APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 5, 331-336 (1991)

The epitaxial growth of GaAs using alkylarsine: Part 2. Molecular orbital calculation

Y Kikuzono* and T Maeda
Sumitomo Chemical Co. Ltd, 5-33, 4-Chome, Kitahama, Chuo-Ku, Osaka 541, Japan

Semi-empirical molecular orbital calculations were carried out for the compounds $(C_2H_5)_3As$, $(C_2H_5)_3Ga$ and $RAsH_2$ ($R = C_2H_5$, i-C_3H_7, i-C_4H_9, and t-C_4H_9) by using the CNDO/2-U program, and their capability of β-elimination reaction is compared on the basis of the torsion energy to the transition state, electrostatic interactions and orbital overlapping between the central atom and the β-hydrogen, and bond order of the metal–carbon, and carbon–hydrogen bond. In the comparison of $(C_2H_5)_3As$ with $(C_2H_5)_3Ga$, we found that the β-elimination of $(C_2H_5)_3As$ could hardly be expected to take place in the thermal decomposition. The capability of β-elimination would be smaller in $C_2H_5AsH_2$ than that in $(C_2H_5)_3As$. Moreover when the ethyl group is replaced by a t-butyl group in $RAsH_2$, the β-elimination reaction appears to become more difficult and a large possibility for a radical process is suggested.

Keywords: Molecular orbital, calculation, MOCVD, source gas, alkylarsine, β-elimination

INTRODUCTION

There is an ongoing interest in developing alternative arsenic sources for the growth of gallium arsenide (GaAs) by metalorganic chemical vapor deposition (MOCVD), because arsine is an extremely toxic high-pressure gas. Several alkylarsines such as trimethylarsine $[(CH_3)_3As]$ have been tried since these sources are liquid at room temperature and safe to handle. However, use of $(CH_3)_3As$, for instance, has resulted in GaAs layers with large amounts of residual carbon originating from the alkyl radical.[1]

In a previous paper,[2] we have investigated the use of triethylarsine $[(C_2H_5)_3As]$, expecting that the carbon incorporation might be reduced as in the case of triethylgallium $[(C_2H_5)_3Ga]$ or triethylaluminum $[(C_2H_5)_3Al]$.[3,4] Degradation of these molecules is generally known to proceed through an interaction of a central metal atom with a hydrogen atom at the β-position (H_b) of the ethyl carbon, forming ethylene (β-elimination) without the production of reactive carbon-containing species which will cause carbon incorporation. However, we had obtained experimental results[2] which suggest that a β-elimination reaction is not essential in the actual epitaxial growth process, and that the use of $(C_2H_5)_3As$ causes carbon incorporation via a radical process similar to that of $(CH_3)_3As$.

In this paper, we report results of molecular orbital calculations for $(C_2H_5)_3As$ by the CNDO/2-U method, and discuss its capability to undergo β-elimination reaction in comparison with that of $(C_2H_5)_3Ga$. The calculations were also carried out for the series of monoalkylarsine, $RAsH_2$ ($R = C_2H_5$, i-C_4H_9 and t-C_4H_9), in order to compare the different effect of the alkyl group

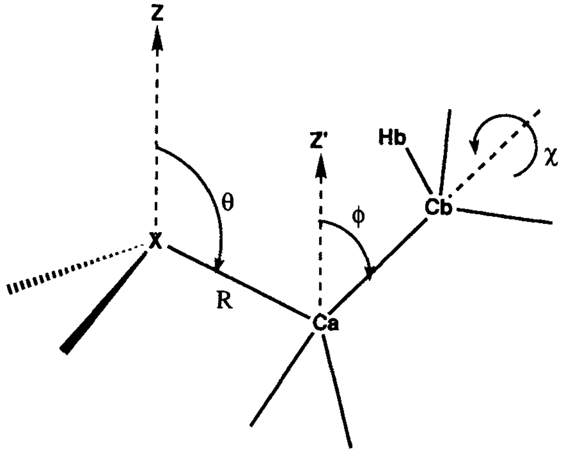


Figure 1 Geometrical parameters in $(C_2H_5)_3As$ and $(C_2H_5)_3Ga$ models (X = As or Ga). C_{3v} symmetry is assumed.

