Synthesis and Thermal Properties of Resorcinol–Furfural Thermosetting Resin

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ABSTRACT: A mild and effective synthesis of resorcinol–furfural (RF) thermosetting resin was proposed with ethanol as a distinctive solvent, which, as a usually neglected factor, was shown to not only help form a homogeneous reaction system but also observably reduce the energy barriers between the early intermediates and transition states in addition reactions by explicit solvent effects, drawn from theoretical calculation conclusions. Besides, the para-additions on aromatic rings were more dominant than ortho-additions with the same reactants, which affected the final link types of monomers verified by Fourier transform infrared spectroscopy and two-dimensional nuclear magnetic resonance tests. The prepared resin can be assigned to a relatively fast gel speed and a high residual mass (65.25%) after pyrolysis in a N₂ atmosphere by adjusting the molar ratios of F to R, and the curing of that was a complex reaction, with a curing temperature around 149 °C and an activation energy of about 49.11 kJ mol⁻¹ obtained by the Kissinger method.

INTRODUCTION

Phenolic resin, which has been utilized in diverse fields for more than a century due to its versatility, was first synthesized in 1872 by Adolph von Baeyer. By altering the preparation conditions, especially the catalyst¹ and molar ratios of phenols to aldehydes, novolac (cold-setting) and resol²³ (thermosetting) can be prepared to meet different applications. For instance, resol can be cured rapidly by heating and eventually become an infusible and insoluble solid with excellent performances, such as pre-eminent dimensional stability, high carbon residue, and low toxic gas release at high temperatures. Therefore, it has been extensively used in gel,⁴ membrane,⁵ and flame-retardant materials⁶ and as an appropriate precursor of diversified kinds of carbon products.⁷⁻⁹

Traditional phenolic resin is prepared from formaldehyde and phenol. However, formaldehyde is known to be an atmospheric pollutant¹⁰ and mainly transformed from non-renewable natural gas. Therefore, a plenty of substitutes for that has been explored during the past decades, such as paraformaldehyde,¹¹⁻¹³ acetaldehyde,¹⁴ glyoxal,¹⁵ and furfural (F). In comparison with the others mentioned above, furfural is a kind of renewable heterocyclic aldehyde with a bright industrialization prospect. It is mainly yielded from biomass wastes, such as corncobs and sugarcane bagasse¹⁶ at present, which is a potential candidate to replace formaldehyde in the synthesis of phenolic resins.¹⁷⁻²¹

However, the synthesis conditions of furfural–phenol thermosetting resin would be much more demanding than that of traditional phenolic resin in most cases. High reaction temperatures (>100 °C) and large amounts of the base catalyst were usually required¹⁷⁻²¹ due to the low reactivity of furfural. In general, the introduction of phenols with high activity is a practical way to promote the synthesis of phenolic resin. For example, resorcinol (R)²²⁻²⁵ is less volatile and more reactive than phenol, which can conspicuously soften synthesis conditions and facilitate further curing of resin. Nevertheless, the preparation of satisfactory thermosetting RF resin with high molar ratios of F to R under alkali conditions remains a challenge in this field. Solvent factors may have contributed to this problem. First, water is almost always used as the solvent in those systems where the RF resin with high F/R molar ratios is less soluble resulted in the difficulty for the reaction system to maintain being uniform and stable as the reaction goes on. Besides, the solvent may also be involved in the resin synthesis, which was often less considered. On the other hand, to prepare the resin with specific link structures, external conditions, such as the catalyst and temperature, were generally in focus, but the
advantage or limitation of raw materials themselves on it was relatively less studied.

Here, a mild and efficient way for the preparation of RF thermosetting resin under alkali conditions was developed. To form a stable homogenous reaction system, ethanol was chosen as the solvent. The properties of RF resin were studied by the analysis of chemical constructions, gelation behaviors, curing processes, and pyrolysis characteristics. Density functional theory (DFT) was adopted to discuss various effects on single addition reactions during the resin synthesis, as well as to study the reaction mechanism of phenolic resin in a different perspective and help in the selection of appropriate reaction conditions.

## RESULTS AND DISCUSSION

### Synthesis and Structures of RF Resin

The basic reaction mechanism of thermosetting RF resin was similar to that of the traditional phenolic resin in general.\(^{17,18,26}\) First, under alkali conditions, resorcinol can form anions in stable resonance states like phenol,\(^{27}\) which can enhance the activity at ortho- (o-) and para- (p-) positions, and then facilitate the process of addition with furfural to form \(\alpha\)-furan hydroxymethyls (\(-\text{CHFu}−\text{OH}\)). Since the two \(\alpha\)-furan hydroxyl groups of resorcinol can interact with each other, the protons could be both captured by \(\text{OH}^−\), as shown in Scheme 1.

