384	0.245	-0.685	0.317
CTR2	0.398	0.327	-0.301	0.251	0.367	-0.693	0.063
CTR3	0.390	0.331	-0.328	0.298	0.331	-0.729	0.305
CTR4	0.452	0.335	-0.330	0.312	0.311	-0.724	0.323
CTA1	0.349	0.425	-0.348	0.763	-0.258	-0.241	0.269
CTA2	0.343	0.450	-0.104	0.733	-0.294	-0.214	0.267
CTA3	0.346	0.434	-0.348	0.762	-0.259	-0.242	0.270
CTA4	0.349	0.488	-0.366	0.758	-0.246	-0.247	0.268
TTN	0.319	0.317	-0.226	0.249	0.281	0.337	-0.338
CTN	0.324	0.320	-0.078	0.086	0.212	0.547	-0.446
TTB1	0.389	0.399	-0.423	0.638	-0.011	-0.487	0.296
TTB2	0.469	0.475	-0.430	0.623	-0.003	-0.488	0.308
TT	0.355	0.346	-0.489	0.596	-0.032	-0.409	0.317
CT	0.354	0.346	-0.451	0.562	0.026	-0.492	0.361

TT=*trans-trans*, CT=*cis-trans*, TTR=*trans-trans*-ring carbonyl oxygen protonated, CTA=*cis-trans*-acyl oxygen protonated etc, TTN=*trans-trans*-nitrogen protonated etc, TTB1=*trans-trans*-proton-bridged form (pentagonal), TTB2=*trans-trans*-proton-bridged form (hexagonal). The other numbers 1, 2, 3 and 4 indicate angles of rotation, ϕ , (clockwise) of O-H⁺ around C-O bonds started from the molecular plane and angles of $\angle\text{COH}^+$, θ , in the molecular plane. For 1: $\theta=120^\circ$, $\phi=0^\circ$, 2: $\theta=120^\circ$, $\phi=90^\circ$, 3: $\theta=120^\circ$, $\phi=180^\circ$, 4: $\theta=180^\circ$, $\phi=0^\circ$.

acid catalyzed hydrolysis since the nucleophile, H₂O, is a hard base¹⁷ and the reaction will be charge-controlled. This trend in the preference of cleavage mode will be the same in an orbital-controlled acid catalyzed nucleophilic substitution reaction, since the AO coefficient of the protonated carbonyl carbon in the LUMO is the largest. Thus irrespective of the hardness (or softness)¹⁷ of the nucleophile the ring carbonyl oxygen protonation leads to the ring cleavage and the acyl oxygen protonation leads to the acyl cleavage. we therefore conclude that the ring

cleavage will be preferred in the acid catalyzed hydrolysis of N-acetylpyrrolidone, since the ring carbonyl oxygen is shown to be protonated preferentially.¹³ This agrees well with the experimental findings reported.¹⁵

It is interesting to note that if the protonation occurs on the nitrogen (N₁) atom, no clear prediction is possible since formal charges of N do not differ much and both of the C-N bonds are bonding in the LUMO. For the bridged proton forms TTB1 and TTB2, the nucleophilic reactivity will remain the same as for the unproto-

nated form in an orbital controlled reaction while it will reverse in a charge-controlled reaction by protonation.

STATIC ORBITAL MIXING

In *Table 3* we have shown the perturbed LUMO's (of the protonated form) in terms of the π -orbitals of unprotonated N-acetylpyrrolidones⁵. As expected from the large energy differences (Eq. 10) contributions of lower energy levels, π_1 and π_2 , were very small and therefore they were neglected and attention has been solely focussed on the mixing of two orbitals π_3 and π_5 into the LUMO(π_4). These two π_3 and π_5 are nearest neighbors for π_4 and the HO and next to the lowest unoccupied (NLU) orbitals respectively. According to the rule, *Table 1*, the contributions of orbitals π_3 and π_5 to π_4 will be positive, i. e., $C_{54}^S > 0$ and $C_{34}^S > 0$ for the ring carbonyl oxygen (O_6) protonation, since the energy differences are $(E_4 - E_5) < 0$ and $(E_4 - E_3) > 0$, and signs of the product of AO coefficients for O_6 are $a_4 a_{5r} > 0$ and $a_4 a_{3r} < 0$. On the other hand the mixing coefficients are both negative i. e., $C_{54}^S < 0$ and $C_{34}^S < 0$ for the acyl oxygen (O_8) protonation judging similarly from *Table 1*. Thus the static orbital mixing rule predicts that both HO and NLU orbitals will give positive contributions in the ring carbonyl oxygen protonation while they will give negative contributions in the acyl oxygen protonation. As a result of these orbital mixing the absolute value of the AO coefficient increases significantly at C_2 in the ring carbonyl oxygen protonation and at C_7 in the acyl oxygen protonation respectively.

