A Theoretical Study of Curing Reactions of Maleimide Resins through Michael Additions of Amines

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I. Introduction

Maleimide resins can be used as materials for composites and electronics-related products, such as printed wiring boards, because they have good thermal stability, high electrical insulation, low dielectric constant, and low dissipation factor. However, the curing reactions for these resins require a high temperature and a long duration.[1−6] Considering the importance of their use in industry, it is necessary to elucidate the mechanism of the curing reaction and to design a more reactive compound. Scheme 1 shows a typical curing reaction. The bismaleimide is a bifunctional electrophilic olefin subject to Michael additions.[7] The benzenamine is a difunctional nucleophile. The multifunctionality gives rise to the curing reaction. In the Michael addition, the nucleophile is neutral, and a proton transfer is involved (Scheme 2).

Besides the curing reaction, many α,β-unsaturated ketones may be Michael acceptors and undergo self-condensation reactions in the presence of bases.[8] Michael additions have been studied theoretically by means of ab initio calculations.[9] But, these studies used anionic nucleophilic reagents, and neutral model systems such as these shown in Scheme 2 have not yet been investigated. To understand the mechanism of the curing reactions of maleimide resins, we must clarify the reaction path in Scheme 2.

In this work, Michael additions compatible with curing reactions were studied theoretically.

Ab initio calculations of a model reacting system composed of maleimide and dimethylamine were carried out. Although use of BMI in Scheme 1 is desirable, the substrate size is too large for reliable calculations and the maleimide was used as an electrophilic olefin. To simulate the neutral nucleophile in “further Michael additions” of Scheme 1, dimethylamine Me_2NH was used. Our aim in ab initio calculations was to reveal structural features of the Michael addition in Scheme 2. Through the present study on model reaction systems, the curing reaction in Scheme 1 is made more understandable; new synthetic approaches are consequently expected.

II. Computational Method

Ab initio calculations were performed using the GAUSSIAN 94[10] program on the CONVEX SPP 1200/XA computer at the Information Processing Center of Nara University of Education and the SGI Indigo2 computer at Matsushita Electric Works, Ltd. The RHF/6-31G* and B3-LYP/6-31G*[11] methods with the SCRF[12] effect were applied to geometry optimizations and subsequent vibrational analyses. Results calculated by B3-LYP/6-31G*-(SCRF) will be discussed. The dielectric constant (ϵ) for SCRF = dipole is 5.26 (dimethylamine). For the large model reacting systems in Figure 4, the RHF/3-21G method was used.

III. Results and Discussion

Figure 1 shows a reaction between a maleimide molecule and a dimethylamine molecule. When these two molecules meet, a weakly bound complex, intermediate 1, is formed. It involves two hydrogen bonds. But, the intermediate is unstable in the change of Gibbs free energies [+3.8 kcal/mol]. Through reorientation of the lone-pair orbital toward the π^* MO in the maleimide, TS1 is formed. The N···C formation and proton transfer take place simultaneously. TS1 has a four-membered shape and a small NHC angle ($\alpha = 110.4°$). This ring strain indicates a difficult proton transfer and a large activation energy, 30.1 kcal/mol. A more facile proton transfer is required for the Michael addition to occur.

Figure 2 shows a reaction containing an amine dimer. Intermediate 2 formed through a N−H···O hydrogen

