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BOND DISSOCIATION ENTHALPY AS A TOOL TO STUDY URETHANE DEGRADATION

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Polyurethane is the most important class of polymers. It contains several urethane bonds, which connect the building blocks of the polymer. Thus, the chemical recycling and the degradation of the polymer depend on the strength of the urethane bond. To better understand polyurethane degradation at the molecular level, three model systems were created, carbamic acid, methyl *N*-methylcarbamate, and phenyl *N*-phenyl carbamate, and studied by using computational chemical tools. Each of the model compounds contained one urethane bond. Thus, the effect of various functional groups around this motif can be studied by comparing the corresponding bond dissociation enthalpies (BDEs) within these compounds. The BDEs were computed by using the B3LYP density functional theory (DFT) method in combination with the 6-31G(d) basis set in the gas phase. It was found that in the case of phenyl *N*-phenyl carbamate, the degradation is more probable because the corresponding BDEs are lower than in the other two compounds.

Keywords: polyurethane, urethane bond, DFT, BDEs

INTRODUCTION

Polyurethanes (PUs) are one of the most versatile industrial polymers, because of their good mechanical, physical, biological, and chemical properties. PUs are applied in products such as furniture, coatings, adhesives, construction materials, and fibers [1], [2]. They are also suitable for thermal and sound insulation due to their low density, and thermal conductivity as well [3]. Their most important unit is the urethane bond (–NH–COO–), which is formed by the reaction of an isocyanate group (–N=C=O) and an –OH group [4] *(Figure 1)*. Although polyurethanes have good properties and many advantages, due to their petroleum-based starting materials, they have an adverse effect on human health and the environment [5]. As PU production continues to rise, dealing with the growing amount of polyurethane-based waste is becoming exceedingly challenging [1].

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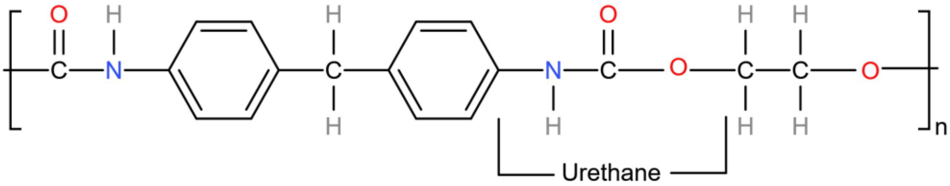
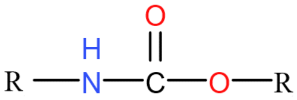


Figure 1

Schematic chemical structure of conventional polyurethanes

Therefore, there is a great need to develop new plastic waste management approaches that are both environmentally friendly and cost-effective [1]. This can be done by finding new biodegradable materials that break down in the environment through physical, chemical, and biological processes or by finding organisms that can degrade conventional polymers [6]. The term "PU biodegradation" refers to the degradation of polyurethane by microbes (or biotic organisms), leading to physical and chemical weakness in the substrate. The mechanism of PU degradation is determined by the presence of microorganisms, and alkaline and oxidative conditions capable of degrading polymer chains [7]. Those living microorganisms (bacteria, fungi, and algae) are known to participate in PU biodegradation, which can produce special enzymes (intracellular or extracellular) capable of catalyzing the necessary degradative processes, thus, contributing to polymer chain decomposition and taking up the final hydrolysis products and metabolize them [8]–[10]. Hydrolysis, oxidation and hydroxylation are examples of enzymatic activities that result in the cleavage of polymer chains into oligomers and monomers, and a decrease in the molecular weight and the viscosity of the chains [8]. Because microbes differ in their characteristics, degradation differs from one microorganism to another [11]. To some extent, the most attractive plastic waste treatment method is enzymatic degradation [11]. The urethane bond is chemically and structurally similar to the urea and peptide bonds, thus, it can be attacked by low-specificity proteases and ureases.



$R-NH-C(=O)-O-R$

Figure 2

Position of the R group in urethane models, where R = H, CH_3, or C_6H_5 for carbamic acid, methyl N-methylcarbamate, and phenyl N-phenyl carbamate, respectively

To further understand urethane formation, various experimental and computational research has been conducted. *(Figure 2)* The bond dissociation enthalpy (BDE) is an important thermosdynamic quantity that represents the strength of the corresponding bond, and the lower the BDEs are, the easier it is to break the bond [12]. In the current work, urethane bond degradation was studied by using computational chemical tools. Thus, to better understand the decomposition mechanism of plastic polymers, bond dissociation enthalpies (BDEs) were computed.