---

* Author to whom correspondence should be addressed.

0268-2605/91/040331-06$05.00

Received 22 March 1991
Revised 27 April 1991

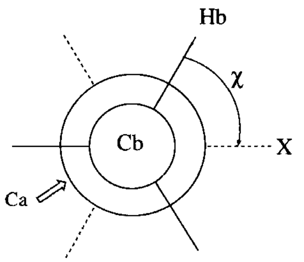


Figure 2 Conformation of methyl group [X = As or Ga; $\chi = 0°$ (eclipsed, $\chi = 60°$ (*gauche*)].

on the β-elimination in relation to other more recent studies using $(C_2H_5)_2AsH$[5] or $t\text{-}C_4H_9AsH_2$.[6,7]

METHODS

Semi-empirical molecular orbital (MO) calculations were carried out by using the CNDO/2-U program[8] from QCPE[9] on an IBM computer system (Model 4381) for $(C_2H_5)_3As$, $(C_2H_5)_3Ga$ and monoalkylarsine, $RAsH_2$ ($R = C_2H_5$, $i\text{-}C_3H_7$, $i\text{-}C_4H_9$ and $t\text{-}C_4H_9$). No experimental data have been reported on the three-dimensional molecular structures of these compounds. Therefore, initial models for the MO calculations were built by combining the partial molecular structures of their homologs, and the total energy of their stable conformations was calculated based on a grid-search method.

The initial geometry for $(C_2H_5)_3As$ was deduced from experimental data of trimethylarsine [$(CH_3)_3As$][10] and chloroethane,[11] and its geometrical parameters (R,θ,ϕ,χ) are illustrated in Fig. 1. This model has C_{3v} symmetry, parameter R is the bond distance from arsenic to the carbon atom, and parameter θ is the bond angle of Z—As—C_a. Parameter θ represents the degree of sp^3 hybridization of the arsenic atom: the value increases with a configuration change from sp^2 to sp^3 around the arsenic atom. Parameter ϕ is the torsional angle from the C_{3v} axis to the C_a–C_b axis, and χ represents the conformation of the methyl group: *gauche* form at $\chi = 60°$ and eclipsed form at $\chi = 0°$ (Fig. 2).

The initial geometry for the other molecules was obtained in the same way: $(C_2H_5)_3Ga$ from $(CH_3)_3Ga$,[12] chloroethane[11] and a series of monoalkylarsines, $RAsH_2$ from AsH_3,[13] $(CH_3)_3As$,[10] and the corresponding alkyl chloride, RCl ($R = C_2H_5$,[11] $i\text{-}C_3H_5$,[14] $i\text{-}C_4H_9$,[15] and $t\text{-}C_4H_9$[16]), respectively. These geometrical parameters are also illustrated in Figs 1 and 2.

On the basis of the initial geometry mentioned above, MO calculations were carried out by means of a grid-search method for various conformers having different geometrical parameter sets (R,θ,ϕ,χ). In the case of organoarsenic compounds, however, the parameters R and θ were fixed to the same values as reported for $(CH_3)_3As$,[10] so only parameters ϕ and χ were changed.

RESULTS AND DISCUSSION

The β-elimination is a unimolecular reaction in which an interaction of H_b and a central atom causes production of a hydride and olefin as shown in Fig. 3. Its reaction is recognized to proceed through a transition state having a plane with a four-membered ring consisting of the Ga—C—C—H_b atoms. We can therefore understand that a compound which has a low torsion energy to the transition state, a large electrostatic interaction and a large orbital overlapping between the central atom and the H_b atom, and a low bond order of As—C or Ga—C, and C_b—H_b, would be preferable for the β-elimination reaction. Here we have assumed that the torsion energy from the most stable geometry to the eclipsed conformation (β-conformation) with the