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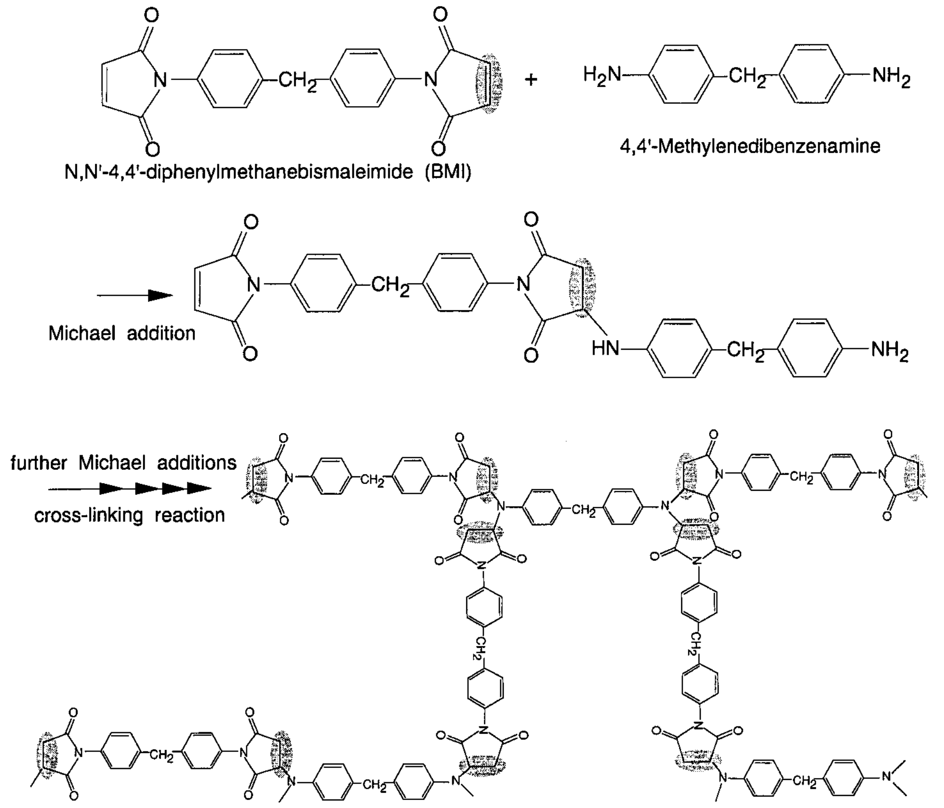
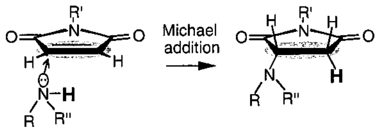
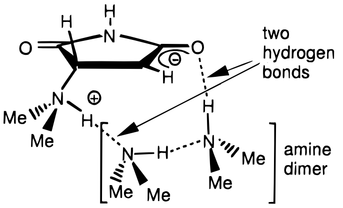
Scheme 1. Curing Reaction of the Maleimide Resin



Scheme 2. Nucleophilic Addition of the Amine Accompanied by a Proton Transfer



Scheme 3. Zwitterionic Intermediate Stabilized by Two Linear Hydrogen Bonds with the Amine Dimer



bond is a good precursor for the nucleophilic addition, TS2. By means of the (N→C) nucleophilic attack, a proton moves to the second amine. Its proton goes to the methine carbon. While the proton transfer between two nitrogen atoms occurs readily at the NHN angle, $\alpha = 163.2°$, that between N and C atoms is difficult at the NHC angle, $\beta = 131.3°$. The angle α is much larger than the 110.4° in TS1 of Figure 1. TS2 is less strained than TS1, and accordingly, E_a(TS2) = 11.6 kcal/mol is much smaller than E_a(TS1) = 30.1 kcal/mol. But, the NHC angle ($\beta = 131.3°$) must be improved if there is to be a ready proton attachment to the methine carbon.

Figure 3 shows a reaction containing an amine trimer. The intermediate 4 has four linear hydrogen bonds. When the hydrogen bond (C−H···N) is replaced in the N→C nucleophilic attack, TS3 is generated. It is noteworthy that the reaction-coordinate vector is almost localized at the N···C bond formation at TS3. On account of the absence of the proton-relay component, a zwitterionic species, intermediate 5, is obtained after TS3 (Scheme 3).

In Figures 1 and 2, such an intermediate was not obtained. The amine monomer and dimer cannot make a linear hydrogen-bond network, as shown Figure 3, to stabilize the intermediate. After the intermediate 5, a proton relay takes place readily along the network; intermediate 5 → TS4 → intermediate 6 → TS5 → intermediate 7. There is no ring strain for the proton migration. The intermediate 7 is a product stabilized by the amine dimer. Thus, the amine trimer is a reasonable reactant of neutral Michael additions (in Scheme 2) structurally.[13]

Energy changes are examined in Figure 3. E_a(TS3) = 5.5 kcal/mol is much smaller than E_a(TS1) = 30.1 kcal/mol (Figure 1) and E_a(TS2) = 11.6 kcal/mol (Figure 2) owing to the stabilization of the linear hydrogen bonds as shown in Figure 3. The relative energies of intermediates 5 and 6 are similar to that of TS3, and they are only transient. An energetic outcome was observed; $E_a(\mathrm{TS3}) < E_a(\mathrm{TS4}) < E_a(\mathrm{TS5})$. The first step, the N→C nucleophilic attack, is apparently not a rate-determing one, as shown in Figure 3. This apparent peculiarity may be related to the electronic distributions described in Scheme 3. The carbonyl oxygen in the enone moiety of maleimide