1. MATERIALS AND METHODS

Three model systems were designed to understand degradation at the molecular level, carbamic acid, methyl *N*-methylcarbamate, and phenyl *N*-phenyl carbamate, each of which contained one urethane bond. The formation of the urethane products was also studied by computing the corresponding reactants and transition states. All calculations were carried out by using the Gaussian 09 program package [13]. Optimizations and frequency calculations were carried out by using the B3LYP density function theory (DFT) method in combination with the 6-31G(d) basis set in the gas phase. [12] The bond dissociation enthalpy (BDE) values of X-Y (where X and Y are C, N, O) or X-H (where X is C) bonds were computed for all structures.

2. RESULTS AND DISCUSSION

All structures were optimized at the B3LYP/6-31G(d) level of theory. The geometries of reactants, transition state (TS), and products and the corresponding thermodynamic properties were computed as well *(Table 1)*. The length of the bonds was measured, and in the case of carbamic acid, the bond lengths varied between 0.971 Å and 1.390 Å. In the case of methyl N-methylcarbamate, the bond lengths were longer (1.361 Å, 1.364 Å, 1.431 Å, 1.448 Å), compared to the corresponding bond length of phenyl N-phenyl carbamate *(Figure 3)*.

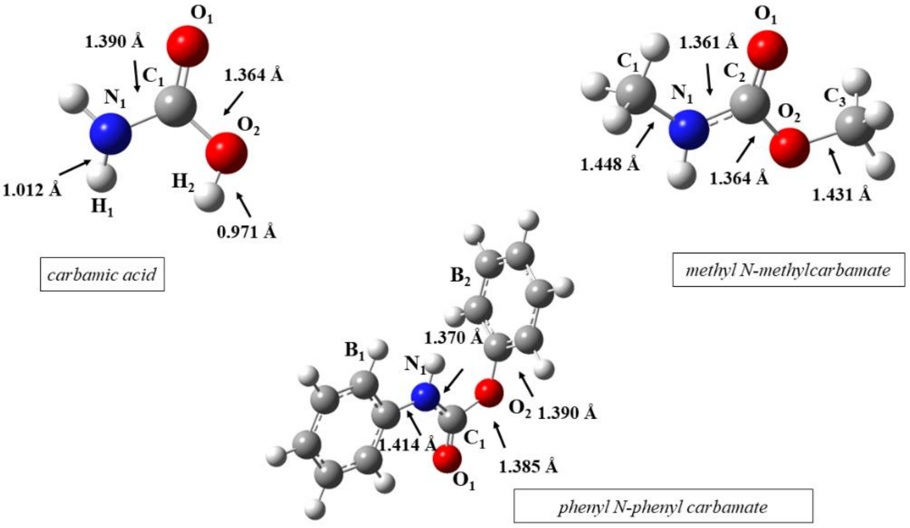
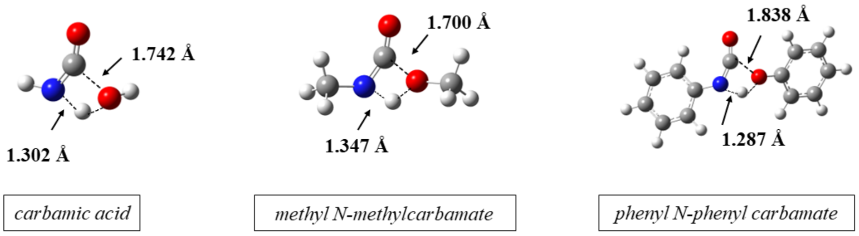


Figure 3

Optimized structures of the studied urethane model systems for carbamic acid, methyl N-methylcarbamate, and phenyl N-phenyl carbamate, respectively

The studied urethane-containing products were formed through concerted transition states (TS). In the case of methyl *N*-methylcarbamate, the N-H distance in the TS was 1.347 Å, while the forming C-O bond between the isocyanate and methanol was 1.700 Å. In the case of carbamic acid, the N-H distance was slightly shorter, 1.302 Å, while the C-O was longer, 1.742 Å, compared to the methyl-substituted structure. This trend was even more pronounced in the case of the phenyl *N*-phenyl carbamate structure, where the N-H was 1.287 Å, while the C-O was 1.838 Å in the corresponding transition state *(Figure 4)*.



carbamic acid *methyl N-methylcarbamate* *phenyl N-phenyl carbamate*

Figure 4
Transition state of the studied urethane model systems carbamic acid, methyl N-methylcarbamate, and phenyl N-phenyl carbamate, respectively