### Scheme 1. Possible Resonance Equilibriums of Resorcinol under Alkaline Conditions and the Relative Energies (\(\Delta E\)) of Different Routes Calculated at the B3LYP/6-311+G (d, p) Level with the PCM (Ethanol) Solvation Model

![Scheme 1](image)

Afterward, the \(-\text{CHFu}−\text{OH}\) groups formed can develop ether bridges by dehydration reaction, which can further generate \(-\text{CHFu}−\) bridges by removing one molecule of furfural. Besides, \(-\text{CHFu}−\text{OH}\) groups can also directly attack the o- or p- position of another aromatic nucleus to form \(-\text{CHFu}−\). As a result, with the development of polycondensation, the polymerization degree of RF resin increases,\(^{19}\) which will eventually result in the formation of an infusible and insoluble solid with three-dimensional molecular networks.

### DFT Analysis

Since the addition of R with F is a precondition for the resin synthesis, the mechanism of that was first studied by the DFT method to further explore the influence of various factors on it and guide the synthesis of phenolic resin more generally. As shown in Scheme 1, in the reaction of R with \(\text{OH}^−\), the heat release in route 1 was 80.1 kJ mol\(^{−1}\), and 110.6 kJ mol\(^{−1}\) in route 2, proving that R\(_1\) and R\(_2\) can both exist in the system, the single addition reactions on which were simultaneously considered.

The effect of reaction sites and the dissociation degree of protons of R on addition were first studied based on intramolecular proton transfers. As shown in Figure 1a,c, o/p\(_2\)-TS were both transition states with four-membered rings of C−C−O−H with R\(_1\) as a reactant. A proton from a benzene ring was transferred directly to the oxygen atom of an aldehyde group, accompanied by the shortening of C−C and O−H bonds to form o/p\(_1\)-Pr eventually. The electrostatic potential\(^{23}\) and atomic charge can predict the active sites of addition reactions. As can be seen in Figure 2, the charge of the C atom at the o- site (−0.398) was lower than that of p\(_2\)- (−0.360), representing an advantage of reacting with an electrophile. However, the reaction barrier of R\(_1\)-o (196.0 kJ mol\(^{−1}\)) was higher than that of R\(_1\)-p\(_2\) (189.3 kJ mol\(^{−1}\)), probably as a result of higher steric hindrance. In contrast with the two paths above, p\(_1\)-IM\(_1\) (Figure 1b) required two transition states, namely, p\(_1\)-TS\(_1\) and p\(_1\)-TS\(_2\), to form the final product p\(_1\)-Pr. That is, when a furfural molecule approached the p\(_1\)- site, a proton on phenolic hydroxyl was first snatched by an aldehyde group to form p\(_1\)-IM\(_1\); afterward, the snatched proton returned to the oxygen of the phenolic hydroxyl; meanwhile, a proton on the p\(_1\)- site shifted to the aldehyde oxygen to form p\(_1\)-TS\(_2\), and eventually generated the final product (p\(_1\)-Pr). On the contrary, the proton on the adjacent phenolic hydroxyl of the o- active site was not captured by an aldehyde group, probably due to the spatial orientation limits of furfural caused by steric resistance, which was larger than that of the p\(_1\)- site. Furthermore, the maximum energy barrier of R\(_1\)-p\(_2\) was much lower than R\(_1\)-o and R\(_1\)-p\(_1\).

On the other hand, as shown in Figure 1d,e, proton transfers of R\(_2\) at o- and p- positions were similar to those of R\(_1\)-o and R\(_1\)-p\(_2\), respectively, but their corresponding energy barriers were all reduced. It might be due to the more negative charges on the reaction sites of R\(_2\) compared with R\(_1\) (Figure 2), which made it more likely to be attacked by an electrophilic reagent. Moreover, the energy barrier in R\(_2\)-p\(_2\) (127.6 kJ mol\(^{−1}\)) was lower than that of R\(_1\)-o (148.6 kJ mol\(^{−1}\)), which was also caused by the steric hindrance, but the energy of the final product in R\(_2\)-o was lower. Overall, the addition reactions at p- sites were more dominant than those at o- mentioned above, which will be further reflected in the final molecular structures of RF resin. Besides, based on the results of Figure 1f, the addition of P-p is similar to that of R\(_2\)-p, but the energy barrier of it was evidently higher and conformed to the trend of the electrostatic potential and atomic charge, proving a relatively lower activity of P than R\(_2\) under the same circumstances.