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[13] Recently, experimental and theoretical studies of amine reactions involving dimers with substrates such as esters and ketenes have been reported. They are basically concerned with the mechanism of hydrogen bonds and proton relays. (a) Raspoet, G.; Nguyen, M. T.; Kelly, S.; Hegarty, A. F. *J. Org. Chem.* **1998**, *63*, 9669. (b) Talvik, A.-T.; Tuulmets, A.; Vaino, E. *J. Phys. Org. Chem.* **1999**, *12*, 747. (c) Spillane, W. J.; Hogan, G.; McGrath, P.; King, J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 309. (d) Adalsteinsson, H.; Bruice, T. C. *J. Am. Chem. Soc.* **1998**, *120*, 3440. (e) Sung, K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1998**, *120*, 3043.

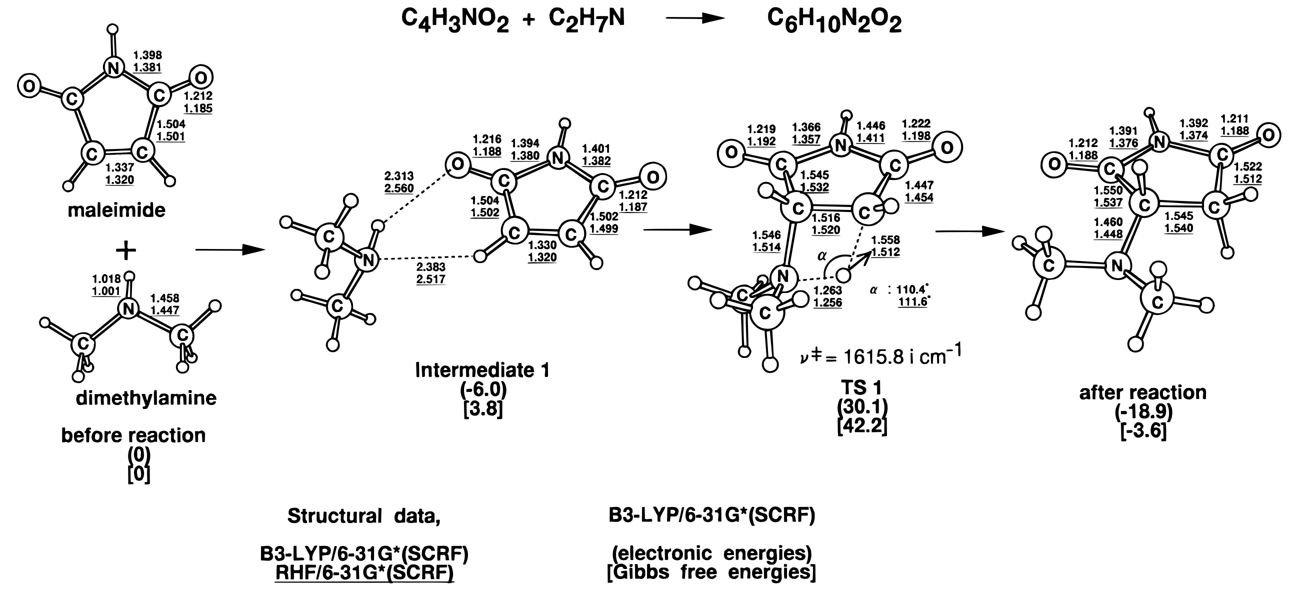


Figure 1. Geometries of reactants, intermediate and transition-state (TS) optimized by the B3-LYP/6-31G*(SCRF) method. Distances are in angstroms. Empty small circles stand for hydrogen atoms. Underlined numbers for distances are those of RHF/6-31G*(SCRF). For TS, B3-LYP/6-31G*(SCRF) reaction-coordinate vectors corresponding to the sole imaginary frequency $\nu^{\ddagger}$are sketched. The combination of one maleimide molecule and one dimethylamine ($n = 1$) molecule is considered. In parentheses, energy differences of B3-LYP/6-31G*(SCRF) are shown (kcal/mol). In square brackets, differences of Gibbs free energies ($T = 300$ K, 1 atm) are given.