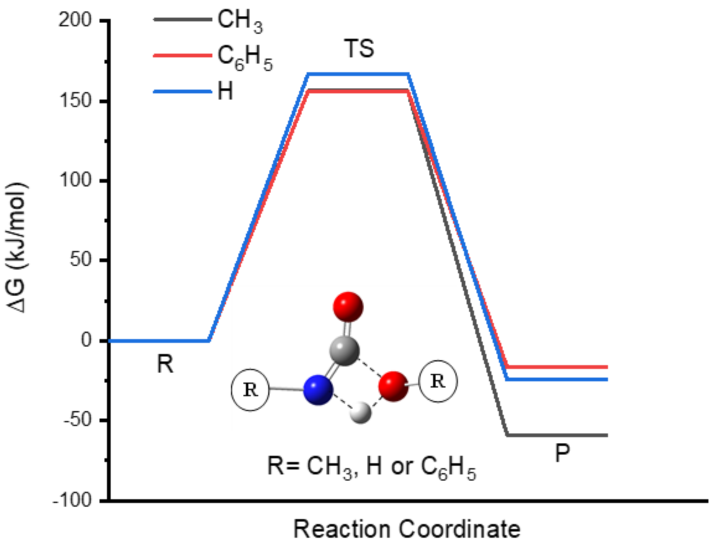


Figure 5
*Relative Gibbs free energies (*DG*) of the studied urethane formation reactions to achieve the model systems for carbamic acid, methyl N-methylcarbamate, and phenyl N-phenyl carbamate, respectively*

The relative Gibbs free energy difference (D*G*) between the *phenyl N-phenyl carbamate* and *methyl N-methylcarbamate* was only 0.2 kJ/mol at the corresponding transition states, while *carbamic acid* was deviating a little bit more compared to the other two cases (~11 kJ/mol) *(Table 1, Figure 5)*. Thus, the activation energy was almost identical for *phenyl N-phenyl carbamate* and *methyl N-methylcarbamate*, while it was higher in the case of *carbamic acid* (167.1 kJ/mol). Higher activation energies indicate slower reactions.

For all three studied model structures, carbamic acid, methyl *N*-methylcarbamate, and phenyl *N*-phenyl carbamate, four bonds involved in the urethane unit have been broken and the corresponding radical species were computed and the BDEs for these bonds have been calculated *(Figures 6–7–8)*. It was assumed that the BDEs are somewhat related to the degradability of the bond. The lower the BDE values are, the breaking bonds would be easier, and the degradation is more probable at the respective position.

Table 1

The zero-point corrected relative energies (ΔE_0), enthalpies (ΔH), and Gibbs free energies (ΔG) of the studied structures: carbamic acid (HNHCOOH), methyl N-methylcarbamate ($H_3CNHCOOCH_3$), and phenyl N-phenyl carbamate ($C_6H_5NHCOOC_6H_5$) calculated at the B3LYP/6-31G(d) level of the theory in the gas phase. R: reactant, TS: transition state, P: product

	methyl *N*-methylcarbamate *($H_3CNHCOOCH_3$)*	**carbamic acid** *(HNHCOOH)*	**phenyl *N*-phenyl carbamate** *($C_6H_5NHCOOC_6H_5$)*
	ΔE_0 (kJ/mol)		
R	0.0	0.0	0.0
TS	110.1	129.5	108.8
P	–102.6	–62.4	–65.5
	Δ*H* (kJ/mol)		
R	0.0	0.0	0.0
TS	106.8	121.9	109.1
P	–109.7	–69.9	–65.9
	Δ*G* (kJ/mol)		
R	0.0	0.0	0.0
TS	156.6	167.1	156.4
P	–59.4	–24.5	–16.6