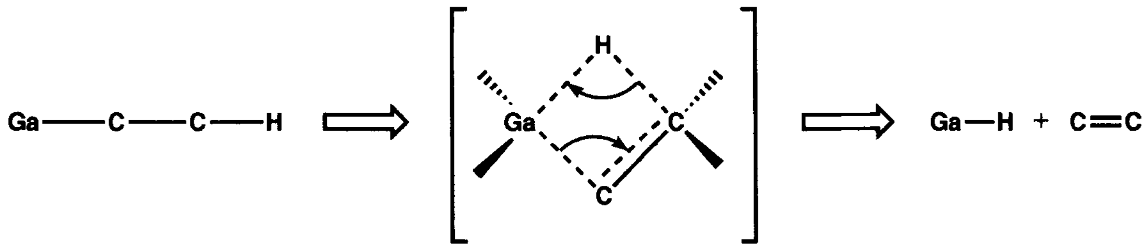


Figure 3 Scheme for β-elimination.

Table 1 Torsion energy of $(C_2H_5)_3$ As model

	Torsion angle (deg)		
Run no.	ϕ	χ	Torsion energy ΔE (kcal mol^{-1})[a]
1	0	60 (*gauche*)	11.79
2	0	0 (eclipsed)	31.06
3	60	60 (*gauche*)	0
4	60	0 (eclipsed)	8.91
5	90	60 (*gauche*)	6.58
6	120	60 (*gauche*)	25.36
7	150	60 (*gauche*)	52.93

[a] Torsion energy in comparison with Run no. 3; 1 kcal = 4.18 kJ.

lowest conformational energy roughly corresponds to the activation energy for β-elimination, because the eclipsed conformation around the C_a—C_b bond as shown in Fig. 2 ($\chi = 0$) should be very similar to the transition state as discussed in general in the context of the Evans–Polanyi principle.[17] The orbital overlapping in the transition state (eclipsed conformer) was examined for the highest occupied molecular orbitals (HOMOs), because this reaction is a thermal, intramolecular, concerted reaction.[18]

Comparison between $(C_2H_5)_3As$ and $(C_2H_5)_3Ga$

Total energies of $(C_2H_5)_3As$ were calculated for seven parameter sets (ϕ,χ). Table 1 shows the torsion energy from the most stable geometry, Run no. 3 ($\Delta E = 0$ kcal mol^{-1}, $\phi = 60°$, $\chi = 60°$: *gauche*). Among the torsion energies to the eclipsed ($\chi = 0°$) conformer, Run no. 4 [$\Delta E = 8.91$ kcal mol^{-1} (37.3 kJ mol^{-1}) $\phi = 60°$] is smaller than Run no. 2 ($\phi = 0°$). So we obtained 8.91 kcal mol^{-1} (37.3 kJ mol^{-1}) for the transition energy for β-elimination in the case of $(C_2H_5)_3As$.

Similarly, the total energy of $(C_2H_5)_3Ga$ was obtained for 12 parameter sets (R,θ,ϕ,χ), as shown in Table 2. The geometry of Run no. 16 was found to have the most stable conformation where R(Ga—C) = 2.067 Å (0.2067 nm), $\theta = 90°$, $\phi = 0°$ and $\chi = 60°$: *gauche*. The Ga—C distance, 2.067 Å (0.2067 nm), would be comparable with that of $(CH_3)_3Ga$, 1.967 Å (0.1967 nm). It is obvious that the torsion energy to the eclipsed form, 2.16 kcal mol^{-1} (9.0 kJ mol^{-1}) (Run no. 19) is considerably lower in comparison with 8.91 kcal mol^{-1} of $(C_2H_5)_3As$. It should be noticed here that this structure has sp^2-type hybridization of the gallium atom in consistency with experimental results obtained by electron diffraction analysis.[12] This hybridization should promote the β-elimination more strongly, because the spatial distance between Ga and H_b atoms can be shorter than in the case of the sp^3 As atom. These results suggest that $(C_2H_5)_3As$ is much more difficult to distort into a configuration suitable for β-elimination.