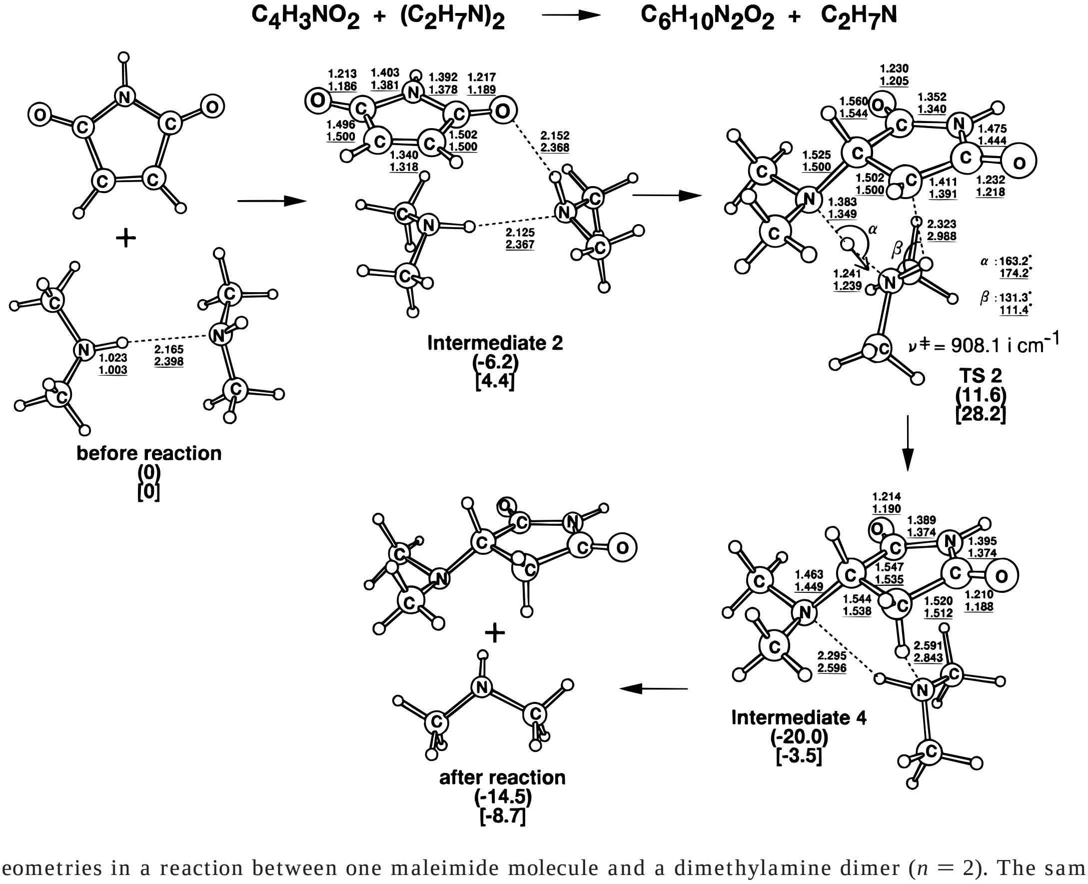


Figure 2. Geometries in a reaction between one maleimide molecule and a dimethylamine dimer ($n = 2$). The same notations as in Figure 1 are used.

becomes anionic in the zwitterionic intermediate and would be subject to further direct solvation. SCRF is not enough to describe the solvation; more hydrogen bonds to the anionic oxygen atom need to be considered. The system shown in Figure 3 is very large and further addition of the dimethylamine molecule is hardly feasible.

In Figure 4, the trimer-participation TSs are shown with an ammonia molecule as a catalyst. Through this addition, a different order, E_a(TS4, 5.9 kcal/mol) < E_a(TS5, 6.1 kcal/mol) < E_a(TS3, 11.0 kcal/mol), is obtained. Now, TS3 is the rate-determing step. The strength of the hydrogen bond $H_2N{-}H{\cdots}O{=}C$ is in the order