These predictions are exactly borne out in the result of our calculations (*Table 3*). Since the magnitude of mixing, i. e., $|C_{Jr}^S|$, is dictated by $|E_I - E_J|$ and $|a_{Jr} a_{Ir}|$, we would expect the contribution of NLU (π_5) orbital to be greater

than that of HO (π_3), as $|E_4 - E_5| > |E_4 - E_3|$ and $|a_{3r}| < |a_{5r}|$. Thus the contribution of the NLU (π_5) orbital is always much larger than that of HO (π_3) orbital as can be seen from *Table 3*.

The static orbital mixing rule does not apply for the N-protonated forms. This may well be due to the approximations introduced in derivations¹⁰ and also due to extremely small, near zero, values of AO coefficient of the N atom in the LUMO, $a_{4r} \cong 0$.

For the bridged protonation the rule is applicable but the mixing coefficients are extremely small and therefore the perturbed LUMO remain nearly the same as that of the unperturbed.

DYNAMIC ORBITAL MIXING

If we assume that a Lewis acid is present near an oxygen atom, O_6 or O_8 , the electrostatic effect will be small but the Lewis acid will provide empty d orbitals that can overlap with both the

Table 3. Mixing coefficients of π_3 (HO), C_{34} , and of π_5 (NLU), C_{54} , into π_4 (LU) of the protonated N-acetylpyrrolidones.

Protonated forms	C_{44}	C_{34}	C_{54}
TTR1	0.766	0.178	0.452
TTR2	0.608	0.342	0.422
TTR3	0.731	0.201	0.497
TTR4	0.748	0.160	0.481
TTA1	0.812	-0.188	-0.201
TTA3	0.827	-0.163	-0.172
CTR1	0.850	0.153	0.294
CTR3	0.795	0.189	0.402
CTA1	0.795	-0.162	-0.299
CTA3	0.795	-0.163	-0.298
TTN	0.014	-0.415	0.393
CTN	0.341	-0.332	0.423
TTB1	0.885	0.012	0.094
TTB2	0.887	0.016	0.103

e. g. The perturbed LUMO can be represented as either, (for TTR1)

$$\psi_{LU'} = 0.766\psi_{LU} + 0.178\psi_{HO} + 0.452\psi_{NLU} \text{ or } \psi'_{4'} = 0.766\psi'_4 + 0.178\psi'_3 + 0.452\psi'_5$$

LU and HO or NLU, and the dynamic orbital mixing will take place. Since the energy of the vacant d orbitals will be relatively large, the orbital overlap can become appreciable in many cases. This type of situation is met in the Meerwein—Ponndorf reaction,¹⁰ in which aldehydes are reduced to alcohols by the catalysis of aluminum isopropoxide. The transition state of this reaction is usually considered to be a cyclic complex¹⁸ by the coordination of the carbonyl oxygen with aluminum, followed by the transfer of the hydride ion (a soft base).¹⁷ In this case Al provides vacant d orbitals which can overlap with π MOs (HO, LU and NLU) of the carbonyl group of aldehydes. However the contribution of HO to LUMO in the dynamic orbital mixing calculated from Eq (8b) was exactly the same as we would have expected if the Al had been replaced by a proton and the static orbital mixing is considered, i. e., the carbonyl carbon was activated (the absolute value of the AO coefficient increased) as a result of coordination with Al (a Lewis acid) with the carbonyl oxygen¹⁰. This means that the Al atom being an acid acts like a proton, or vice versa. The difference between the two cases is that in the Lewis acid catalysis the reaction is normally orbital controlled (as in the case of hydride ion transfer) and the absolute magnitude of the AO coefficient of the carbonyl carbon has the predominant effect in determining the reactivity, while in the proton catalysis the reaction is likely to be charge-controlled and the magnitude of formal atomic charge(positive) of the protonated carbonyl carbon dictates the reactivity.

We therefore conclude that in the acid catalysis of carbonyl compounds all the acid, whether it is a Lewis type or a proton, acts the same way in activating the carbonyl carbon. Both the static and dynamic orbital mixings increase the positive charge¹⁹ and the absolute

value of the AO coefficient of the carbonyl carbon whose oxygen is coordinated with the acid. Thus the reactivities of both charge-controlled (by a hard base) and orbital controlled (by a soft base) S_N reaction¹⁶ increase by the coordination of oxygen with acid.

ACKNOWLEDGMENT

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However the second-order polarization of the occupied π -orbitals by mixing in of unoccupied π -orbitals, i. e., by dynamic orbital mixing, is expected to increase positive charge of the carbonyl carbon atom when an acid is coordinated with the carbonyl oxygen.⁷