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Reaction Paths toward Isocyanate Adducts

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Addition reactions of isocyanates were theoretically investigated. The simplest model compounds for urethanes, thiourethanes, and ureas were analyzed to find bimolecular reaction profiles. The transition states suggested intramolecular hydrogen-transfer processes, in which highly acidic hydrogens hopped.

Isocyanate adducts are one of the most important ingredients of industrial polymers. For example, urethane compounds are derived from isocyanates and alcohols.[1] A general scheme is shown in Figure 1a. This is a reversible reaction. Recently, thiols have also been employed instead of the usual alcohols as shown in Figure 1b, the products of which are called thiourethanes. These reactions have been widely applied for coatings, adhesives, and foams. The reaction mechanism has also been speculated by classical reaction rate analyses. Early workers reported that the reaction rate of urethane formation is approximately proportional to the square of the concentration of alcohols.[1,2] For this reason, little attention has been paid to direct addition of alcohol molecules to isocyanates,[3,4] which is first order with respect to the alcohol concentration. However, considering the unimolecular decomposition of urethanes as a reverse reaction in Figure 1a, which is often observed by heating,[5] there should be direct addition in urethane formation. In general, various mechanisms are disputed among many organic chemists.

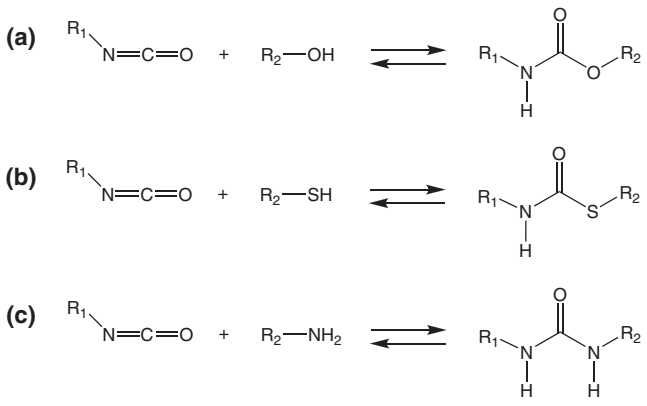

Figure 1. Scheme of (a) urethane and (b) thiourethane, and (c) urea formations. R_1 and R_2 are substituents.

A direct addition mechanism probably plays a significant role in urethane formation, because the isotope effects is small.[6] That is, when a deuterium is substituted in the hydroxy in methanol, the reaction rate of 1,1′-methylenebis(4-isocyanatobenzene) and methanol is 1.58 times slower than usual.[6] If two or more alcohol molecules are involved in the rate-determining step, the reaction rate of the heavy isotope system should be 10–20 times slower due to the lower zero-point energy of –OD bonds.[7] Thus, the elementary reaction of the direct addition should be crucial for urethane formation. In particular, in decomposition of urethanes in solid states such as polyurethanes, the reverse of direct addition should be important. The decomposition of solid-state urethanes has been applied to one-pot coatings, in which protective group blocked isocyanates and polyols react at ca. 100–200 °C to form robust thermosetting resins.[8] Thus, the elementary reaction of direct addition is important from both fundamental and engineering points of view.

Theoretical analysis of the transition state of the reaction in Figure 1a has not been reported except for two brief descriptions.[9,10] In these reports however, the relationship between reactivity and electronic characteristics of the transition states have not been discussed in detail. In this article, the reaction process is described by molecular-orbital theory and the remarkable characteristics of the transition states are reported including sulfur- and nitrogen-containing analogs. The simplest model compound dimethylurethane ($R_1 = R_2 = CH_3$ in Figure 1a), which is derived from methyl isocyanate and methanol, was analyzed. As analogs, dimethylthiourethane ($R_1 = R_2 = CH_3$ in Figure 1b) and dimethylurea ($R_1 = R_2 = CH_3$ in Figure 1c) were also analyzed.

All the calculations were done at PM3 level of theory by using MOPAC,[11,12] which is suitable for thermodynamic description of organic reactions.[10] The transition states were first optimized, and IRC (intrinsic reaction coordinate) paths to initial and final states were also calculated. The transition states were confirmed by vibrational analysis.