The net atomic charge and bond order were also calculated in the $(C_2H_5)_3As$ and $(C_2H_5)_3Ga$ molecules for both the most stable state and the transition state for β-elimination. These results

Table 2 Torsion energy of $(C_2H_5)_3Ga$ model

			Torsion angle (deg)		
Run no.	Bond distance, R (Å)	Bond angle, θ (deg)	ϕ	χ	Torsion energy, ΔE (kcal mol^{-1})[a]
8	1.967	90	90	60	61.05
9	1.967	90	60	60	54.77
10	1.967	90	30	60	51.34
11	1.967	90	0	60	42.07
12	1.967	90	0	60	47.38
13	1.967	95	0	60	53.87
14	1.987	100	0	60	36.75
15	2.007	90	0	60	29.01
16	2.067	90	0	60	0
17	2.167	90	0	60	121.38
18	2.067	90	0	30	0.54
19	2.067	90	0	0	2.16

[a] Torsion energy in comparison with run no. 16; 1 kcal = 4.18 kJ.

Table 3 Net atomic charge and bond order in $(C_2H_5)_3As$ and $(C_2H_5)_3Ga$

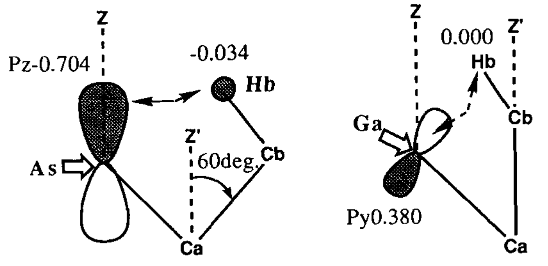
		Most stable conformation								β-conformation[a]						
		Net atomic charge				Bond order				Net atomic charge				Bond order		
Molecule	Run no.	X^b	C_a	C_b	H_b	X^b—C_a	C_a—C_b	C_b—H_b	Run no.	X^b	C_a	C_b	H_b	X^b—C_a	C_a—C_b	C_b—H_b
$(C_2H_5)_3As$	3	0.293	−0.073	0.007	−0.007	0.970	1.048	0.976	4	0.299	−0.075	0.007	−0.019	0.971	1.044	0.975
$(C_2H_5)_3Ga$	16	0.386	−0.144	0.036	−0.009	0.958	1.012	0.969	19	0.386	−0.147	0.038	−0.021	0.952	1.008	0.946

Bond orders of ethane: C_a—C_b (1.064), C_b—H_b (0.978).
[a] Eclipsed form, [b] X = As or Ga.

Table 4 Net atomic charge and bond order in $RAsH_2$

		Most stable conformation								β-conformation[a]						
		Net atomic charge				Bond order				Net atomic charge				Bond order		
Molecule $RAsH_2$	Run no.	As	C_a	C_b	H_b	As—C_a	C_a—C_b	C_b—H_b	Run no.	As	C_a	C_b	H_b	As—C_a	C_a—C_b	C_b—H_b
R = C_2H_5	23	0.222	−0.049	0.009	−0.007	1.010	1.045	0.977	20	0.229	−0.055	0.005	−0.018	1.009	1.044	0.976
i-C_3H_7	29	0.234	−0.027	0.012	−0.010	0.980	1.022	0.978	27	0.243	−0.033	0.001	−0.022	0.981	1.028	0.977
i-C_4H_9	32	0.226	−0.052	0.054	−0.018	1.015	1.002	0.941	31	0.227	−0.056	0.054	−0.034	1.015	0.998	0.941
t-C_4H_9	36	0.254	−0.014	0.012	−0.014	0.946	1.003	0.979	33	0.261	−0.020	0.008	−0.025	0.947	1.000	0.976

[a] Eclipsed form.



