

Figure 4. The ratio of R/R_0 for the bistable system with $\nu=0.2$. The curves 1, 2, and 3 correspond to $\mu=0.5$, $\mu=1$, and $\mu=2$, respectively.

and $\nu=0.9$, respectively. In Figure 4 we have taken μ to be 0.5, 1, and 2, respectively, when $\nu=0.2$. As D increases the ratio in large μ value decreases faster than the ratio in small μ does. As shown in Figure 3, it is obvious that in the region $\nu < 1$ the transition rates decrease with increasing D . As the exponent ν increases, the transition rates decrease and relaxation times increase. In the limit $\nu \rightarrow 1$, the transition rate approaches zero.

In the result, in the region for which $\nu < 1$ the transition rates decrease as ν increases and ν decreases shown in Figure 3 and 4. However, in the case that $\nu > 1$, it is obvious that in Eq. (17) never probability can be reach $y \rightarrow \infty$ in any finite time. It means that the system cannot be reach the unstable state since the concentration $x \rightarrow 0$ (unstable point) corresponds to $y \rightarrow \infty$. When $\nu > 1$ the random force is so weak

that the system is entirely controlled by the deterministic term in the vicinity of the unstable state. The transition between the two deterministic stable states cannot occur and the initial distribution is continuously retained.

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Orbital Interactions in BeC_2H_2 and LiC_2H_2 Complexes

Ikchoon Lee* and Jae Young Choi

Department of Chemistry, Inha University, Incheon 402-751. Received August 17, 1992

Ab initio calculations are carried out at the 6-311G** level for the C_{2v} interactions of Be and Li atoms with acetylene molecule. The main contribution to the deep minima on the $^3\text{B}_2$ BeC_2H_2 and $^2\text{B}_2$ LiC_2H_2 potential energy curves is the b_2 ($2p(3b_2) - |\pi_g^*(4b_2)|$) interaction, the a_1 ($2s(6a_1) - |\pi_u(5a_1)|$) interaction playing a relatively minor role. The exo deflection of the C-H bonds is basically favored, as in the b_2 interaction, due to steric crowding between the metal and H atoms, but the strong in-phase orbital interaction, or mixing, of the a_1 symmetry hydrogen orbital with the $5a'_1$, $6a'_1$ and $7a'_1$ orbitals can cause a small endo deflection in the repulsive complexes. The Be complex is more stable than the Li complex due to the double occupancy of the 2s orbital in Be. The stability and structure of the MC_2H_2 complexes are in general determined by the occupancy of the singly occupied frontier orbitals.

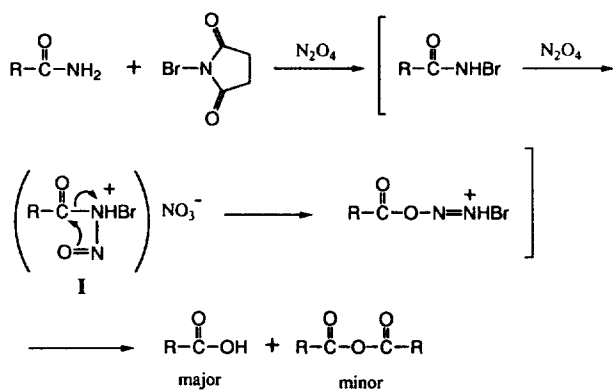
Introduction

The interactions of metal atoms with molecules have been

the subject of many experimental and theoretical studies.¹ The main purpose of the research in this field is a fundamental understanding of catalysis. It has been suggested that

Table 1. Deamination of Amides by Dinitrogen Tetroxide with *N*-Bromosuccinimide
$$\text{R-CONH}_2 + \text{NBS} \xrightarrow[\text{CH}_3\text{CN, r.t., 20 min}]{\text{CH}_3\text{CN, r.t., 20 min}} \xrightarrow[\text{CH}_3\text{CN, } -20^\circ\text{C}]{\text{N}_2\text{O}_4} \text{R-CO}_2\text{H} + (\text{R-CO})_2\text{O}$$

Run	Amides	NBS (eq.)	N ₂ O ₄ (eq.)	Time (h)	1 (%) ^a	2 (%) ^a
1	PhCONH ₂	1.2	1.8	0.5	96	2
2	PhCONH ₂	none	4.0	3.0	86	b
3	<i>p</i> -Me-PhCONH ₂	1.2	1.8	0.5	92	6
4	<i>p</i> -Me-PhCONH ₂	none	4.0	3.0	85	b
5	<i>p</i> -Cl-PhCONH ₂	1.2	1.8	0.5	94	2
6	<i>p</i> -Cl-PhCONH ₂	none	4.0	3.0	85	b
7	<i>o</i> -Me-PhCONH ₂	1.2	1.8	0.5	94	trace
8	<i>p</i> -NO ₂ -PhCONH ₂	1.2	2.0	0.5	93	4
9	<i>m</i> -NO ₂ -PhCONH ₂	1.2	2.0	0.5	92	2
10	<i>p</i> -Br-PhCONH ₂	1.2	1.8	0.5	95	trace
11	<i>p</i> -MeO-PhCONH ₂	1.2	1.8	0.5	96	trace

^a Isolated yields, ^b Not checked**Scheme 1.**

and its anhydride which were separated by SiO₂ column chromatography to give benzoic acid (117 mg, 96%) and benzoic anhydride (2 mg, 2%).

The reaction appears to be initiated *via* bromination and then subsequent formation of transient nitronium bromide intermediate I.¹² Dinitrogen tetroxide is known to be in equilibrium with NO⁺ + NO₃⁻ ion in solution.¹³ Nitrosation may occur rapidly on nitrogen to form a nitronium intermediate I which converts to the product of carboxylic acid. Rapid reaction in short time and the mild conditions may restrain formation of carboxylic acid anhydride from the carboxylic acid.

Although the reaction mechanism is not yet clear, this new interesting reaction is practical and may be available for the cleavage of C-N bond of amides. Additional research will be required to better understand the reaction mechanism.

This work was supported by the Basic Science Research Institute Program, Ministry of Education.

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- The possible intermediate I was detected by careful NMR and IR study, and TLC monitoring of the reaction mixture. It was identified not to be *N*-bromosuccinimide by comparing their spectral data with those from authentic *N*-bromosuccinimide. The reaction mixture solution of benzamide and NBS in CD₃CN was taken for ¹H-NMR and TLC each other after 5, 10, 30 min and 1 h.
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Catalytic Enantioselective Reactions. Part 2.¹ A Comparison Study of Asymmetric Borane Reduction of Prochiral Ketones Catalyzed by Chiral Oxazaborolidines

Byung Tae Cho^{*†}, Yu Sung Chun[†], Ch. Dauelsberg[‡], Sabine Wallbaum[‡], and Jürgen Martens[‡]

[†]Department of Chemistry, Hallym University
Chunchon 200-702

[‡]Fachbereich Chemie, Universität Oldenburg,
Heerstraße 114-118, D-2900 Oldenburg i.O., Germany

Received September 10, 1993

Recently much attention has been focused on the asymmetric reduction of prochiral ketones catalyzed by a variety of chiral oxazaborolidines.² However, the direct comparison study on the catalytic effectiveness of these oxazaborolidines