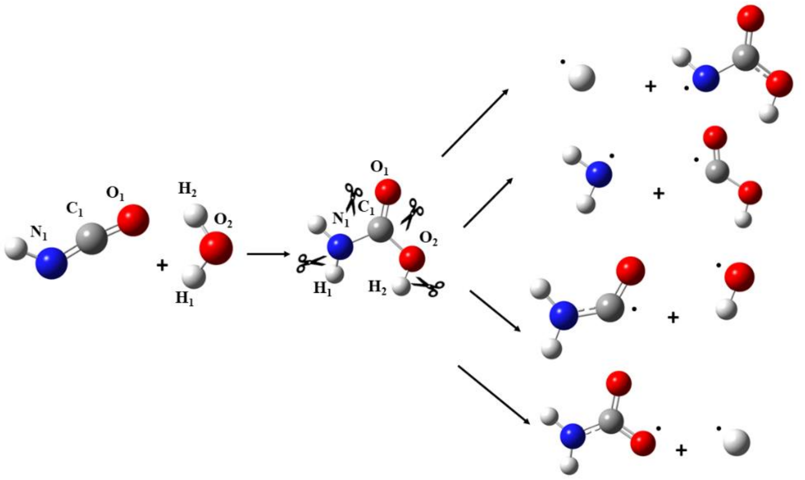


Figure 6

The formation and degradation pathways of carbamic acid (H_2NCOOH). The species have been computed at the B3LYP/6-31G(d) level of theory in the gas phase and BDEs has been computed. The scissors refer to breaking the bond.

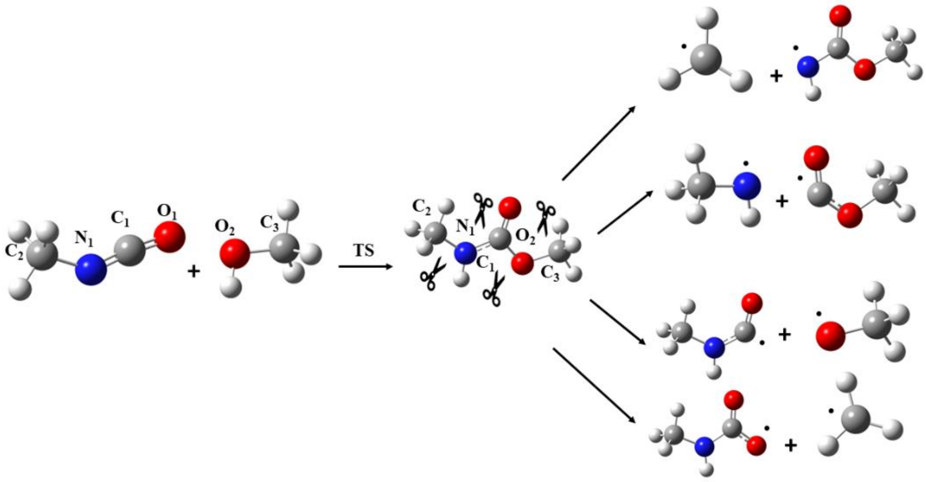


Figure 7
The formation and degradation pathways of methyl N-methylcarbamate ($H_3CNHCOOCH_3$). The species have been computed at the B3LYP/6-31G(d) level of theory in the gas phase and BDEs has been computed. The scissors refer to breaking the bond.

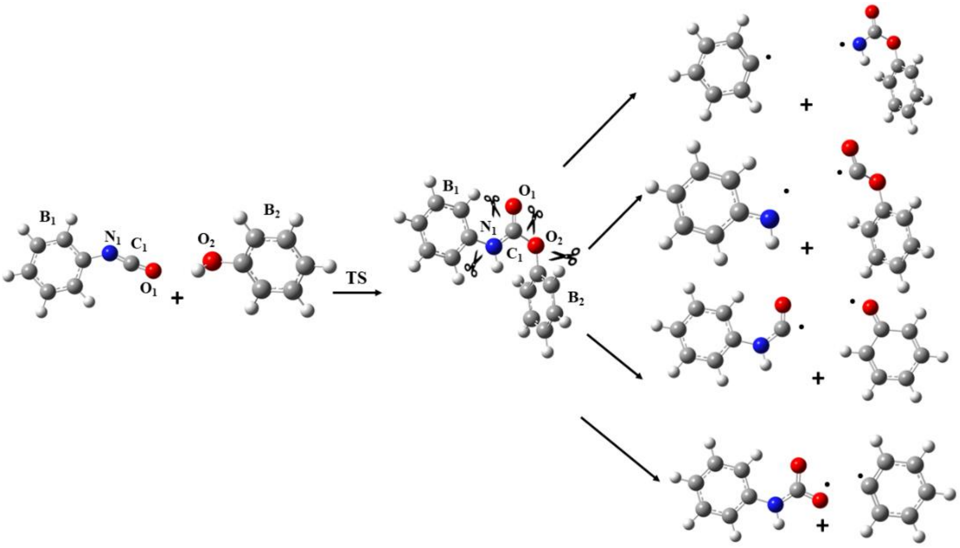


Figure 8
The formation and degradation pathways of phenyl N-phenyl carbamate ($C_6H_5NHCOOC_6H_5$). The species have been computed at the B3LYP/6-31G(d) level of theory in the gas phase and BDEs has been computed. The scissors refer to breaking the bond.

