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**Centrosymmetric imidazolium hydrogen squarate structure:
Catalytic properties, chemical reactivity and electronic structure**

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Abstract

The catalytic performance, chemical reactivity and electronic structure of the centrosymmetric ion pair imidazolium hydrogen squarate ($[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$) were investigated experimentally and theoretically in this paper for the first time. This comprehensive evaluation was carried out using Hammett acidity (H_0) measurements, molecular electrostatic potential (MEP) analysis, frontier molecular orbital (FMO) theory, Fukui function and natural population analysis (NPA). Density functional theory (DFT) calculations were performed at the B3LYP/6-311++G(2d,2p) level of theory. The catalytic activity of $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ was assessed in the butyl acetate synthesis. The reaction kinetics, thermodynamic parameters, as well as the effects of reaction temperature (60-80°C) and catalyst content (5-12 wt.%) were methodically inspected. Intrinsic reaction coordinate (IRC) calculations were made and a catalytic cycle for butyl acetate synthesis was proposed. The nucleophilic and electrophilic reactivity of $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ is associated with the cation and anion, respectively. The positively charged site within the $[\text{C}_3\text{H}_5\text{N}_2]^+$ was denoted the compound's Brønsted acidity ($H_0 = 1.909$). Moieties in the hydrogen squarate anion were found to govern the catalytic performance of the ion pair $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ in butyl acetate synthesis. The reaction proceeded through the formation of an active complex, as confirmed by the IRC calculations.

Keywords: Imidazolium hydrogen squarate; Chemical reactivity; Electronic structure; DFT calculations; Catalytic properties; Reaction kinetics

1. Introduction

Ionic liquids (ILs), which consist entirely of molecular ions, have gained significant attention in recent years due to their unique physicochemical properties. These include a broad liquid-phase temperature range, high electrochemical stability, negligible vapor pressure and their possible use as environmentally friendly solvents [1-3]. Owing to these characteristics, the imidazolium-based ILs have emerged as promising materials for a wide range of applications, including thermal energy storage [4, 5], electrochemical technologies [6, 7], lubrication systems [8, 9], fuel cells [10, 11], biomedical technologies [12, 13]. For example, Li and co-workers [5] investigated the energy storage capacity (ESC) of the imidazolium ion pairs $[C_4C_1Im]^+[C(C\equiv N)_3]^-$ and $[C_4C_1Im]^+[SC\equiv N]^-$. The authors demonstrated that the $[C_4C_1Im]^+[SC\equiv N]^-$ ionic liquid exhibited superior ESC performance, which was attributed to the smaller size of the thiocyanate anion. In another study, the incorporation of $[C_1(C_4Si-OCH_3)Im]^+[Cl]^-$ into tetramethylene glycol was found to enhance friction behavior in steel-steel contacts [9]. Furthermore, several imidazolium ionic liquids, including $[(CH_3)_2Im]^+[Cl]^-$, $[(C_6H_5SO_3H)Im]^+[NO_3]^-$, and $[C_2C_1Im]^+[BF_4]^-$, were examined for their interactions with C_2N surfaces to gain deeper insights into electrode-electrolyte interactions in super-capacitor systems [11]. Among these compounds, $[(CH_3)_2Im]^+[Cl]^-$ was identified as the most promising candidate due to its favorable interfacial properties.

In addition to the aforementioned applications, imidazolium-based ILs have been extensively investigated as catalytic systems for a wide range of chemical reactions [14-20]. Friedel-Crafts alkylation reaction for synthesis of 2,5-dimethyldiphenylmethane using $[FeCl_4]^-$ anion-based imidazolium ionic liquids ($[C_6H_5Im]^+[FeCl_4]^-$, $[C_6H_4CH_3Im]^+[FeCl_4]^-$, $[C_6H_4OCH_3Im]^+[FeCl_4]^-$ and $[C_6H_4NO_2Im]^+[FeCl_4]^-$) as catalysts was investigated in a paper of Yang et al. [15]. The authors reported that the $[C_6H_4OCH_3Im]^+[FeCl_4]^-$ sample exhibited the highest selectivity and reactant conversion under the investigated reaction conditions. Dicationic ionic liquids ($[Pyr-C_2-Im(C_1C_6)]^+[Cl]^-$, $[Pyr-C_6-Im(C_1C_6)]^+[Cl]^-$ and $[Pyr-C_{10}-Im(C_1C_6)]^+[Cl]^-$), containing pyridinium and imidazolium moieties, were explored as catalytic systems for the synthesis of benzyl butyrate [17]. It was stated that the optimal spacing between the two aromatic rings in the $[Pyr-C_6-Im(C_1C_6)]^+[Cl]^-$ ionic liquid promotes the formation of a highly acidic hydrogen atom between the nitrogen centers of the imidazolium moiety, which contributes to its enhanced catalytic activity. DBU-based imidazolium ionic liquids ($[DBU-H]^+[Im]^-$, $[DBU-H]^+[1-C_1Im]^-$, and $[DBU-H]^+[2-C_1Im]^-$) were investigated as basic catalysts for the methanolysis of flaxseed oil [19]. Among the studied

ion pairs, $[\text{DBU-H}]^+[\text{2-C}_1\text{Im}]^-$ demonstrated the highest catalytic efficiency, which was attributed not solely to the basicity of the system but primarily to the influence of the anion structure.

It is well known that the catalytic performance of a compound depends on its chemical reactivity and electronic structure [21-25]. Using QM/MM Monte Carlo simulations, Allen and colleagues [22] demonstrated that the presence of $[\text{C}_4\text{C}_1\text{Im}]^+[\text{BF}_4]^-$ and $[\text{C}_4\text{C}_1\text{Im}]^+[\text{PF}_6]^-$ enhanced the $\text{S}_\text{N}\text{Ar}$ reaction between cyclic secondary amines and nitrothiophenes. This improvement was attributed to the increased nucleophilicity of the cyclic amines within the IL environment, as well as favorable π - π interactions between the $[\text{C}_4\text{C}_1\text{Im}]^+$ moieties and the aromatic rings. In another paper, the catalytic performance of the $[\text{C}_8\text{C}_1\text{Im}]^+[\text{Cl}]^-/\text{ZnCl}_2$ system for the conversion of $\text{CO}(\text{NH}_2)_2$ into cyclic carbonates was demonstrated [24]. It was shown that the $[\text{C}_8\text{C}_1\text{Im}]^+$ cation impacts the formation of $[\text{Zn}_2\text{Cl}_5]^-$ fragments, which are responsible for the acidity strength of the catalytic system.

Inspired by the published literature data for imidazolium-based ion pairs, the centrosymmetric compound imidazolium hydrogen squarate ($[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$) was prepared and studied in this paper with respect to its catalytic performance, chemical reactivity and electronic structure. Although the centrosymmetric form of $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ was first defined by Karle et al. [26], only its crystal structure was described. The centrosymmetric form of $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ was investigated by Harsha and Das [27] as well, who evaluated the thermosalt behavior of the compound. A detailed review of the literature revealed that a non-centrosymmetric form of $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ also exists [28]. However, only limited spectroscopic and nonlinear optical studies have been conducted for this form. It is worth noted that catalytic performance, chemical reactivity and electronic structure of the centrosymmetric and/or non-centrosymmetric form of the imidazolium hydrogen squarate ion pair have not been indicated in the literature so far. Consequently, this paper explores the catalytic activity, chemical reactivity and electronic structure of the centrosymmetric $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ by means of experimental (Hammett acidity) and theoretical (molecular electrostatic potential surface, global and local reactivity descriptors, net atomic charges) methods. The catalytic performance of $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ was investigated in the synthesis of butyl acetate. The reaction kinetics, thermodynamic parameters and the effects of reaction temperature and catalyst loading were systematically examined. In addition, a catalytic cycle for butyl acetate synthesis mediated by the $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ catalyst was proposed. The findings reached in this study, together with the observed reaction behavior, provide valuable insights into the catalytic performance of organic salts and may serve as a useful reference for future investigations in this field.

2. Experimental details

2.1. Preparation of the centrosymmetric ion pair $[C_3H_5N_2]^+[C_4O_4H]^-$

The title compound was produced from equimolar quantities of imidazole ($C_3H_4N_2$) and squaric acid ($H_2C_4O_4$) at room temperature (Scheme 1). Upon accomplishment of the reaction, the solvent was removed using a rotary evaporator. The resulting solid mass (Fig. S1) was then dried at 70°C and 0.09 MPa. Single-crystal X-ray diffraction measurements (CIF file and checkCIF/PLATON report added in the Supporting Information, CCDC 2532605) discovered that the crystallographic parameters of the prepared ion pair were reliable with those previously described [26]. These data established the positive synthesis of the centrosymmetric form of the imidazolium hydrogen squarate ion pair.