The reaction profile of urethane formation is depicted in Figure 2. The initial state corresponds to methyl isocyanate and methanol. The transition state was found 170.7 kJ mol^{-1} above the initial state. The final state was obtained as dimethylurethane, which was 249.9 kJ mol^{-1} below the transition state. The difference of heat of formation between initial and final states was 79.2 kJ mol^{-1}, as noted in Figure 2. The transition state contained an almost planar four-membered N–C–O–H ring, in which N–H and O–H bond lengths were 1.481 and 1.206 Å, respectively. The detailed structure of the transition state is shown in Figure 2. This situation suggests hydrogen transfer, in which an active hydrogen is directly transferred from oxygen to nitrogen. Qualitatively, this is consistent with the preceding work.[9,10] Whereas the net atomic charges of the active hydrogens in methanol and methylurethane were calculated to be +0.181 and +0.085, respectively, the charge of the hydrogen in the transition state was +0.295. This is clearly acidic. The acidity of the hydrogen suggests possible base catalysis. Indeed, urethane formation is highly catalyzed by basic compounds such as triethylenediamine and dibutyl(dilauroyloxy)tin.[6] From reaction rate analysis, early workers described self-catalyzed processes in urethane formation, in

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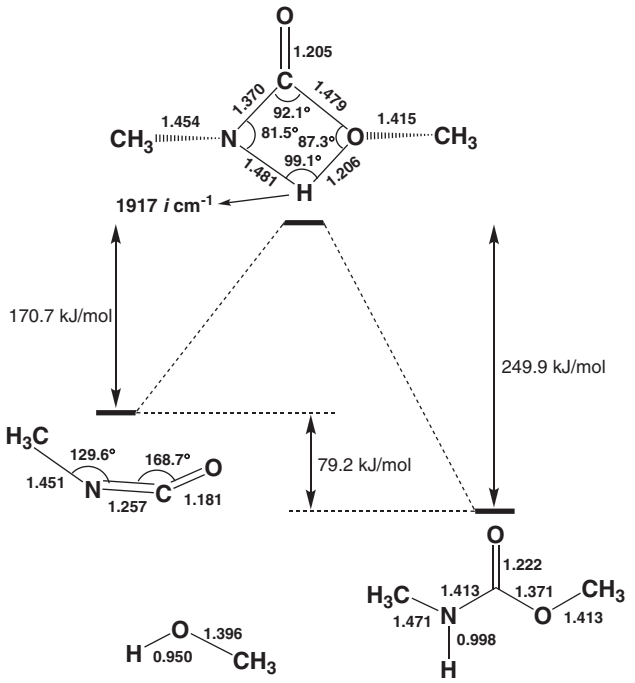

Figure 2. Reaction profile of urethane formation. Heats of formation at initial and final states were −293.5 and −372.7 kJ mol^{-1}. Optimized parameters are given in Å and degrees.

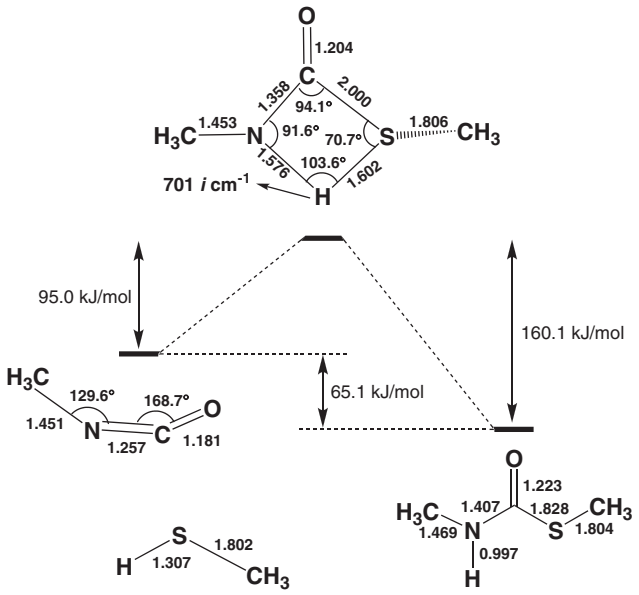

Figure 3. Reaction profile of thiourethane formation. Heats of formation at initial and final states were −99.5 and −164.6 kJ mol^{-1}. Optimized parameters are given in Å and degrees.