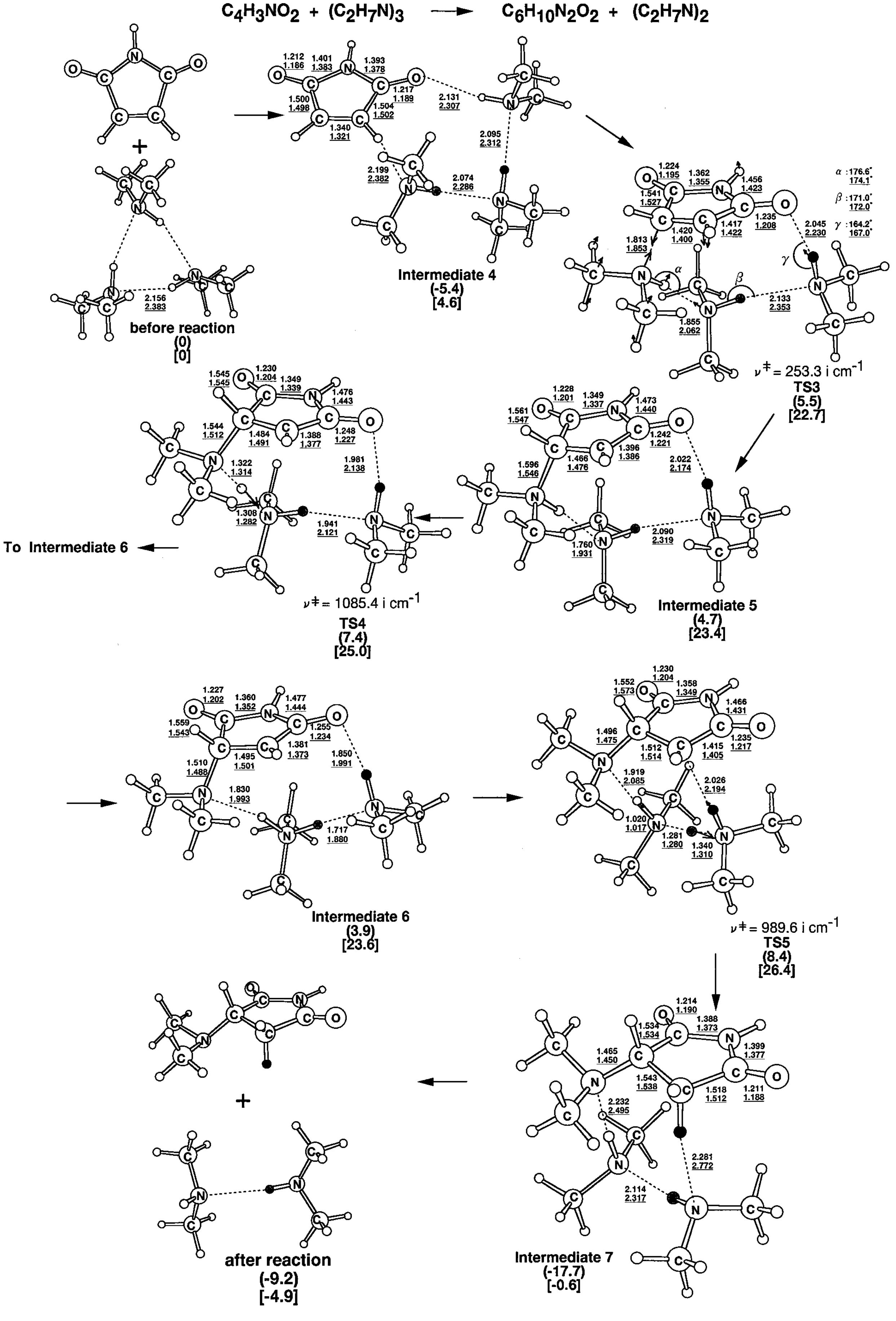


Figure 3. Geometries in a reaction between one maleimide molecule and a dimethylamine trimer ($n = 3$).