The computed BDE values of the N-C bond for the three models varied from 325.1 to 400.3 kJ/mol *(Table 2)*. The N-C bond with the lowest BDE (325.1 kJ/mol) corresponds to phenyl *N*-phenyl carbamate. In the case of the C-O, the strongest bond was found in carbamic acid

(H_2NCOOH) (410.4 kJ/mol) which was followed by methyl N-methylcarbamate ($H_3CNHCOOCH_3$) (387.2 kJ/mol), and phenyl *N*-phenyl carbamate ($C_6H_5NHCOOC_6H_5$) (269.3 kJ/mol).

Table 2

The computed and measured bond dissociation enthalpy (BDE_{calc} and BDE_{exp}) values of the studied structures: carbamic acid (H_2NCOOH), methyl N-methylcarbamate ($H_3CNHCOOCH_3$), and phenyl N-phenyl carbamate ($C_6H_5NHCOOC_6H_5$). The calculations were carried out at the B3LYP/6-31G(d) level of theory. The corresponding calculated bond length values are also listed.

Bond	**BDE_{calc} (kJ/mol)**	**BDE_{exp} (kJ/mol)** [14]	**Bond Length (Å)**
carbamic acid *(HNHCOOH)*			
H_1-N_1	423.1	343.9	1.012
-N_1-C_1-	388.9	–	1.390
-C_1-O_1-	410.4	–	1.364
-O_2 -H_2	380.9	380.3	0.971
methyl *N*-methylcarbamate *($H_3CNHCOOCH_3$)*			
-C_2-N_1-	384.6	-	1.448
-N_1-C_1-	400.3	343.9	1.361
-C_1-O_2-	387.2	-	1.364
-O_2-C_3-	384.6	380.3	1.431
phenyl *N*-phenyl carbamate *($C_6H_5NHCOOC_6H_5$)*			
-B_1-N_1-	442.5	420.9	1.414
-N_1-C_1-	325.1	–	1.370
-C_1-O_2-	269.3	316.7	1.385
O_2 -B_2	366.3	–	1.390

The results indicate that the longer the bond length is, the smaller the bond dissociation enthalpy is. By comparing the BDE values for all structures, it was found that the lower values of the BDEs were in the case of phenyl *N*-phenyl carbamate in C_1-O_2 (1.385 Å, BDE = 269.3 kJ/mol). The lower the BDE values are, the higher ability to break the bond and the degradation is more probable. By comparing the calculated values with the experimental BDEs, it was found that in some cases there was an excellent agreement between the calculated and measured values such as in the case of carbamic acid, BDE_{exp} for O_2-H_2 was 380.3 kJ/mol which is largely similar to calculated value 380.9 kJ/mol. However, there were bonds where significant deviations were found between the computed and experimentally measured BDEs, such as in the case of phenyl *N*-phenyl carbamate the BDE_{exp} for C_1-O_2 was 316.7 kJ/mol which differed by 47.4 kJ/mol compared to the calculated value. Based on the differences between calculated and experimental values the level of theory has to be changed to finetune the results and reproduce the experimentally measured data. For this purpose, composite methods (e.g. G3MP2B3) can be applied to achieve results that are closer to the experimental values.

CONCLUSION

In terms of synthesis and applications, polyurethanes (PUs) are a versatile class of polymers. They are useful for a wide range of applications due to their exceptional properties. The possible formation and degradation mechanisms of three model systems, carbamic acid, methyl *N*-methylcarbamate, and phenyl *N*-phenyl carbamate were studied and compared. The corresponding potential energy curves and bond dissociation enthalpies (BDEs) were calculated by using the B3LYP/6-31G(d) level of theory in the gas phase. The forming C-O bond in the TS in the case phenyl *N*-phenyl carbamate is 1.838 Å, whereas the N-H is 1.287 Å. The highest relative Gibbs energy along the reaction was found in the case of carbamic acid (167.1 kJ/mol) and it is belonging to the corresponding TS. The results of the degradation showed that the weakest bonds were located in the phenyl *N*-phenyl carbamate, the C_1-O_2 with a BDE of 269.3 kJ/mol, while the BDE for the N_1-C_1 is 325.1 kJ/mol. Experimentally measured BDE values were used to validate the calculations, and although the results were good in some cases, the deviation was significant in others. Therefore, additional calculations are planned in the future to finetune the results.

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