which the bimolecular reaction of isocyanate and alcohol is enhanced by another alcohol molecule.[1,2] The apparent second-order reaction rate is often observed in liquid states. Even in such cases, the hydrogen and alkoxy group should be supplied intramolecularly rather than intermolecularly, because the latter necessitates association of alcohol[2] and leads to quite large isotope effects. In solid states, non-associated or well-separated –OH groups in polyols can form polyurethanes. The second catalytic alcohol in the liquid state probably stabilizes the direct addition transition state by weak basicity. Vibrational analysis gave a unique imaginary frequency of the transition state at 1917 *i*cm^{-1}, which corresponds to simple hydrogen transfer. The eigenvector of the imaginary frequency is depicted in Figure 2. It is noteworthy that the transition state has a highly acidic hydrogen. This suggests that possible decomposition agents for urethane resins should be basic rather than acidic. Indeed, diethanolamine is used in a possible recycling process for polyurethanes.[13]

The reaction profile of thiourethane is similarly described in Figure 3. The activation energies for the forward and reverse reactions are 95.0 and 160.1 kJ mol^{-1}, respectively, which are ca. 80 kJ mol^{-1} lower than those of the urethane. The difference of heat of formation between initial and final states is 65.1 kJ mol^{-1}, which is slightly lower than that in the urethane. As shown later, this leads to a smaller equilibrium constant. The transition state also contains a planer four-membered N–C–S–H ring, in which N–H and S–H bond lengths are 1.576 and 1.602 Å, respectively, as depicted in Figure 3. This geometry also suggests hydrogen transfer. The unique imaginary frequency is 701 *i*cm^{-1}, which is much smaller than that of the urethane due to the large S–H bond length. The charge of the active hydrogen in the transition state is +0.260, which is also highly acidic.

Finally, the reaction path for urea is shown in Figure 4. In this case, the reaction profile consists of two steps. First, one of the carbon atoms in isocyanate and a nitrogen in amine form a 1.623 Å C–N bond. This complexation results from the strong basicity of amines. The activation energy for the complexation is 36.1 kJ mol^{-1}, which is sufficiently small. The first transition state is characterized by an imaginary frequency 282 *i*cm^{-1}, which corresponds to weak C–N stretching. Next, addition of the hydrogen takes place, as shown in Figure 4. The activation energy for the second step is 104.2 kJ mol^{-1}, which is much larger than that of the first step. Thus, the second step is rate-determining. The second step is used later for calculation of the activation free energy. In this reaction, the first complexation reduces the entropy of the system, and the second activation energy is also reduced due to the C–N bonding. The transition state for the second step was similarly obtained, in which one of the N–H bond lengths is 1.479 Å, and the other is 1.370 Å, as shown in Figure 4. The charge of the active hydrogen is +0.243, which is also highly acidic. It can be seen that the right methylamino group is oriented so as to release the active hydrogen. The imaginary frequency was found at 1919 *i*cm^{-1}, which also corresponds to hydrogen transfer. For the reverse reaction, there exists 217.6 kJ mol^{-1} of activation energy. The difference of heat of formation between initial and final states is 95.3 kJ mol^{-1}. This is larger than those in the urethane and thiourethane. Therefore, the equilibrium is thought to be strongly inclined toward urea, which is consistent with our common sense that isocyanates and amimes react very rapidly and the reactions are essentially irreversible.[1] This is confirmed later by using activation free energies.