However, the energy barriers of the intramolecular proton transfers discussed above were so high that the proceeding of it needs harsh experimental conditions. Therefore, the synergistic effect of polar solvents on the proton transfer process\(^{30−32}\) was also compared as shown in Figure 1g,h. In these paths, water and ethanol both participated in the formation of early complexes through hydrogen bonds, leading to further formation of the transition states with hexatomic ring structures. As can be seen from Figure 1g, the energy barrier (31.2 kJ mol\(^{−1}\)) was significantly decreased compared with that of R\(_2\)-p, which was probably due to the fact that the formation of the hexatomic ring greatly reduced the ring tension of transitional structures. For comparison purposes, the water-catalyzed proton transfer (Figure 1h) was also calculated, the process of which was similar to ethanol, but the energy barrier (30.4 kJ mol\(^{−1}\)) was slightly lower, probably because the introduction of solvents with higher polarity was beneficial to reduce the energy barrier in view of the dipole moments of p-TS, which were all higher than p-1M in all three paths (Table 1). In addition, all atoms involved in hexatomic rings of p-TS (Figure 1g,h) were all basically in the same plane, in accord with the reported results on water-involved proton transfers.\(^{31,33}\) Therefore, the solvent in the
reaction system can not only form a homogeneous reaction system but also reduce the energy barrier in addition reactions by explicit solvent effects, conducive to soften reaction conditions.

Chemical Structures. The Fourier transform infrared (FT-IR) spectra (Figure 3) were first used to study the functional groups and structures of RF resin. For distinct comparison, all spectra were normalized with the intensity of the band at 1605 cm\(^{-1}\), assigned to the stretching of C=C in benzene rings, the intensity of which was regarded as a constant.\(^{19,26}\)

As can be seen in Figure 3a, the relatively weak peak at 1653 cm\(^{-1}\) indicated the existence of unreacted F in the reaction system, which decreased with the extension of reaction time. The peak at 1506 cm\(^{-1}\) was referred to the phase stretching of C=C conjugated to a saturated group in F,\(^{19}\) and the peak at 1073 cm\(^{-1}\) corresponded to the symmetrical stretching vibration...
of ether bonds in the furan nucleus. Besides, the peak at 1467 cm$^{-1}$ referred to $-\text{CHFu}$ between two benzene rings,26,34 and the peak around 1093 cm$^{-1}$ referred to the antisymmetric C–O stretching of ether bridges,19 both of which proved the occurrence of polycondensation.6 The broad peak at 1301 cm$^{-1}$ was the characterization of the stretching vibration of $-\text{OH}$ of secondary alcohols generated from addition. With the reaction time, the absorption intensity of $-\text{CHFu}$ increased obviously, representing a gradual increase in the polymerization degree, while the peak intensity of C=C groups in furan rings and $-\text{OH}$ groups of secondary alcohols were not much different. This is probably because the polycondensation took place along with the formation of new $-\text{CHFu}$–$\text{OH}$ groups by addition, and the F involved in it might come from the unreacted F added at the beginning and the byproduct from the formation of $-\text{CHFu}$. On the other hand, according to the possible substitutions on the aromatic ring of R (Chart 1), the peak at 813 cm$^{-1}$ ($\nu_{\text{CH}}$ for two adjacent H atoms) can be referred to B and/or C,34 and the weak peak at 772 cm$^{-1}$ ($\nu_{\text{CH}}$ for three adjacent H atoms) referred to A,34 with a band at 734 cm$^{-1}$ for $\delta_{\text{ring}}$. The peak at 884 cm$^{-1}$ ($\nu_{\text{CH}}$ for an isolated H atom) can correspond to D, E, and/or as an additional absorption band of B. Particularly, E is the key to the formation of cross-linked molecular structures.