(C2H5)3As: RUN NO.4 (C2H5)3Ga: RUN NO.19

Figure 4 Orbital interaction for β-elimination of $(C_2H_5)_3As$ and $(C_2H_5)_3Ga$: MO coefficients in HOMO.

Table 5 Torsion energy of $C_2H_5AsH_2$ model

Run no.	Torsion angle (deg) ϕ	χ	Torsion energy, ΔE(kcal mol^{-1})^a
20	0	0 (eclipse^d)	12.75
21	0	60 (*gauche*)	7.94
22	30	60 (*gauche*)	1.20
23	60	60 (*gauche*)	0
24	90	60 (*gauche*)	0.93
25	120	60 (*gauche*)	5.37
26	150	60 (*gauche*)	8.50

[a] Torsion energy in comparison with Run no. 23; 1 kcal = 4.18 kJ.

are shown in Table 3. From the point of view of net atomic charge, it is clear that the electrostatic interaction between the central atom and the β-hydrogen is significantly stronger in the ground-state $(C_2H_5)_3Ga$ due to a large electronegativity of the gallium atom, and this interaction becomes much stronger when $(C_2H_5)_3Ga$ distorts into the transition state. Moreover, the C_b—H_b bond order in $(C_2H_5)_3Ga$ was found to become weaker, in contrast to the case of $(C_2H_5)_3As$ in which it becomes stronger. It shows that the β-hydrogen of $(C_2H_5)_3As$ will become rigid, whereas that of $(C_2H_5)_3Ga$ will tend to be removable by the torsion. These results indicate that in comparison with $(C_2H_5)_3Ga$, the β-elimination reaction would hardly take place by a thermal decomposition of $(C_2H_5)_3As$.

Table 6 Torsion energy of i-$C_3H_7AsH_2$ model

Run no.	Torsion angle (deg) ϕ	χ	Torsion energy, ΔE (kcal mol^{-1})^a
27	0	0 (eclipsed)	11.13
28	0	60 (*gauche*)	5.66
29	60	60 (*gauche*)	0
30	120	60 (*gauche*)	9.77

[a] Torsion energy in comparison with Run no. 29; 1 kcal = 4.18 kJ.

Table 7 Torsion energy of i-$C_4H_9AsH_2$ model

Run no.	Torsion angle (deg) ϕ	χ	Torsion energy ΔE (kcal mol^{-1})^a
31	0	0 (eclipsed)	194.87
32	60	60 (*gauche*)	0

[a] Torsion energy in comparison with Run no. 32; 1 kcal = 4.18 kJ.

On the other hand, as shown in Fig. 4, there exists a very small orbital interaction in the eclipsed conformer of $(C_2H_5)_3As$, but none in $(C_2H_5)_3Ga$. Hence we can assume that this orbital interaction does not play an important role as a driving force for the β-elimination reaction.

Comparison among $RAsH_2$ compounds

Alkylarsines which have a hydrogen atom attached to the arsenic atom, such as ethylarsine $(C_2H_5AsH_2)$ and t-butylarsine (t-$C_4H_9AsH_2$), have been reported to give high-quality GaAs films with low carbon contamination.[5,6] Therefore we have also carried out MO calculations on these monoalkyl-type compounds, and their torsion energy, electrostatic interaction between As and H_b, and bond order of As—C_a and C_b—H_b are summarized in Table 4. It is clear, by comparing the results of Table 4 with those of Table 3, that the torsion energy, electrostatic interaction and bond order become more unfavorable for β-elimination by the change from triethylarsine to

Table 8 Torsion energy of t-$C_4H_9AsH_2$ model

Run no.	Torsion angle (deg) ϕ	χ	Torsion energy, ΔE (kcal mol^{-1})^a
33	0	0 (eclipsed)	40.12
34	0	60 (*gauche*)	19.96
35	30	60 (*gauche*)	6.32
36	60	60 (*gauche*)	0

[a] Torsion energy in comparison with Run no. 36; 1 kcal = 4.18 kJ.

monoethylarsine, so that the capability of β-elimination is relatively smaller in monoethylarsine.