2.2. UV–Vis determining the sample acidity

The degree of acidity of $[C_3H_5N_2]^+[C_4O_4H]^-$ was evaluated on an Evolution 300 UV–Vis instrument, using $C_6H_6N_2O_2$ indicator [29]. The Hammett acidity function (H_0) was estimated from the changes in absorbance observed after the addition of imidazolium hydrogen squarate, Eq. (1). Hence, the sample acidity can be established through the indicator absorbance variations.

$$H_0 = pK(I)_{aq} + \log \left(\frac{[I]_s}{[IH^+]_s} \right) \quad (1)$$

The parameter $pK(I)_{aq}$ (0.99) denotes the pK_A value of *p*-nitroaniline ($C_6H_6N_2O_2$) in water. The concentrations of the protonated and non-protonated forms of $C_6H_6N_2O_2$ are represented by $[IH^+]_s$ and $[I]_s$, respectively. The $[I]_s/[IH^+]_s$ ratio is determined from the absorption profile.

2.3. Batch esterification and chemical kinetics

The ester synthesis was performed consuming equimolar quantities of acetic acid (CH_3COOH) and butanol ($CH_3(CH_2)_2CH_2OH$), Scheme 2. The catalyst was employed at changing contents (5–12 wt.% qualified to the CH_3COOH amount) and the reaction was conducted at temperatures within 60–80°C.

The reaction rate constant for catalyzed esterification process was valued by a non-linear least squares method, Eq. (2).

$$\text{SRS} = \sum_{\text{samples}} (x_{\text{measured}} - x_{\text{calculated}})^2 \quad (2)$$

The SRS signifies the minimized difference between the experimentally determined and theoretically calculated ester yields (x).

3. Theoretical section

3.1. Molecular optimization

Molecular optimization (Fig. S2) was carried out by means of Gaussian 16 software package [30] at B3LYP/6-311++G(2d,2p) level of theory [31]. The molecular visualization was achieved with Gauss View [32]. The optimized were exposed to vibrational frequency calculations at the same DFT level to validate that the geometries agreed to true minima on the potential energy surface. The absence of imaginary frequencies in the designed vibrational spectra supported that the optimized structures represent stable minimum-energy configurations. The calculations were performed in a condensed matter (water).

3.2. Frontier molecular orbital (FMO) analysis

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are vital perceptions in quantum chemistry, providing valuable understandings into molecular stability and reactivity [33]. Based on the FMO theory, a smaller energy gap ($\Delta E_{\text{LUMO-HOMO}}$) between the HOMO and LUMO corresponds to enhanced chemical reactivity. In general, the HOMO functions as an electron donor, whereas the LUMO acts as an electron acceptor. The HOMO and LUMO energies are used to calculate global quantum chemical descriptors –hardness (η), softness (σ), electronegativity (χ), chemical potential (μ) and electrophilicity index (ω).

3.3. Molecular electrostatic potential (MEP) surface

The molecular reactivity of the title compound was examined via MEP surface. MEP maps enable the identification of molecular areas that are most prone to electrophilic or nucleophilic interactions. Furthermore, MEP surface offers valuable information on the distribution and orientation of possible connections, contributing to a better understanding of reaction mechanisms and the identification of favored reactive sites [34].

4. Results

4.1. Electronic structure

The electronic structure of the centrosymmetric form of the organic compound imidazolium hydrogen squarate (characterized by its MEP surface) is shown in Fig. 1. The corresponding net atomic charges are listed in Table 1. To facilitate the interpretation of the MEP surface of $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$, the following color scheme is used: (i) dark red represents regions of high electron density, (ii) yellow indicates areas of weak negative electrostatic potential, (iii) green corresponds to electrostatic potential close to zero, (iv) light blue denotes regions of slight positive electrostatic potential, and (v) dark blue identifies the most positively charged regions of the compound.

The data presented in Table 1 show that oxygen atom O^4 (-0.7384) carries the highest negative charge in the ion pair $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$, followed by O^1 (-0.6941), O^2 (-0.6602) and O^5 (-0.6524). A pronounced negative electrostatic potential is also associated with the nitrogen atoms in the imidazolium ring, namely N^{10} (-0.4982) and N^{11} (-0.4826). Conversely, the highest positive electrostatic potential is localized on the hydrogen atom H^3 ($+0.5062$) in the hydrogen squarate anion, followed by hydrogen atoms H^{18} ($+0.4677$) and H^{19} ($+0.4527$) of the imidazolium cation. In addition to these hydrogen atoms, significant positive electrostatic potential (net atomic charges ranging from $+0.3323$ to $+0.4086$) is observed for carbon atoms (C^7 , C^8 and C^9) in the $[\text{C}_4\text{O}_4\text{H}]^-$ fragment.

4.2. Chemical reactivity

The chemical reactivity of the investigated ion pair (including its electrophilic and nucleophilic behavior) was evaluated using FMO theory, specifically through the analysis of the HOMO and

LUMO energies and the corresponding global reactivity descriptors (Fig. 2). In addition, the Fukui functions (local reactivity descriptors) were determined as well, Table 2.

FMO calculations revealed that the HOMO orbital is completely delocalized on the hydrogen squarate anion, while the LUMO orbital fully denotes the imidazolium cation. Considering the energies of HOMO (−6.127 eV) and LUMO (−1.101 eV), a value of 5.026 eV was calculated for the magnitude $\Delta E_{\text{LUMO-HOMO}}$.

Based on the HOMO–LUMO energy gap, the global reactivity descriptors were calculated. The chemical hardness ($\eta = \frac{\Delta E}{2}$) was found to be 2.513 eV, while the corresponding chemical softness ($\sigma = \frac{1}{\eta}$) was 0.398 eV, indicating that the compound is highly polarizable and chemically reactive. This interpretation is consistent with the MEP surface, which exposes the presence of negatively and positively charged areas in $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$. The electronegativity (χ), calculated according to $\chi = -\frac{(E_{\text{HOMO}}+E_{\text{LUMO}})}{2}$, was determined to be 3.614 eV, indicating a strong tendency of the compound to attract electrons. Consequently, the chemical potential (μ), abbreviated as the opposite of the electronegativity, is −3.614 eV. Additionally, the electrophilicity index (ω), which measures the stabilization energy associated with electron transfer between an electron donor and an electron acceptor, was calculated using $\omega = \frac{\mu^2}{2\eta}$ and found to be 2.599 eV. The valued global reactivity descriptors confirm the high chemical reactivity and pronounced electrophilic performance of the centrosymmetric ion pair $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$. The chemical reactivity of the $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ compound was further investigated using the local reactivity descriptors $\Delta f_k(r)$, $\Delta\sigma_k$ and $\Delta\omega_k$ (Table 2). A positive value of the dual descriptor $\Delta f_k(r)$ (as well as the corresponding descriptors $\Delta\sigma_k$ and $\Delta\omega_k$), indicates a negatively charged centers that is disposed to electrophilic attack [35]. On the other hand, negative values identify positively charged centers, prone to nucleophilic attack. The results exposed that the oxygen atom O¹ in the $[\text{C}_4\text{O}_4\text{H}]^-$ anion exhibits the highest $\Delta f_k(r)$ value (+0.9669), identifying it as the most favorable site for electrophilic attack. This finding is supported by the corresponding $\Delta\sigma_k$ and (+0.3847) and $\Delta\omega_k$ (+2.5126) values, which are also the highest among the investigated atomic sites. Contrary, a hydrogen atom (H¹⁹) in the $[\text{C}_3\text{H}_5\text{N}_2]^+$ cation displays the lowest values of $\Delta f_k(r)$ (−0.5056), $\Delta\sigma_k$ (−0.2012) and $\Delta\omega_k$ (−1.3140) indicating that it is the most favorable site for nucleophilic attack.

4.3. Acidity extent

Hammett acidity measurements on the centrosymmetric $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ compound are illustrated in Fig. 3. The reference material (*p*-nitroaniline) displayed absorbance of 1.079. Upon the addition of $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$, the absorbance diminished to 0.956, corresponding to a H_0 value of 1.909. These findings are an indication for the acidic nature of the title compound.

4.4. Catalysis and reaction kinetics

This subsection focused on the catalytic performance of the centrosymmetric form of the ion pair imidazolium hydrogen squarate in the esterification of acetic acid with butyl alcohol. The investigated aspects include its catalytic activity, the effects of reaction temperature and catalyst loading. In addition, all investigated process variables were supported by chemical kinetics analyses, including the estimation of the reaction rate constants. Moreover, the activation energy (E_A) and pre-exponential factor (A) were valued as well.

