THEORETICAL INVESTIGATION OF THE ROLE OF CLAY EDGES IN PREBIOTIC PEPTIDE BOND FORMATION

II. Structures and Thermodynamics of the Activated Complex Species

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Abstract. Amino acid activation by anhydride formation in model tetrahedral silicate and aluminate sites in clays and neutral phosphates have been studied by semi-empirical molecular orbital calculations. The results have been compared to previous ab initio studies on the reactant species and were found to be in good agreement. The geometries of all species were totally optimized and heats of formation obtained. Relative heats of formation of the anhydrides indicate the extent of anhydride formation to be Al > Si > P which is the same order as the stability of hydrolysis. The relative efficacy of the anhydrides in promoting peptide bond formation has been evaluated using both thermodynamic and chemical reactivity criteria. Heats of reaction for model reactions were calculated from calculated enthalpies of formation of the products and reactants. The electrophilicity of the carbonyl carbon and the nucleophilicity of the oxygen were specifically used as indicators of chemical reactivity towards dipeptide formation by the activated amino acids. Our results indicate that if the reaction mechanism is dominated by the nucleophilic character of the oxygen, tetrahedral Al sites should be more active than Si, and if the electrophilic character dominates, the order would be reversed.

1. Introduction

The condensation of amino acids to form polypeptides in the early stages of earth’s history has been a subject of considerable interest (Bernal, 1951; Paecht-Horowitz et al., 1970; Theng, 1974; Cairns-Smith, 1975; Otroschenko and Vasilyeva, 1977; Lahav et al., 1978; Friebele et al., 1980; Laszlo, 1987). The question of how dilute solutions of relatively simple molecules could form the more complex biomolecules found in living organisms is of utmost importance. One plausible mechanism for this condensation invokes the role of a catalyst which binds the simpler molecules and activates them for reaction with other molecules also bound by the supporting surface. This proposed hypothesis has the attractive features of explaining the buildup of concentration for large scale synthesis and of offering a plausible route for the activation of otherwise stable molecules to polymer formation.

The formation of biopolymers from biomonomers through various mechanisms involving clays has been studied by a number of investigators. (Lahav and Chang, 1976; Lahav et al., 1978; Lahav and White, 1980; Lawless and Levi, 1979; Lawless and Edelson, 1980; White and Erickson, 1980; Jewett and Lawless, 1982; White et
Clays are especially attractive as a supporting catalyst in the prebiotic synthesis of biopolymers because of their general abundance, large surface area, and catalytic properties. In one approach, preactivated amino acyl adenylates are added to clay slurries (Paecht-Horowitz et al., 1970; Paecht-Horowitz, 1973). In a second approach, in situ activation of biomonomers by complex formation with metal ions in the interlamellar regions of ion-exchanged clays has been investigated both experimentally (Lawless and Levi, 1979; Lawless and Edelson, 1980) and theoretically (Liebmann et al., 1982; Gupta et al., 1983).

In a third approach (Lahav and Chang, 1976; Lahav et al., 1978; Lahav and White, 1980; White and Erickson, 1980; Jewett and Lawless, 1982; White et al., 1984), activation of amino acids by formation of an anhydride with either silicon or aluminum sites on the surfaces of clays is proposed as a key step in formation of oligopeptides. In this approach, alternate wetting and drying conditions, such as those found in tide pools, are envisioned. The anhydrides formed serve as activated centers for condensation with free amino acids to form peptide bonds during the drying cycle. In order to further verify and elucidate key features of this proposed model, we report here theoretical studies of: (1) the thermodynamics of activated complex formation by tetrahedral silicates, aluminates, and phosphates and their susceptibility to hydrolysis, and (2) the properties of these activated complexes that could be reliable indicators of the extent of activation to peptide bond formation. To this end, we have investigated the model activation reaction:

$$Z-\text{CH}_2-\text{C}-\text{OH} + \text{XO}_4\text{H}^{n+} \rightarrow Z-\text{CH}_2-\text{C}-\text{O}-\text{XO}_3\text{H}^n + \text{H}_2\text{O}$$  \hspace{1cm} (1)

where $Z = \text{H}$ and $\text{NH}_2$ for acetic acid and glycine respectively. Since it is believed that the reactions actually occur at the broken edges, we have chosen $X$ to be $\text{Si}$ and $\text{Al}$ in the forms $\text{Si(OH)}_4$ and $\text{Al(OH)}_4^-$ to model the clays. Also, since it is known that phosphates are amino acid activators in the biochemistry of contemporary living organisms, we have included $\text{H}_3\text{PO}_4$ in our model study for comparison.

In a previous publication (Luke et al., 1984), hereupon referred to as Paper I, the structures of the reactants $\text{CH}_3\text{COOH}$, $\text{NH}_2\text{CH}_2\text{COOH}$, $\text{H}_3\text{PO}_4$, $\text{Si(OH)}_4$, and $\text{Al(OH)}_4^-$ were determined by ab initio quantum chemical techniques in the first step to model the reaction given above. We report here the characterization of the structure of the resulting activated complexes and the thermodynamics of the reaction leading to its formation. In addition we have calculated properties of the activated complexes which should serve as reliable indicators of the relative activation of the complexes to form longer peptides. Among these are the heats of reaction of model peptide bond formation where $\text{NH}_3$ acts analogously to an incoming amino acid:

$$Z-\text{CH}_2-\text{C}-\text{O}-\text{XO}_3\text{H}^n + \text{NH}_3 \rightarrow Z-\text{CH}_2-\text{C}-\text{NH}_2 + \text{HOXO}_3\text{H}^n$$  \hspace{1cm} (2)