As shown in Figure 3b, with the augmentation of furfural, the peak intensities of C=C groups in furan rings and $-\text{OH}$ groups of secondary alcohols both increased, indicating the greater formation of $-\text{CHFu}$–$\text{OH}$, which was beneficial to further generation of ether and $-\text{CHFu}$ bridges. As evidence of it, the peak intensities of ether and $-\text{CHFu}$ bridges also increased simultaneously, representing the gradual increase of the polycondensation degree. However, it was not efficient to enhance the polymerization of RF resin by increasing the amount of the F/R molar ratio from 1.5 to 2 under the experimental conditions, probably limited by the number of substitution sites of R and the relatively low reaction temperature.

To further verify the structure of the prepared RF resin, 2D NMR tests were performed (Figure 4); the probable assignments of $^1$H–$^{13}$C signals17,18,35–37 according to a hypothetical structural unit were listed in Table 2, combined with the $^1$H and $^{13}$C NMR results (Figure S1). As can be seen from Figure 4, with the increase of the amount of F initially added, the signals of F3 and F5 were all enhanced, proving that the amount of unreacted and reacted furfural were all respectively increased. In addition, the signals of $-\text{CHFu}$ bridges were also heightened, representing the increase of the polycondensation degree.
consistent with the results of FT-IR analysis. Furthermore, the signals of p–p–CHFu– bridges were notably higher than those of o–p and o–o, which confirmed that the addition at p- was more dominant than that of o- positions in accord with the theoretical calculation results.

Through the above analysis, a synthesis mechanism of the RF resin prepolymer was proposed as shown in Scheme 2, and the theoretical calculation results. Also, the rate of curing reaction can be expressed by eq 2.40,41

$$\frac{dx}{dt} = \beta \frac{dx}{dT} = k(T)f(\alpha) = A \exp \left(-\frac{E}{RT}\right)f(\alpha)$$

where $dx/dt$ is the reaction rate of curing (s^{-1}); $T$ is the absolute temperature (K); $\beta = \frac{dT}{dt}$ is the constant heating rate (K s^{-1}); $k(T)$ is the constant of reaction rate related to temperature and following the Arrhenius equation; $R$ is the ideal gas constant, namely, 8.3145 J (mol K)^{-1}; $A$ is the prefactor (s^{-1}); $E$ is the activation energy (J mol^{-1}).

Table 2. Chemical Shifts and Probable Assignments of Carbons and Protons of RF Resin

| 13C/1H chemical shifts (ppm) | assignments |
|-----------------------------|-------------|
| 178.0/9.62                  | phenolic quinones or aldehyde groups of the unreacted furfural |
| 158.43                      | $C_p$ for unsubstituted R |
| 152.52–156.48               | $C_p/H_p$ ($F_p$) for unreacted furfural |
| 149.15/8.08                 | $C_p/H_p$ ($F_p$) for $-\text{CHFuOH}$ and $-\text{CHFur}$, respectively |
| 141.08, 140.81/7.26–7.52     | $C_p/H_p$ ($F_p$) for unreacted furfurals |
| 139.66/6.39–6.77            | $C_p/H_p$ ($R_p$) |
| 118.45–119.23               | $C_o$ and $C_p$ substituted |
| 112.89/6.77                 | $C_p/H_p$ ($R_p$) for unreacted furfural |
| 109.75/6.2                  | $C_p/H_p$ ($R_p$) for $-\text{CHFurOH}$ or $-\text{CHFur}$– |
| 105.59/6.18                 | $C_p/H_p$ ($R_o$) of unreacted R |
| 102.52/6.23                 | $C_o/H_o$ ($R_p$) of unreacted R |
| 56.05/3.41                  | $-\text{CHFurOH}$ |
| 35.44/5.75                  | o–p bridges |
| 30.0/1.25                   | o–o bridges |
| 27.5/1.9                    | o–o bridges |

Figure 4. 2D NMR chromatograms of (a) RFB-3 and (b) RFD-3.
Taking the logarithm of both sides of eq 2, eq 3 can be obtained.

\[ \beta \alpha \alpha = + - i \]

\[ \sigma \beta \alpha \alpha \]

\[ T_{p} \]
$E_a$ can be obtained by the linear regression of $\ln(\beta d\alpha dT^{-1})$ and $T^{-1}$ at various heating rates, and eq 4 can be obtained by using the Kissinger\(^{42}\) method.

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p}$$

where $T_p$ is the peak temperature ($K$), and a line can be obtained by plotting $T_p^{-1}$ with $\ln(\beta T_p^{-2})$, via changing the heating rate (Figure 5b). The calculated $E_a$ was 49.11 kJ mol\(^{-1}\) obtained by the slope ($-E_a/R-1$), and an $A$ value of $4.18 \times 10^5$ s\(^{-1}\) by the intercept, with the sample of RFB-3, as shown in Figure 5c.