4.4.1. Catalytic activity

The catalytic activity of $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ for butyl acetate synthesis is illustrated in Fig. 4. The data for the blank (non-catalyzed) reaction were added for comparison. The results showed that, in the absence of a catalyst (blank reaction), the butyl acetate yield reached only 13.9% after 6 h of reaction. This finding indicates that the esterification of acetic acid proceeds only to a limited extent without a catalyst. In contrast, the addition of $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ to the reaction mixture significantly enhanced the ester yield to 36.2% under the same reaction conditions. Favored butyl acetate synthesis in the presence of the $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ catalyst was confirmed by the calculated forward reaction rate constants (k_1): 9.33×10^{-3} l/mol $\times$ h (blank reaction) and 26.89×10^{-3} l/mol $\times$ h (catalyzed process), Table 3. Regarding the catalytic activity of $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$, a good agreement between the experimental and calculated butyl acetate yields was established. Thus, Eq. (2) was considered sufficiently reliable for studying the kinetics of butyl acetate production by means of $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ sample. A comparison of the catalytic activity of the centrosymmetric form of the imidazolium hydrogen squarate compound with that of other imidazolium-based catalytic systems published in the literature for butyl acetate production [36-39] is shown in Table 4. It is seen that the catalytic behavior of the $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ compound (abbreviated as $[\text{Im}]^+[\text{C}_4\text{O}_4\text{H}]^-$) is similar to $[\text{C}_1\text{Im}]^+$ cation-based catalysts such as $[\text{C}_1\text{Im}]^+[\text{BF}_4]^-$ [36] and $[\text{C}_1\text{Im}]^+[\text{HSO}_4]^-$ [39].

4.4.2. Effect of the reaction temperature

Catalytic performance of the title compound as a function of the reaction temperature is represented in Fig. 5. A correlation between experimental and calculated ester yield is added as well. The results showed that the title reaction produced a butyl acetate yield of 21.5% at 60°C (Table 3). Increasing the reaction temperature up to 70 and 80°C favored the esterification process, resulting in higher butyl acetate yields of 29.9 and 36.2%, respectively. These findings implied that the reaction of butyl acetate synthesis is an endothermic process. The latter is in accordance with the estimated k_1 values as a function of the reaction temperature: 14.56×10^{-3} l/mol $\times$ h (60°C), 21.40×10^{-3} l/mol $\times$ h (70°C) and 26.89×10^{-3} l/mol $\times$ h (80°C), Table 3. Similar to the data described in the previous subsection, a strong linear correlation between measured and calculated ester yields was observed.

4.4.3. Influence of the catalyst loading

Effect of the catalyst loading on the butyl acetate yield and a correlation between measured and calculated butyl acetate yield are demonstrated in Fig. 6. The blank reaction is added for comparison. The results revealed that the addition of a small amount (5 wt.%) of the $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ catalyst significantly increased the butyl acetate yield from 13.9% in the non-catalyzed reaction to 25.5%. A similar trend was observed when 7 and 10 wt.% of $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ were used for the esterification reaction, resulting in ester yields of 29.9% and 36.2%, respectively. It was found that increasing the $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ loading up to 12 wt.% resulted in an ester yield of 37.9%, which was only marginally higher than the 36.2% yield obtained with 10 wt.% catalyst. Therefore, 10 wt.% of $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ was identified as the optimal catalyst loading for the esterification of acetic acid with butyl alcohol, as further increasing the catalyst amount provided no significant improvement in ester yield. The improved butyl acetate yield with rising the catalyst content was confirmed by means of the calculated forward and backward (k_2) reaction rate constants (Fig. 7). As a result, the following relations were produced: $y_{\text{forward}} = 1.6729x + 9.3323$ ($R^2 = 0.9934$) and $y_{\text{backward}} = 0.2296x + 1.2768$ ($R^2 = 0.9869$). When the x-axis equals zero, the generated intercepts (9.3323 and 1.2768) correspond to k_1 and k_2 for the blank reaction. These were established to be in close agreement with the experimentally determined k_1 (9.33×10^{-3} l/mol $\times$ h) and k_2 (1.27×10^{-3} l/mol $\times$ h), Table 3.

4.4.4. Activation energy and pre-exponential factor

Once the k_1 and k_2 values at different reaction temperatures were determined, important kinetic parameters, including the activation energy and the pre-exponential factor, were calculated using the Arrhenius law, Eq. (3). A graphical representation of Eq. (3) is illustrated in Fig. 8.

$$\ln k = \ln A - \frac{E_A}{RT} \quad (3)$$

The results showed that the activation energy (E_{A_f}) and pre-exponential factor (A_f) for the forward reaction were 30.0 kJ/mol and 767.1 l/mol $\times$ h, respectively. In contrast, lower values were obtained for the backward reaction, with an activation energy (E_{A_b}) of 13.8 kJ/mol and a pre-exponential factor (A_b) of 0.41 l/mol $\times$ h.

4.5. Thermodynamics

The thermodynamic behavior of the esterification of acetic acid with butyl alcohol in the presence of the $[C_3H_5N_2]^+[C_4O_4H]^-$ catalyst was investigated by determining the equilibrium constant (K_C) as well as the standard reaction enthalpy (ΔH_r°), standard reaction entropy (ΔS_r°) and standard Gibbs free energy (ΔG_r°). Furthermore, the activation thermodynamic parameters for both the forward and backward reactions were evaluated, including the enthalpy of activation ($\Delta H_f^\ddagger$ and $\Delta H_b^\ddagger$), entropy of activation ($\Delta S_f^\ddagger$ and $\Delta S_b^\ddagger$) and Gibbs free energy of activation ($\Delta G_f^\ddagger$ and $\Delta G_b^\ddagger$).

The equilibrium constant was calculated using Eq. (4), where X_{A_e} symbolizes the substrate conversion at equilibrium for each reaction temperature.

$$K_C = \frac{k_1}{k_2} = \frac{X_{A_e}^2}{(1 - X_{A_e})^2} \quad (4)$$

Within the investigated temperature range (60–80°C), the equilibrium constant (K_C) increased from 5.231 at 60°C to 6.208 at 70°C and 7.295 at 80°C, Table 3. The observed increase in K_C with increasing reaction temperature supports the statement that the esterification of acetic acid with butyl alcohol is an endothermic reaction. The ΔH_r° (16.2 kJ/mol) and ΔS_r° (0.624 kJ/mol $\times$ K) for the esterification of acetic acid with butyl alcohol catalyzed by the ion pair

$[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ were determined using the graphical representation of the Van't Hoff equation (Eq. (5)), as shown in Fig. S3. The positive ΔH_r° is another indication that the elevated temperatures promote the reaction of butyl acetate synthesis.

$$\ln K_C = \left(-\frac{\Delta H_r^\circ}{RT} \right) + \left(\frac{\Delta S_r^\circ}{R} \right) \quad (5)$$

where, R exposes the universal gas constant ($8.314 \text{ J/mol} \times \text{K}$).

Based on the determined values of ΔH_r° and ΔS_r° , the standard Gibbs free energy over the temperature range of $60\text{--}80^\circ\text{C}$ was estimated in accordance with the equation $\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ$. In details, the following ΔG_r° values were obtained: -4.567 kJ/mol (60°C), -5.191 kJ/mol (70°C) and -5.816 kJ/mol (80°C). The progressively more negative values of ΔG_r° with increasing temperature indicate that the reaction becomes thermodynamically more favorable at higher temperatures, further supporting the endothermic nature of the esterification process. To calculate $\Delta H_f^\ddagger$, $\Delta H_b^\ddagger$, $\Delta S_f^\ddagger$ and $\Delta S_b^\ddagger$, the Eyring equation (Eq. (6)) and its graphical form (Fig. 9) were applied.

$$\ln \left(\frac{k}{T} \right) = \ln \left(\frac{k_B}{h} \right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (6)$$

where, k_B is Boltzmann's constant ($1.38 \times 10^{-23} \text{ J/K}$), h is Planck's constant ($6.63 \times 10^{-34} \text{ J} \times \text{s}$).

Hence, values of 27.2 kJ/mol and $-0.19 \text{ kJ/mol} \times \text{K}$ were calculated as $\Delta H_f^\ddagger$ and $\Delta S_f^\ddagger$, respectively. For comparison, significantly lower $\Delta H_b^\ddagger$ (10.9 kJ/mol) and $\Delta S_b^\ddagger$ ($-0.26 \text{ kJ/mol} \times \text{K}$) were observed for the backward reaction. Considering the relationship $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, the Gibbs free energy of activation for both the forward and backward reactions was readily calculated. $\Delta G_f^\ddagger$ and $\Delta G_b^\ddagger$ are positively valued because, for an endothermic reaction (such as butyl acetate synthesis studied in this work) the formation of products requires an input of energy to break the chemical bonds in the reactants. In addition to the thermodynamic parameters represented above, intrinsic reaction coordinate (IRC) calculations were performed to investigate the formation of the active complex (Fig. 10). As can be seen, the IRC identified the following key stages: (i) interaction between isolated CH_3COOH and $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ species, (ii) formation of an active complex and (iii) generation of protonated acetic acid ($[\text{CH}_3\text{CO}(\text{H})\text{OH}]^+$) together with the deprotonated catalyst ($[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4]^{2-}$).