Here, we consider the reaction rates for the three model cases. For a given temperature T, the rate constants $k_{1,-1}$ (the

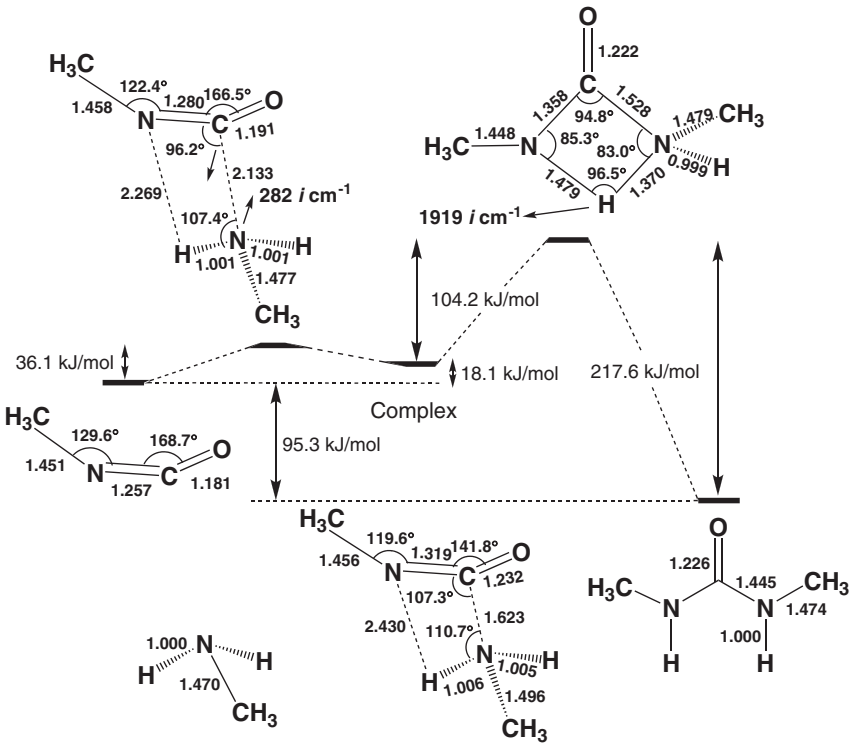

Figure 4. Reaction profile of urea formation. Heats of formation at initial and final states were −98.1 and −193.4 kJ mol^{-1}. Optimized parameters are given in Å and degrees.

subscripts 1 and −1 correspond to forward and reverse reactions) are expressed as follows:

$$k_{1,-1} \propto \kappa \frac{kT}{h} \exp\left(-\frac{\Delta G^{\ddagger}_{1,-1}}{RT}\right) \quad (1)$$

where $\Delta G^{\ddagger}_{1,-1}$ are activation Gibbs energies. R is the gas constant. k and h denote the Boltzmann and Plank constants, respectively. κ is the transmission coefficient, which is regarded as constant among analogous reactions.

The activation free energies for forward reactions were calculated by thermodynamic computation options in MOPAC. In these calculations, the activation entropies, which are about −150 J mol^{-1} K^{-1} at 298 K, are not negligible for quantitative results, because the reactions are triggered by collision. The activation free energies $\Delta G^{\ddagger}_1$ were ordered as:

$$\Delta G^{\ddagger}_1 \text{ (kJ mol}^{-1}) = 105.4 \text{ (–NH}_2) < 140.2 \text{ (–SH)} < 218.8 \text{ (–OH)} \quad (2)$$

In general, thiols are very much less reactive toward isocyanates than alcohols.[1] Therefore, the controversy of the order in reactivities lies in not kinetic but thermodynamic control, which includes the rate of reverse reactions as well as forward reactions. Thus, the rate constant ratios k_1/k_{-1}, which are identical to the overall equilibrium constants K, are suitable for estimation of the reactivities. Logarithms of K can be calculated from the differences of free energies between the initial and final states at 298 K. These were ordered as;

$$\log_{10} K = 4.8 \text{ (–NH}_2) > 3.2 \text{ (–OH)} > 2.1 \text{ (–SH)} \quad (3)$$

This is consistent with the general tendency,[1] and the experimental data for equilibrium constants for urethane formations are on the order of 10^3,[5,10] also consistent with the present estimation. Taking account of the reversible character, the author thinks that thiourethanes are suitable for blocked isocyanates, in which –NCO groups are easily released by heating and thus also well adapted for one-pot coating.

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