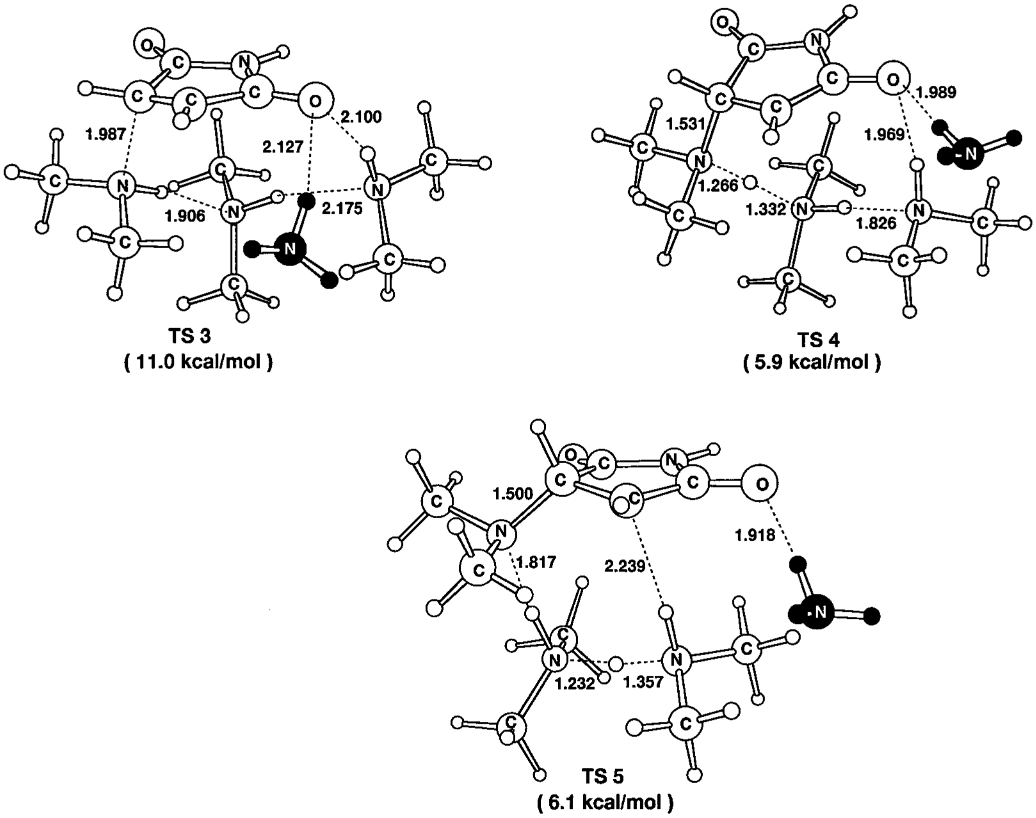


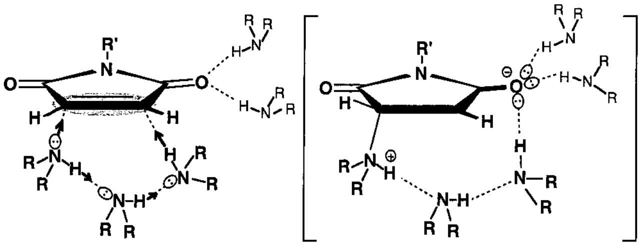
Figure 4. Geometries of three TSs of $n = 3$ including an ammonia molecule as a catalyst. The NH_3 molecule is specified by black atoms. Those geometries were optimized by the RHF/3-21G method. In parentheses, energy differences between TSs and the intermediate 4 are shown.

TS3 < TS4 < TS5, because O···HN distances are 2.127, 1.989, and 1.918 Å, respectively. The hydrogen bond stabilizes TS5 most effectively [in Figure 3, E_a(TS3) < E_a(TS4) < E_a(TS5)]. If more outer ammonia (amine) molecules are included, the order E_a(TS3) $\gg$ E_a(TS4) > E_a(TS5) will be obtained. The catalytic role of outer amine molecules is indispensable for proper description of the neutral Michael addition.

VI. Concluding Remarks

This paper presents a theoretical study of the fundamental mechanism of curing reactions of maleimide resins. In a model reaction between maleimide and dimethylamine, the combination of the Michael addition and proton relays was examined by ab initio calculations. The amine trimer fits into the combination. Proton relays can take place through linear hydrogen bonds readily. Apparently, it is not the N→C nucleophilic attack but the proton relay that is the rate-determining step. Since zwitterionic intermediates are involved during proton relays, the catalytic role of outer amines needs to be included to describe properly the potential energy of the reaction and the rate-determing step. The catalyst makes the N→C addition the rate-determining step. Scheme 4 exhibits the mechanism proposed here.

Scheme 4. Nucleophilic Attack and Proton Relays in the Neutral Michael Addition[a]



[a] The zwitterionic intermediate subject to strong hydrogen bonds at the carbonyl oxygen.

Supporting Information Available: Total energies and Cartesian coordinates of geometries in Figures 1−3 optimized by B3-LYP/6-31G*(SCRF) and RHF/6-31G*(SCRF). This material is available free of charge via the Internet at http://pubs.acs.org.

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