5. Discussion

The previous section noted that the O⁴ atom carries the highest negative charge (−0.7384) in the ion pair [C₃H₅N₂]⁺[C₄O₄H][−], which would normally suggest that O⁴ should be: (i) located in a region of high electron density (red color) and (ii) responsible for the electrophilic reactivity of the title compound. However, these expectations appear to contradict the molecular electrostatic potential surface (Fig. 2), which indicates that the O⁴ atom is situated in an area with effectively neutralized electrostatic potential. To resolve this apparent inconsistency, the charges of the atoms participating in chemical interactions with O⁴ were examined. In the studied compound, the O⁴ atom is involved in C⁸=O⁴...H¹⁸ interactions. The combined positive charge (+0.8000) of the carbon and hydrogen atoms interacting with O⁴ is substantially greater than the negative charge localized on the oxygen atom (−0.7384). Therefore, the effective compensation of the negative electrostatic potential around O⁴ is consistent with the observed MEP distribution. Nevertheless, an important question remains: which of the two interacting atoms (C⁸ or H¹⁸) contributes more significantly to this compensatory effect? This issue was discussed from two perspectives: (i) the net atomic charges on C⁸ and H¹⁸ and (ii) the nature of the C⁸=O⁴ and O⁴...H¹⁸ interactions. Considering the first factor, namely the net atomic charges, the positive charge on the H¹⁸ atom (+0.4677) is substantially greater than that on the C⁸ atom (+0.3323). Therefore, H¹⁸ appears to be the more likely contributor to the compensation of the negative charge localized on the O⁴ atom. The second factor, however, suggests a different interpretation. The C⁸ atom is covalently bonded to O⁴, whereas the O⁴...H¹⁸ interaction is predominantly electrostatic in nature. Consequently, the compensation of the negative electrostatic potential around the O⁴ atom is not governed by either C⁸ or H¹⁸ alone but rather results from their synergistic contributions. Thus, both the covalent C⁸=O⁴ bond and the electrostatic O⁴...H¹⁸ interaction cooperate to effectively compensate the negative potential localized on the O⁴ atom.

Similar to the O⁴ atom, the second most negatively charged site, O² (−0.6602), is also located in a region of nearly neutral electrostatic potential. This observation can be attributed to the combined influence of the positively charged C⁶ (+0.2225) and H³ (+0.5062) atoms. Because both atoms are directly (covalently) bonded to O², the atom carrying the larger positive charge is expected to make the greater contribution to compensating the negative charge localized on the oxygen atom. In this case, H³ plays the dominant role. Since the combined positive charge (+0.7287) of the C⁶ and H³ atoms exceeds the negative charge on O², and the positive charge on H³ is substantially greater than that on C⁶, the residual positive charge (around +0.0685) is expected to remain localized on the H³ atom. This interpretation is fully consistent with the MEP surface, which shows both C⁶ and O² located in areas of nearly neutral electrostatic potential,

whereas H³ is situated in a light blue region, indicating the presence of a weak residual positive electrostatic potential.

To analyze the third most negatively charged atom (O⁵, -0.6524) in the compound under investigation, the C⁹=O⁵...H¹³ bond was examined. Since the combined positive charge (+0.6640) of the C⁹ and H¹³ atoms is nearly equal to the negative charge localized on O⁵, the C⁹=O⁵...H¹³ fragment would be expected to exhibit the same behavior as the C⁸=O⁴...H¹⁸ moiety, namely, to be located in a region of nearly neutral electrostatic potential. However, the MEP analysis reveals that this statement is fulfilled only for the C⁹ and H¹³ atoms. In contrast, the O⁵ atom is situated in a yellow-colored region, indicating the presence of a pronounced negative electrostatic potential. This behavior can be rationalized by considering the nature of the interactions involving O⁵. Whereas the C⁹=O⁵ bond is covalent, the O⁵...H¹³ interaction is purely electrostatic and is characterized by a relatively long intermolecular distance. Consequently, the influence of H¹³ on the electronic environment of O⁵ is expected to be weak. Therefore, the negative electrostatic potential around O⁵ is governed primarily by the covalent C⁹=O⁵ bond rather than by the O⁵...H¹³ interaction.

Among all oxygen atoms in the [C₃H₅N₂]⁺[C₄O₄H]⁻ compound, O¹ is unique in that it participates only in the covalent C⁷=O¹ bond and does not engage in either intra- or intermolecular O...H electrostatic interactions. Consequently, the compensation of the negative charge localized on O¹ depends exclusively on the positive charge of the covalently bonded C⁷ atom. Because the positive charge on C⁷ (+0.3708) is substantially smaller than the negative charge on O¹ (-0.6941), the latter remains only partially compensated. This interpretation is fully consistent with the molecular electrostatic potential surface, where O¹ is located in a dark red region, indicative of a pronounced negative electrostatic potential. Based on these findings, the O¹ atom was identified as the most nucleophilic site in the imidazolium hydrogen squarate ion pair, i.e., the O¹ atom is the primary center governing the electrophilic reactivity of the title compound.

It was already assumed that the positive charge on the C⁸ atom is completely compensated by the negative charge on the O⁴ atom through the covalent C⁸=O⁴ bond, then a residual positive charge of +0.0616 should remain localized on the H¹⁸ atom. This value corresponds to the difference between the combined positive charge of C⁸ and H¹⁸ (+0.8000) and the negative charge on the O⁴ atom (-0.7384). In other words, the H¹⁸ atom is expected to be surrounded by a light blue region on the MEP surface, corresponding to a relatively weak positive electrostatic potential. However, the MEP surface indicates that the atoms in the C⁸=O⁴...H¹⁸ fragment are located in a region of nearly neutral electrostatic potential, implying that no appreciable positive electrostatic

potential remains localized on the H¹⁸ atom. This observation suggests that the residual positive charge (+0.0616) on H¹⁸ is compensated by the negative charge (−0.4982) localized on the N¹⁰ atom of the imidazolium ring.

Speaking for the N¹⁰ atom, interesting observation was presented – although its negative atomic charge (−0.4982) is substantially greater than the residual positive charge (+0.0616) localized on the H¹⁸ atom, the MEP surface places N¹⁰ in a region of nearly neutral electrostatic potential. This finding suggests that the negative charge on N¹⁰ is effectively compensated by electron density withdrawn effect (C¹⁴–H¹⁵ → N¹⁰) by neighboring positively charged atoms. Since the negative charge localized on the N¹⁰ atom is already partially compensated by the residual positive charge on the H¹⁸ atom, the overall positive electrostatic potential (+0.5295) associated with the C¹⁴–H¹⁵ fragment cannot be completely neutralized. This interpretation is consistent with the MEP surface, which shows the C¹⁴ atom located in a region of nearly neutral electrostatic potential, whereas the H¹⁵ atom remains surrounded by a pale blue region, indicative of a weak residual positive electrostatic potential (around +0.0313).

The above findings further suggest that the negative charge localized on the other nitrogen atom, N¹¹ (−0.4826), in the [C₃H₅N₂]⁺ cation is influenced by both the positive charge on the H¹⁹ atom (+0.4527) and the overall positive potential associated with the C¹⁶–H¹⁷ fragment (+0.2762). Since the positive charges on the C¹⁶, H¹⁷ and H¹⁹ atoms are +0.0317, +0.2445 and +0.4527, respectively, it is evident that the positive potentials on H¹⁷ and H¹⁹ are the principal contributors to the compensation of the negative charge on N¹¹, whereas the contribution of C¹⁶ is negligible. The MEP surface supports this interpretation – both the H¹⁷ and N¹¹ atoms are located in regions of nearly neutral electrostatic potential (green colored area), indicating that the positive charge on H¹⁷ is effectively compensated by the negative potential on N¹¹. In contrast, the H¹⁹ atom is situated in a dark blue region, corresponding to a pronounced positive electrostatic potential. This shows that only a small fraction of the positive charge localized on H¹⁹ is involved in compensating the negative potential on N¹¹, while the majority remains uncompensated. Accordingly, the H¹⁹ atom was recognized as the most electrophilic center in the organic sample [C₃H₅N₂]⁺[C₄O₄H][−], preferred for nucleophilic attack.