Among the monoalkylarsines examined (Table 4), it is shown that the electrostatic interaction increases in the order i-C_4H_9 > t-C_4H_9 > i-C_3H_7 > C_2H_5, whereas the torsion energy increases in the order i-C_4H_9 > t-C_4H_9 > C_2H_5 > i-C_3H_5 (Tables 5–8). Judging from the torsion energy, β-elimination becomes more difficult when the ethyl group is replaced by a t-butyl group in $RAsH_2$ although the electrostatic interactions become larger and more favorable. At the same time, the fact that the As—C bond order in t-butylarsine is drastically weakened would suggest that a radical degradation process is highly possible, as is discussed elsewhere[7] in an experiment study of its thermal decomposition.

On the basis of these calculations, we can conclude that the reduction of carbon contamination in GaAs layers, as reported for monoalkylarsine, might not be attributable to β-elimination, but rather to the reactive hydrogen attached to the arsenic atom, as is discussed in the literature.[5,6]

CONCLUSION

We have shown that β-elimination of $(C_2H_5)_3As$, which is a group V compound in the Periodic Table and which has different outer orbital electron configuration, can hardly be expected to take place, when compared with $(C_2H_5)_3Ga$, a Group III compound. The capability of β-elimination would be rather lower in monoethylarsine than in triethylarsine. Moreover, when the ethyl group is replaced by a t-butyl group in monoalkylarsine, β-elimination appears to become more difficult and it is suggested that a radical process is highly possible.

REFERENCES

1. Stringfellow, G B *J. Electronic Materials*, 1988, 17: 327

2. Maeda, T, Hata, M, Zempo, Y, Fukuhara, N, Matsuda, Y and Sawara, K *Appl. Organomet. Chem.*, 1989, 3: 151

3. Seki, Y, Tanno, K, Iida, K and Ichiki, E, *J. Electrochem. Soc.*, 1975, 122: 1108

4. Yoshida, M, Watanabe, H and Uesugi, F *J. Electrochem. Soc.*, 1985, 132: 677

5. Bhat, R, Koza, M and Skromme, B *J. Appl. Phys. Lett.*, 1987, 50: 1194

6. Larsen, C A, Buchan, N I, Li, S H and Stringfellow, G B *J. Crystal Growth*, 1988, 93: 15

7. Larsen, C A, Buchan, N I, Li, S H and Stringfellow, G B *J. Crystal Growth*, 1989, 94: 663

8. Baba-Ahmed, A, Gayoso, J, Maouche, B and Ouamerali, O *CNDO/2-U: Enhanced CNDO Calculation Program*, QCPE Catalog No. 474, 1989

9. Counts, R W *Quantum Chemistry Program Exchange* (QCPE), 1962

10. Landolt–Boernstein, 7:LB-No.437, 1976, Lide, D R, *Spectrochim. Acta*, 1959, 14: 473

11. Landolt–Boernstein, 7:LB-No.262, 1976

12. Landolt–Boernstein, 7:LB-No.448, 1976; Beagley, B, Schmidling, D G and Steer, I A *J. Mol. Struct.*, 1974, 21: 437

13. Landolt–Boernstein, 1976, 7:LB-No.21

14. Landolt–Boernstein, 1976: 7:LB-No.41, Tobiason, F L and Schwendeman, R H *J. Chem. Phys.*, 1964, 40: 1014

15. Landolt–Boernstein, 1976, 7:LB-No.545; Pauli, G H, Momany, F A and Bonham, R A *J. Am. Chem. Soc.*, *1964,* 86: 1286

16. Landolt–Boernstein, 1976, 7:LB-No.544; Hilderbrandt, R L and Wieser, J D *J. Chem. Phys.*, *1972,* 56: 1143

17. Evans, M G and Polanyi, M *Trans. Faraday Soc.*, 1935, 31: 875

18. Fujimoto, H and Fukui, K *Chemical Reactivity and Reaction Paths*, Klopman, G (ed), John Wiley, New York, 1974