The reaction order can be calculated by the Crane equation, as shown in eq 5.

$$\frac{d\ln \beta}{d(1/T_p)} = -\frac{E_a}{nR}$$

$n$ can be obtained from the linear regression of $\ln \beta$ and $T_p^{-1}$ at various heating rates (Figure 5d), the calculated value of which was 0.88 for RFB-3.

By substituting $E_a$, $A$, and $n$ into eq 2, the $n$th order curing kinetic equation (eq 6) can be obtained.

$$\frac{d\alpha}{dt} = 4.18 \times 10^5 \exp\left(-\frac{49114.43}{RT}(1-\alpha)^{0.88}\right)$$

To determine the curing temperature of RF resin and eliminate the influence of $\beta$ on the temperature of heat release during curing, fitted lines were obtained by adopting the method of $\beta$–$T$ extrapolation\(^{43}\) as can be seen in Figure 5e and Table 5 where $T_i$, $T_p$, and $T_f$ are the initial, peak, and termination temperatures, respectively. According to the fitting results, when $\beta = 0$, $T_i = 75.2 \degree C$, $T_p = 121.6 \degree C$, and $T_f = 202.2 \degree C$. To make the solidification more complete, the curing process of RF resin was chosen as 75 \degree C/1 h $\rightarrow$ 125 \degree C/2 h $\rightarrow$ 165 \degree C/2 h $\rightarrow$ 200 \degree C/1 h.

In order to verify that the curing process can improve the polycondensation degree of the resin, FT-IR spectra of the cured resins were also obtained by the same normalization. As can be seen in Figure 5f, after curing, the polymerization degree of RFB-3 was obviously increased, while it was relatively the highest for cured RFD-3 compared with others.

TABLE 5. Characteristic Temperatures of RFB-3 with Different Heating Rates

| $\beta$ (K min\(^{-1}\)) | 5   | 10  | 15  | 20  |
|-------------------------|-----|-----|-----|-----|
| $T_i$ (°C)              | 81.2| 99.1| 107.1| 111.1|
| $T_p$ (°C)              | 129.5| 149.1| 159.6| 164.8|
| $T_f$ (°C)              | 207.2| 225.1| 227.1| 235.1|

Figure 6. (a,c) TG curves of RFA-3, RFB-3, RFC-3, and RFD-3, uncured and cured, respectively; (b,d) DTG curves of RFA-3, RFB-3, RFC-3, and RFD-3, uncured and cured, respectively.
decreased with the increase of the F/R molar ratio, probably due to the thermostability enhancement caused by the increasing of the cross-linking degree of the resins by the initial heating. Afterward, there was a shoulder peak that started at about 620 °C (Figure 6b), representing the occurrence of carbonization, and the final residual mass was the comprehensive result of the processes mentioned above.

The pyrolysis behavior of the cured resin is more significant in the application fields as flame-resistant materials and precursors of carbon materials. TG and DTG curves of the cured resins are shown in Figure 6a,b, and extrapolated onset temperatures ($T_{\text{onset}}$), temperatures related to $\ln(\alpha)$ ($T_{\text{max}}$), and final residual masses ($w_f$) are listed in Table 6. The initial weightlessness was also caused by the volatilization of adsorbed small molecules on mass was eliminated.

The effect of the volatilization of adsorbed small molecules, but there was no obvious weightlessness between 150 and 200 °C unlike with the uncured resin, proving the well curing effect according to the designed procedure. As the temperature continued to rise, pyrolysis occurred and was similar to that of the uncured resins in general. Although the residual mass of phenolic resin after pyrolysis is mainly contributed by phenols generally, which will be reduced with the increased proportion of aldehyde, the concomitant enhancement of the cross-linking degree is beneficial for improving the thermal stability simultaneously. As a consequence of that, the residue mass of RFB-3 (Table 6) was relatively the highest, which can reach up to 65.25% under the experimental conditions.

## CONCLUSIONS

In summary, a thermosetting RF resin was successfully synthesized with ethanol as the solvent, which can serve as satisfactory gels and carbon precursors by altering the molar ratios of F to R. On the other hand, charge distributions and the character of molecular structures were proven to be significant factors on addition positions, which were further reflected in the final molecular structures of phenolic resin. As a result of that, the appropriate selection of raw materials is beneficial to the synthesis of the resins with specific link types. Moreover, the solvent presented in this reaction system not only formed a homogeneous phase but also participated in the addition through explicit solvent effects, which greatly reduced the energy barriers between early complexes and transition states. Therefore, the assistance by appropriate polar solvents, such as water and ethanol, can enable the proton transfer reactions that are difficult to occur in dynamics and increase the selection of reaction materials.