The statement that the O¹ and H¹⁹ atoms are the primary sites governing the electrophilic and nucleophilic reactivity, respectively, of the imidazolium hydrogen squarate ion pair is further supported by the calculated local reactivity descriptors ($\Delta f_k(r)$, $\Delta \sigma_k$ and $\Delta \omega_k$, Table 2). As discussed, the O¹ atom exhibits the highest positive values of $\Delta f_k(r)$ (+0.9669), $\Delta \sigma_k$ (+0.3847) and $\Delta \omega_k$ (+2.5126), confirming it as the most favorable site for electrophilic attack. Conversely, the

most negative values of $\Delta f_k(r)$ (-0.5056), $\Delta \sigma_k$ (-0.2012) and $\Delta \omega_k$ (-1.3140) were obtained for the hydrogen atom attached to the N^{10} atom of the imidazolium ring, identifying it as the preferred site for nucleophilic attack. The presence of distinct regions of negative and positive electrostatic potential on the MEP surface is in excellent agreement with the FMO analysis (Fig. 2), which characterizes the title compound as a highly polarizable and chemically reactive system. The pronounced positive electrostatic potential localized on the H^{19} atom reflects the acidity of the ion pair $[C_3H_5N_2]^+[C_4O_4H]^-$, as evidenced by its Hammett acidity function ($H_o = 1.909$, Fig. 3).

To elucidate the role of the $[C_3H_5N_2]^+[C_4O_4H]^-$ compound as a catalyst in the synthesis of butyl acetate (Fig. 4), two aspects were considered: (i) the thermodynamic parameters, particularly the entropy of activation and (ii) the reactive centers of both the catalyst and the primary reactant involved in the esterification process, namely acetic acid. The first aspect is associated with the value of $\Delta S_f^\ddagger = -0.19 \text{ kJ/mol} \times K$ (Fig. 9), which indicates that the esterification of acetic acid with butyl alcohol proceeds via the formation of an active complex involving both the $[C_3H_5N_2]^+[C_4O_4H]^-$ catalyst and CH_3COOH . The second aspect concerns the chemical reactivity of the $[C_3H_5N_2]^+[C_4O_4H]^-$ sample, previously identified through the O^1 and H^{19} atoms, as well as that of acetic acid. In the CH_3COOH molecule, the carbonyl oxygen atom ($O^2=C^1$) and the hydrogen atom of the hydroxyl group (H^4-O^3) are well established as the principal nucleophilic and electrophilic centers, respectively (Fig. S4) [41]. Based on these findings, several possible pathways for the formation of the active complex can be proposed: (i) generation of a single hydrogen bond between the most electrophilic center of the catalyst and the most nucleophilic one of the acetic acid, i.e., $[N^{10}-H^{19}]_{cat} \cdots [O^2=C^1]_{acid}$, (ii) formation of a single hydrogen bond between the most nucleophilic center of the catalyst and the most electrophilic site of the acetic acid, namely $[C^7-O^1]_{cat} \cdots [H^4-O^3]_{acid}$ and (iii) simultaneous catalyst-acetic acid interaction through both hydrogen bonds ($[N^{10}-H^{19}]_{cat} \cdots [O^2=C^1]_{acid}$ and $[C^7-O^1]_{cat} \cdots [H^4-O^3]_{acid}$). IRC calculations (Fig. 10) revealed that the formation of the activated catalyst-acetic acid complex involves two hydrogen bonds, indeed. Furthermore, the carbonyl oxygen atom and the hydroxyl hydrogen atom of CH_3COOH were confirmed to participate directly in these interactions. However, it was found that the H^{19} atom, despite carrying the highest positive charge, does not significantly influence the catalytic behavior of the $[C_3H_5N_2]^+[C_4O_4H]^-$ compound. Instead, the hydrogen atom H^3 of the hydrogen squarate anion plays a key role in the formation of the active complex.

To rationalize why the center (H^{19}) bearing the highest positive charge does not actually influence the catalytic activity of $[C_3H_5N_2]^+[C_4O_4H]^-$, attention was focused on the structure of the active complex. This structure clearly indicates that the formation of an active complex between

the catalyst and acetic acid requires the establishment of two hydrogen bonds. In this context, if the formation of the active complex involved the H¹⁹ atom (through [N¹⁰–H¹⁹]_{cat}...[O²=C¹]_{acid} bond), the “second hydrogen bond” would necessarily have to involve one of the two hydrogen atoms (H¹⁵ or H¹⁷) of the imidazolium ring. Such a scenario appears highly unfavorable, as it would involve hydrogen bonding between chemically similar fragments, namely [C¹⁴–H¹⁵]_{cat}...[H⁴–O³]_{acid} or [C¹⁶–H¹⁷]_{cat}...[H⁴–O³]_{acid}. Interactions of this type are expected to be predominantly repulsive rather than structure-stabilizing in nature. On the other hand, the positive electrostatic potential associated with the hydroxyl hydrogen atom (H³) of the [C₄O₄H][–] anion enables the formation of one of the two required hydrogen bonds ([O²–H³]_{cat} ... [O²=C¹]_{acid}) with the carbonyl oxygen atom (O²) of acetic acid. Similarly, the strongly negative charge localized on the carbonyl oxygen atom (O¹) of the [C₄O₄H][–] anion can interact with the hydroxyl hydrogen atom (H⁴) of CH₃COOH, leading to the formation of the second hydrogen bond in the active complex [C⁷–O¹]_{cat}...[H⁴–O³]_{acid}.

The formation of an active complex due to catalyst-acetic acid interaction can provide a plausible explanation for the significantly higher butyl acetate yield and rate constants obtained in the presence of the [C₃H₅N₂]⁺[C₄O₄H][–] catalyst (36.2%) compared with the non-catalyzed process (13.9%) after 6 h of reaction, Fig. 4 and Table 3. This interpretation is also consistent with the experimentally observed effect of catalyst loading, whereby both the butyl acetate yield and the reaction rate constant increased with increasing concentration of the [C₃H₅N₂]⁺[C₄O₄H][–] catalyst (Figs. 6 and 7; Table 3). In other words, the enhanced esterification rate at higher catalyst loadings can be attributed to the formation of a greater number of active complexes, thereby promoting the conversion of reactants to butyl acetate. The statements above correlate with the factors influencing the blank reaction, namely: (i) pure acetic acid and butanol are relatively stable, neutral species that do not readily generate the reactive intermediates required for ester formation in the absence of a catalyst and (ii) the carbonyl carbon atom of CH₃COOH is insufficiently electrophilic to efficiently undergo nucleophilic attack by butanol [42]. Consequently, without a catalyst, butanol exhibits limited nucleophilic reactivity toward acetic acid, resulting in a very slow esterification process.

To gain further insight into the nature of the active complex, a comparison between the experimentally determined enthalpy of activation ($\Delta H_f^\ddagger = 27.2$ kJ/mol, Fig. 9) and the total energy required for the formation of the active complex as obtained from IRC calculations (28.9 kJ/mol, Fig. 10) was made. As can be seen, there is excellent agreement between the experimental data and the theoretical results, thereby providing additional support for the proposed mechanism of active complex formation.

Baring in mind the data presented in Table 4, the observed catalytic performance of the imidazolium-based samples can be explained by two main factors: (i) the overall acidity of the catalysts and (ii) the nature of the cation and anion. Regarding the first factor, the catalytic activity increases with increasing acidity of the catalyst. For example, the activity follows the order: $[\text{C}_3\text{SO}_3\text{HBnzIm}]^{2+}[\text{HSO}_4]^{2-}$ (0.98) > $[\text{C}_3\text{SO}_3\text{HIm}]^+[\text{HSO}_4]^-$ (1.57) $\approx$ $[\text{C}_3\text{SO}_3\text{HIm}]^+[\text{CH}_3\text{SO}_4]^-$ (1.54) > $[\text{C}_1\text{Im}]^+[\text{HSO}_4]^-$ (1.94) $\approx$ $[\text{Im}]^+[\text{C}_4\text{O}_4\text{H}]^-$ (1.90), where the values in parentheses correspond to the H_0 parameter. However, the observed acidity trend does not correlate with the nature of the cation and anion. Indeed, the pK_A values of the corresponding conjugate acids follow the order: $[\text{CH}_3\text{SO}_4]^-$ (-1.82) < $[\text{HSO}_4]^-$ (+1.96) < $[\text{C}_4\text{O}_4\text{H}]^-$ (+3.4), indicating a decrease in anion basicity. Based solely on these values, $[\text{C}_3\text{SO}_3\text{HIm}]^+[\text{CH}_3\text{SO}_4]^-$ would be expected to exhibit higher catalytic activity than $[\text{C}_3\text{SO}_3\text{HIm}]^+[\text{HSO}_4]^-$, while the $[\text{Im}]^+[\text{C}_4\text{O}_4\text{H}]^-$ sample would not be expected to display catalytic performance comparable to that of $[\text{C}_1\text{Im}]^+[\text{HSO}_4]^-$. These observations suggest that the catalytic activity cannot be explained simply by the intrinsic acidity of the anion, i.e., the nature of the cation and anion as well as the cation-anion interactions affect the catalytic activity.

The kinetics and thermodynamics of the endothermic butyl acetate production reaction catalyzed by the ion pair imidazolium hydrogen squarate were examined by analyzing the relationships among the forward and backward activation energies (E_{A_f} and E_{A_b}), the standard reaction enthalpy (ΔH_r°) and the forward and backward enthalpies of activation ($\Delta H_f^\ddagger$ and $\Delta H_b^\ddagger$) were examined. Specifically, according to the relationship $E_{\text{A}_f} - E_{\text{A}_b} = \Delta H_r^\circ$, the difference between E_{A_f} (30.0 kJ/mol) and E_{A_b} (13.8 kJ/mol) is 16.2 kJ/mol, which is identical to the experimentally determined ΔH_r° . A similar relationship ($\Delta H_f^\ddagger - \Delta H_b^\ddagger = \Delta H_r^\circ$) can be represented for the activation enthalpies as well. In that case, the variance between $\Delta H_f^\ddagger$ (27.2 kJ/mol) and $\Delta H_b^\ddagger$ (10.9 kJ/mol) also equals to the measured ΔH_r° value. These results ($E_{\text{A}_f} - E_{\text{A}_b} = \Delta H_r^\circ = \Delta H_f^\ddagger - \Delta H_b^\ddagger$) indicate that the positive reaction enthalpy contributes to the higher energy barrier of the forward reaction (ester synthesis) relative to the backward reaction (ester hydrolysis).

6. Reaction mechanism

The mechanism of butyl acetate production in the presence of the centrosymmetric ion pair imidazolium hydrogen squarate (Scheme 3) is entirely governed by the electronic, kinetic and thermodynamic factors: namely (i) the O^1 and H^3 atoms in $[\text{C}_4\text{O}_4\text{H}]^-$ and the most reactive sites ($\text{C}=\text{O}$ and $\text{O}-\text{H}$ groups) in CH_3COOH and (ii) catalyst-acetic acid interaction (through the hydrogen

bonds $[O^2-H^3]_{cat} \cdots [O^2=C^1]_{acid}$ and $[C^7-O^1]_{cat} \cdots [H^4-O^3]_{acid}$) for generation of an active complex. The proposed reaction mechanism is initiated by hydrogen bonding between the centrosymmetric $[C_3H_5N_2]^+[C_4O_4H]^-$ catalyst to the main reactant ($[C_3H_5N_2]^+[C_4O_4H]^- \leftrightarrow CH_3COOH$), producing protonated acetic acid, $[CH_3CO(H)OH]^+$, and deprotonated catalyst, $[C_3H_5N_2]^+[C_4O_4]^{2-}$, (STEPS I–II). Subsequently, the O–H moiety of $CH_3(CH)_2CH_2OH$ nucleophilically interacts with $[CH_3CO(H)OH]^+$, leading to the creation of a tetrahedral intermediate (STEP III). An intramolecular proton transfer then converts this species into a second intermediate (STEP IV). Removal of a molecule of H_2O (a by-product of the esterification process) yields a dehydrated intermediate (STEP V). Finally, proton transfer from the dehydrated intermediate to the deprotonated catalyst restores the initial $[C_3H_5N_2]^+[C_4O_4H]^-$ form (STEP VI), followed by the release of butyl acetate as a product (STEP VII).

Conclusions

The centrosymmetric form of the organic compound imidazolium hydrogen squarate ($[C_3H_5N_2]^+[C_4O_4H]^-$) was explored in terms of its catalytic behavior, chemical reactivity and electronic structure. For this purpose, Hammett acidity (H_0), MEP surface, HOMO-LUMO theory, global and local reactivity descriptors, NPA method and IRC calculations were applied. The theoretical background was in the field of DFT-B3LYP/6-311++G(2d,2p) level of theory. The catalytic performance of $[C_3H_5N_2]^+[C_4O_4H]^-$ was evaluated in the reaction of butyl acetate synthesis. MEP surface, FMO theory, Fukui parameters and NPA method established that the oxygen O^1 atom (in $[C_4O_4H]^-$) and the H^{19} atom (in $[C_3H_5N_2]^+$) are the principal electrophilic and nucleophilic reactive sites, respectively, of the title compound. Due to electronic limitations, the O^1 and H^3 (rather than H^{19}) atoms were found to dictate the catalytic behavior the ion pair $[C_3H_5N_2]^+[C_4O_4H]^-$ for butyl acetate production. IRC calculations together with the entropy of activation ($\Delta S_f^\ddagger = -0.19$ kJ/mol $\times$ K) verified that the catalytic process proceeds through the formation of an active complex between the catalyst and acetic acid via $[O^2-H^3]_{cat} \cdots [O^2=C^1]_{acid}$ and $[C^7-O^1]_{cat} \cdots [H^4-O^3]_{acid}$ hydrogen bonds. The formation of this active complex provides a mechanistic explanation for the enhanced esterification efficiency observed with increasing catalyst loading. A good agreement between the experimentally determined enthalpy of activation ($\Delta H_f^\ddagger = 27.2$ kJ/mol) and the total energy (28.9 kJ/mol) required for the formation of the active complex was observed. Furthermore, the relationships $E_{A_f} - E_{A_b} = \Delta H_r^\circ$ and $= \Delta H_f^\ddagger - \Delta H_b^\ddagger = \Delta H_r^\circ$ verified that the positive reaction enthalpy (16.2 kJ/mol) increases the energy barrier of the forward esterification reaction with

respect to the reverse hydrolysis process, consistent with the experimentally determined kinetic and thermodynamic functions.

List of abbreviations

H₀ – Hammett acidity function

MEP – molecular electrostatic potential

FMO – frontiers molecular orbitals

NPA – natural population analysis

DFT – density functional theory

IRC – intrinsic reaction coordinate

ESC – energy storage capacity

C₃H₄N₂ – imidazole

H₂C₄O₄ – squaric acid

C₆H₆N₂O₂ – *p*-nitroaniline

CH₃COOH – acetic acid

CH₃(CH₂)₂CH₂OH – butanol

Declarations section

A data availability statement

The datasets generated and analyzed during the current study are available from the corresponding author.

Author contributions

Ivaylo Tankov – Writing - original draft preparation, Conceptualization, Methodology, Formal analysis and investigation, Funding acquisition

Rumyana Yankova – Formal analysis

Zilya Mustafa – Formal analysis

Compliance with Ethical Standards

This declaration is “not applicable”.

Competing Interests

The authors declare that they have no known competing interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figure Legend section

Figure 1. Molecular electrostatic potential surface for the ion pair $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$

Figure 2. Frontier molecular orbitals for the centrosymmetric ion pair $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$.

Figure 3. Hammett acidity measurements for the ion pair $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$.

Figure 4. Catalytic performance of $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ for butyl acetate synthesis (left). Correlation between measured and calculated butyl acetate yields (right). Reaction conditions: 10 wt.% catalyst, initial reactants molar ratio of 1.0 and reaction temperature of 80°C.

Figure 5. Effect of the reaction temperature on butyl acetate yield (right). Correlation between measured and calculated butyl acetate yields (left). Reaction conditions: initial reactants molar ratio of 1.0 and 10 wt.% $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$.

Figure 6. Effect of the catalyst loading on the butyl acetate yield (left). Correlation between measured and calculated butyl acetate yield (middle). Reaction conditions: initial reactants molar ratio of 1.0, reaction temperature of 80°C.

Figure 7. Rate constant values as a function of the catalyst loading. Reaction conditions: initial reactants molar ratio of 1.0, reaction temperature of 80°C, 6 h time of reaction.

Figure 8. Arrhenius plot for finding the activation energy and the pre-exponential factor. Reaction conditions: 10 wt.% $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ catalyst, initial reactants molar ratio of 1.0, 6 h of reaction.

Figure 9. Eyring plot for determine the entropy and enthalpy of activation for butyl acetate synthesis. Reaction conditions: 10 wt.% $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ catalyst, initial molar ratio of 1.0, 6 h of reaction.

Figure 10. Total energy along intrinsic reaction coordinates.

Scheme 1. Preparation of the centrosymmetric ionic compound $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$.

Scheme 2. Synthesis of butyl acetate in the presence of the ion pair $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$.

Scheme 3. Catalytic cycle for butyl acetate production using the centrosymmetric $[\text{C}_3\text{H}_5\text{N}_2]^+[\text{C}_4\text{O}_4\text{H}]^-$ catalyst.