## EXPERIMENTAL SECTION

### Chemicals.

Resorcinol was supplied by Macklin Chemical Co., Ltd. (China). Sodium hydroxide, ethanol, and furfural were purchased from Xilong Scientific Co., Ltd. (China). All chemical reagents were used without further purification.

### Preparation of RF Resins.

First, 0.1 mol of R and 3.5 mL of NaOH aqueous solution (1 mol L$^{-1}$) (C) were added in 50 mL of ethanol and stirred at room temperature until a uniform solution was formed. The solution was then transferred to a three-neck flask equipped with condensing equipment, heated, and stirred constantly. When the temperature reached 60 °C, an 80% amount of F was added in the solution dropwise and reacted for 50 min; the molar ratios of total F to R were 1, 1.25, 1.5, and 2. Next, 1.5 mL of C and the rest of F were added in sequence and reacted for another several hours. Synthesis parameters of RF resin are shown in Table 7.

| Table 7. Types of RF Resin with Different Reactant Molar Ratios and Reaction Times |
|-------------------------------|----------------|----------------|----------------|----------------|----------------|
| samples                        | RFB-1 | RFB-2 | RFB-3 | RFA-3 | RFC-3 | RFD-3 |
| n(F)/n(R)                      | 1.25  | 1.25  | 1.25  | 1     | 1.5   | 2     |
| $t^*$ (h)                      | 1     | 2     | 3     | 3     | 3     | 3     |

$^*$Timing started after all the reactants and catalyst were added.

### Characterization.

Functional groups were analyzed by a Fourier transform infrared spectrometer (Thermo Fisher Nicolet iS5); all samples were triturated and mixed with KBr in advance. $^{13}$C$-^{1}$H 2D NMR tests were performed by the heteronuclear single quantum coherence (HSQC) method on a Bruker AV-III 400 MHz spectrometer with CD$_3$OD as the solvent at 25 °C. DSC and TG tests of RF resins were both performed using a simultaneous thermal analyzer (Netzsch STA449FS) under a N$_2$ atmosphere (30 mL min$^{-1}$) with a constant pressure. Curing processes were analyzed by DSC tests in capped aluminum crucibles, with different heating rates of 5, 10, 15, and 20 °C min$^{-1}$ and roughly identical sample weights of about 5 mg. Pyrolysis behaviors were studied by TG tests with a constant heating rate of 10 °C min$^{-1}$ and all sample weights of about 10 mg in alumina crucibles. Gelation times of RF resins were measured according to the standard of ISO 9396-1997, with a solid content range of 75% ± 2% and a test temperature held at 130 °C. To reduce the influence of solvent volatilization and thermal treatment, all test samples were dried at 40 °C, except for the tests of gelation time.

### Calculation Method.

The DFT method was used to optimize molecular geometries and study reaction mechanisms of single addition reactions by Gaussian 09W software, with the B3LYP functional and 6-311+G (d, p) basis set adopted in all calculations. Optimized structures of reactants, intermediates (IM), transition states (TS), and products (Pr) were first acquired, the vibration frequencies of which were all guaranteed to be positive, except for TS with only one imaginary frequency (IMG) (Tables S1,S2) each self. All of the energies of each structure along the reaction path were corrected by zero-point energy (ZPE) (Tables S1,S2) to obtain corrected relative energies ($\Delta E$). Intrinsic reaction coordinate (IRC) calculations were adopted to verify whether the connections between TS and IM or Pr were correct. For comparison purposes, the total energy of initial reactants was taken as the reference energy in each reaction path. Natural population analysis (NPA) charge distributions, electrostatic potential (EPS) distribution on molecular van der Waals surfaces, and electron density contours of R$_{ij}$, R$_{P}$, and F were also calculated to discuss the effect of molecular structures on addition reactions. Since the main solvent was ethanol in this reaction system, a polarizable continuum model (PCM) of ethanol in
self-consistent field response (SCRF) was adopted in all calculations.

■ ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00365. IMAG and ZPE results and 1H and 13C NMR spectra (PDF)

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Notes
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