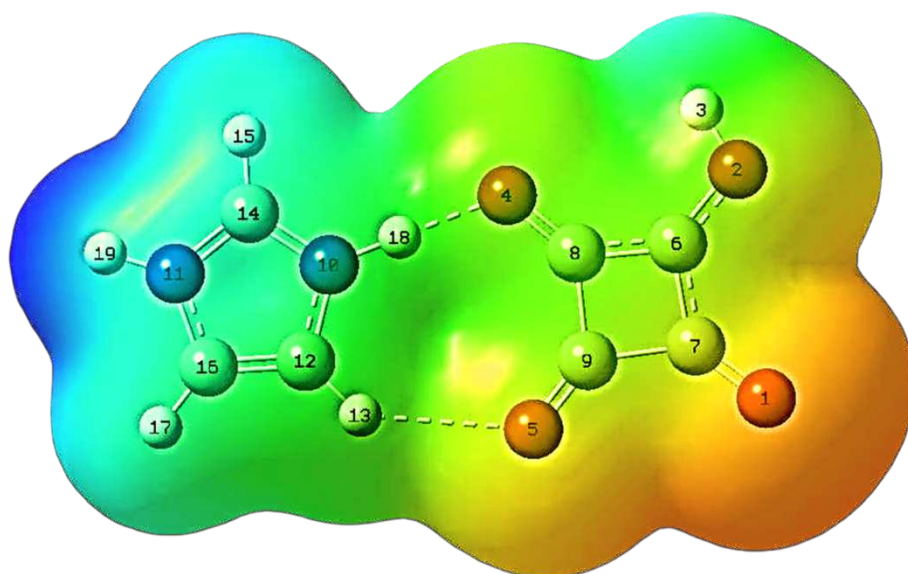


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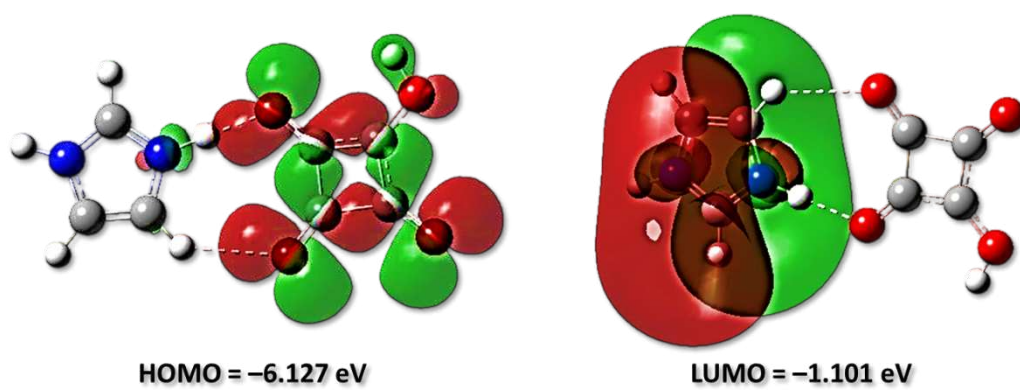


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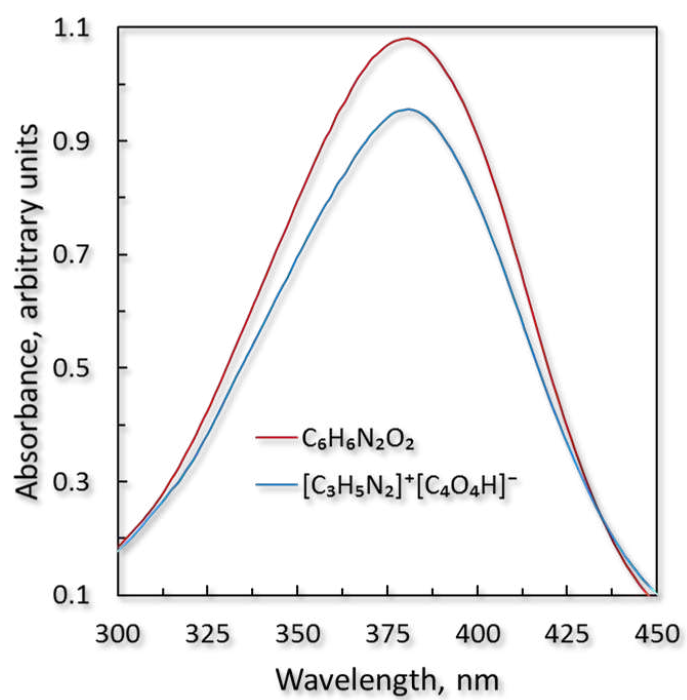


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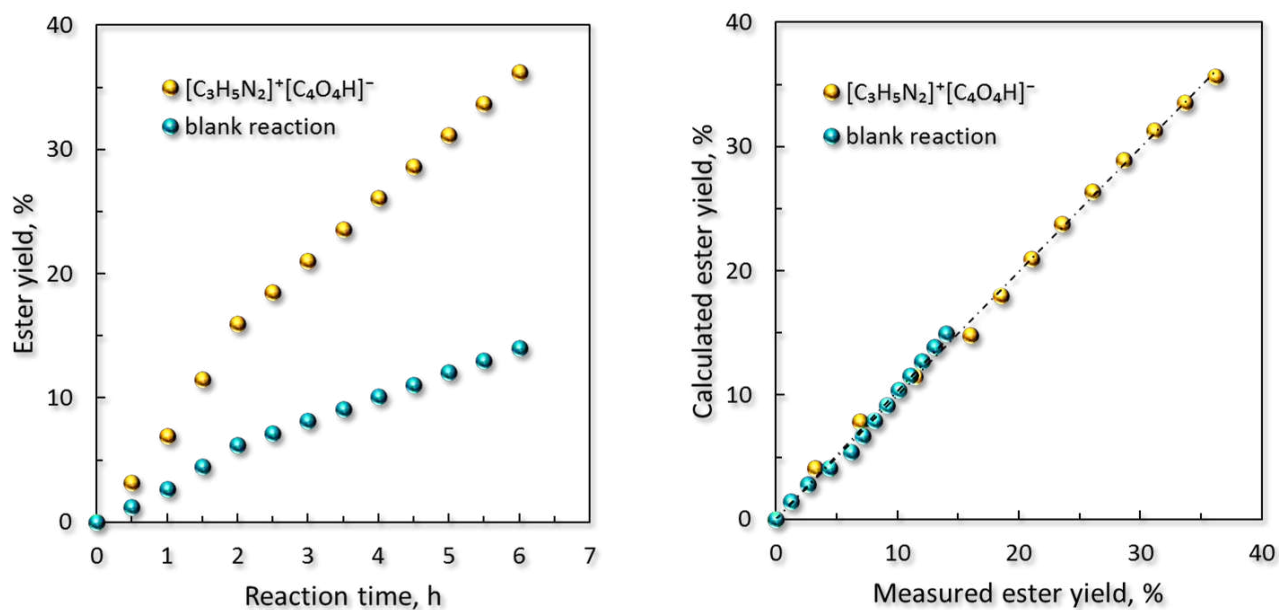


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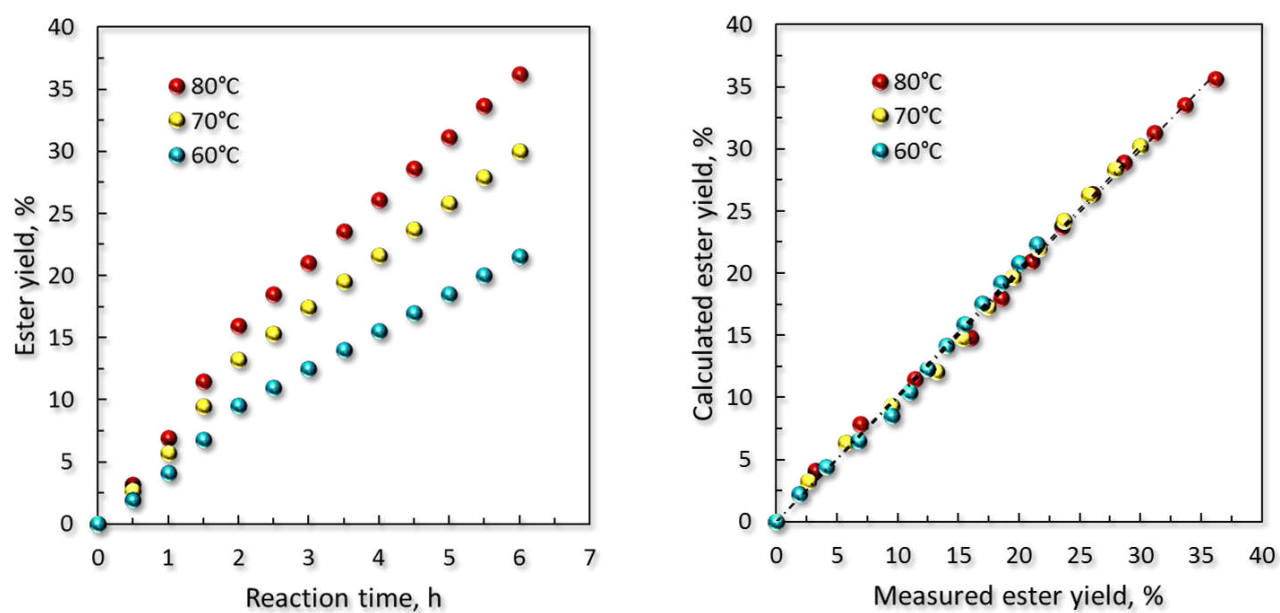


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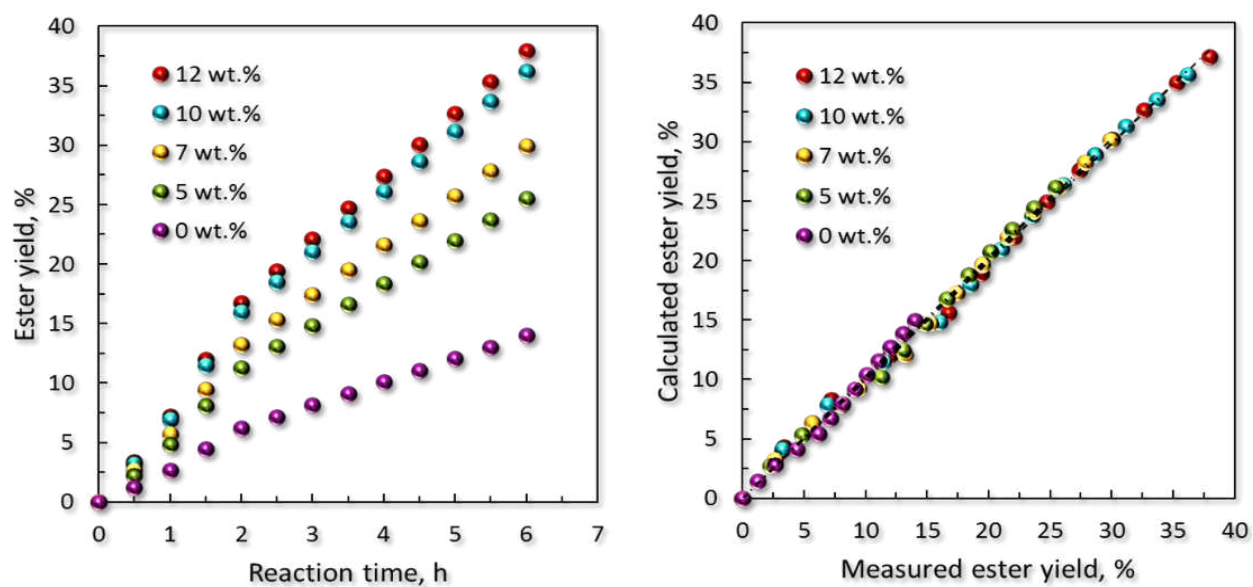


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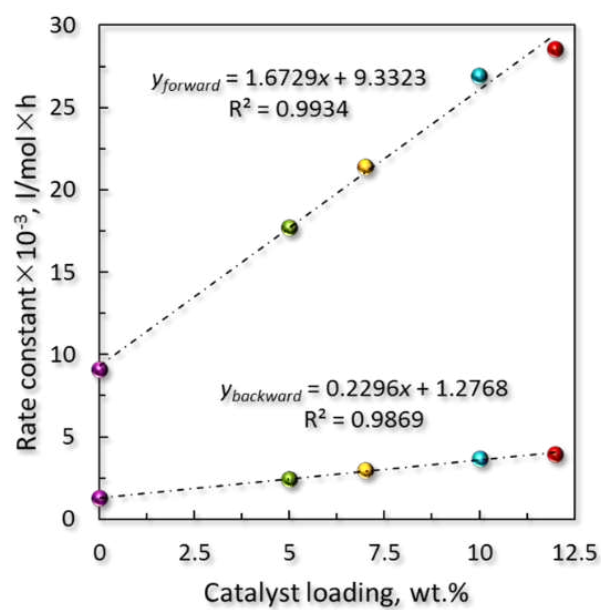


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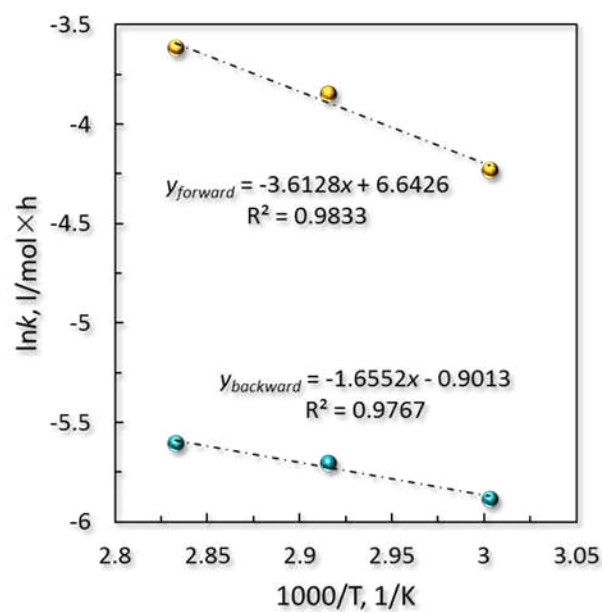


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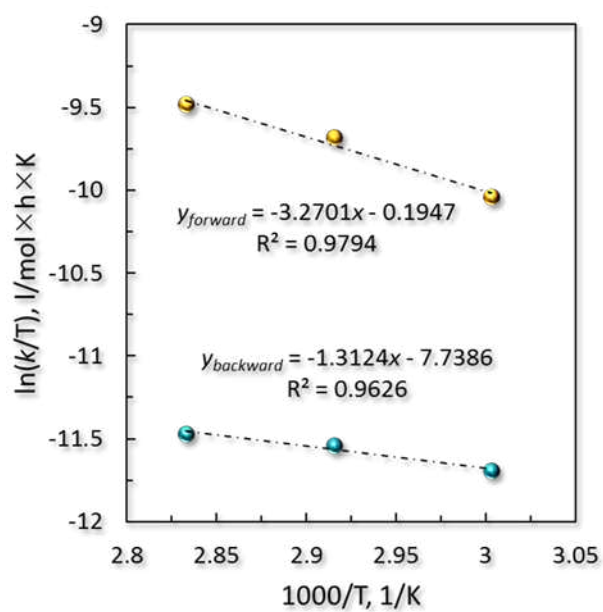


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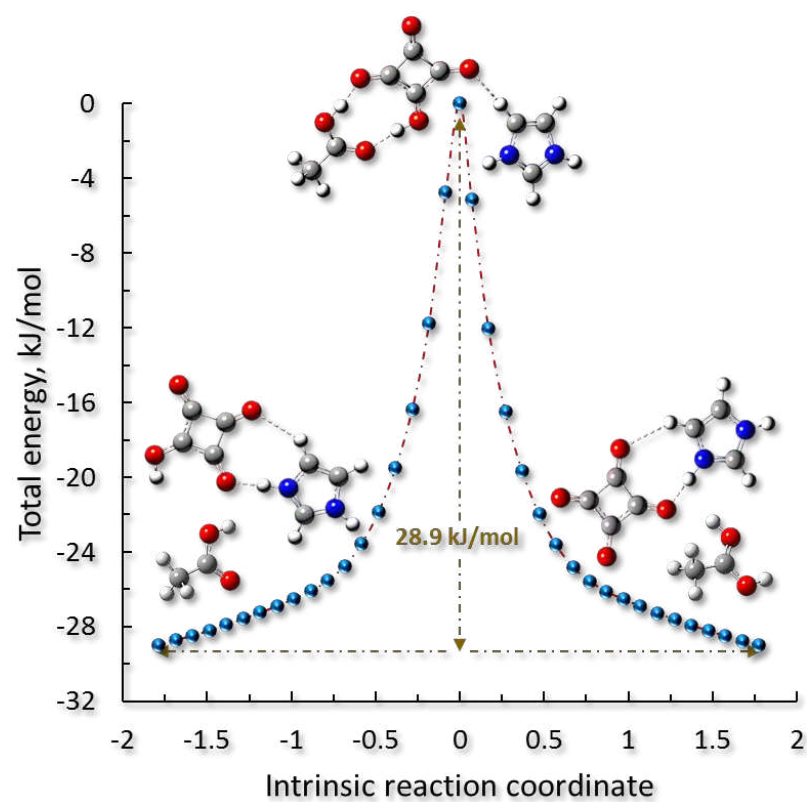


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