Critical Temperatures and Pressures of the Reacting Mixture in the Acylation of Anisole with Acetic Anhydride

Xiangfei Ji, Zhangfeng Qin, Guofu Wang, Mei Dong, Xianglin Hou, and Jianguo Wang*

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, P.O. Box 165,
Taiyuan, Shanxi 030001, People's Republic of China

To determine the supercritical reaction conditions of anisole acylation with acetic anhydride using certain solvents such as carbon dioxide or propane, the critical temperatures and pressures of the nominal reacting mixture (anisole + acetic anhydride + *p*-methoxyacetophenone + acetic acid + carbon dioxide or propane) were measured with the composition representing the extent of reaction (conversion of acetic anhydride) by using a high-pressure viewing cell. The effects of the initial composition, the addition of suitable solvent, and the extent of reaction on the critical properties of the reacting mixture were then investigated. Such information may be helpful to those who intend to carry out the acylation of anisole with acetic anhydride under supercritical conditions to improve the efficiency of current processes in the gas or liquid phase.

Introduction

The Friedel−Crafts acylation of the aromatic compounds is one of the most important routes for the synthesis of aromatic ketones in the fine chemical and pharmaceutical industry.[1] In a conventional homogeneous process, aromatics and carboxylic acid derivatives are used as reactants and Lewis acid anhydrous metal halides are used as catalysts, which may cause serious corrosion and pollution problems.[2] Therefore, considerable effort has been made to develop heterogeneous processes using solid acid catalysts;[3−10] of them, especially, zeolites combine acidic properties with shape selectivity and exhibit accordingly good catalytic activity and selectivity in the acylation of aromatic compounds.[3−7]

However, the solid acid as acylation catalyst often suffers from fast deactivation and then needs frequent regeneration. The reasons for the catalyst deactivation can be the dealumination of zeolites by the acidic byproducts and the stable adsorption of heavy products and the permanent deposition of carbonaceous substances on the catalyst that may block the accesses to the active sites.[11]

Performing reactions under supercritical conditions rather than in the gas or liquid phase could be an interesting option for improving the equilibrium conversion, enhancing the reaction rate, increasing throughput, prolonging catalyst lifetime, and making the process more environmentally benign.[12−14] Moreover, the environmentally undesirable solvents and byproducts may be avoided and the yield of desired products may be enhanced through the addition of a suitable supercritical media.[15−19] The reaction behavior is often very sensitive to the reaction conditions; the operation in the regions near the critical point of the reacting system was most desirable to make the most of the unique characteristics of supercritical fluid.[14] The addition of suitable solvents is an effective way to tune the critical properties of the reacting mixture and to alter the reaction behavior.[16−18] The chemically inert substances such as alkanes, carbon dioxide, and water are often used as the supercritical solvent.

It is supposed that the acylation of anisole and acetic anhydride under supercritical conditions may provide an approach to the synthesis of *p*-methoxyacetophenone (*p*-MAP) with improved catalyst activity and stability; however, such an investigation has not been reported. We are intent on carrying out a systematical study on the acylation under supercritical conditions. To determine the phase behaviors of the reacting mixture and the operating parameters for the reaction under supercritical conditions, it is essential to be cognizant of the critical properties of the reacting mixture along with the reaction course.

In this work, the critical temperatures and pressures of the nominal reacting mixture (anisole + acetic anhydride + *p*-MAP + acetic acid + carbon dioxide or propane) for anisole acylation with acetic anhydride using carbon dioxide or propane as solvent were measured with the composition representing the extent of reaction (conversion of acetic anhydride) by using a high-pressure viewing cell. The effects of the initial composition, the addition of suitable solvent, and the extent of reaction on the critical properties of the reacting mixture were then investigated. The selection of suitable solvent and the determination of the operating conditions were hereby clarified.

Experimental Section

Anisole (mass fraction $w > 98.0$ %) and *p*-MAP ($w > 98.0$ %) were purchased from Shanghai Chemical Reagent Corporation. Acetic anhydride ($w > 98.6$ %) and acetic acid ($w > 99.5$ %) were obtained from Tianjin Tian-Da Chemical Corporation; they were further purified before use by distillation. Carbon dioxide (mole fraction $x > 99.95$ %) from the Beijing Analytical Instrument Corporation and propane ($x > 99.5$ %) from Beijing Haipu Corporation of Gas Reagents were used without further treatment. The purity of all chemicals was checked before measurement by gas chromatography and proven to be $x > 99.5$ %.

For the acylation of anisole and acetic anhydride using zeolites or heteropoly acids as catalysts, the selectivity to *p*-MAP is very high (> 98 %),[3,8] and only trace amounts of the ortho isomers as byproducts are detected. The byproducts are then

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* To whom correspondence should be addressed. E-mail: iccjgw@sxicc.ac.cn. Phone: +86-351-4046092. Fax: +86-351-4041153.

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Table 1. Critical Properties of the Pure Substances

	T_c/K		P_c/MPa		ρ_c/g·cm^{-3}	
substance	this work	ref 22	this work	ref 22	this work	ref 22
carbon dioxide	304.9	304.1	7.38	7.38	0.473	0.469
propane	370.1	369.8	4.24	4.25	0.217	0.217

neglected in the determination of critical properties of the reacting mixture, and following reaction scheme is assumed to prepare the nominal reacting mixture:

$$C_6H_5OCH_3 + (CH_3CO)_2O \rightarrow CH_3OC_6H_4COCH_3 + CH_3COOH$$

The composition of the nominal reacting mixture was then determined according to the initial reactants constitutes (anisole, acetic anhydride, carbon dioxide, or propane) and the reaction extent (conversion of acetic anhydride).

The critical properties of the mixtures were measured with the same view cell and procedure as described previously.[20] Briefly, a known mass of liquid mixture based on the composition of the nominal reacting mixture was first charged into the pre-evacuated cell, and then a gaseous substance (carbon dioxide or propane) was pressurized into the cell through a sampling tube. The amount of the mixture in the cell was controlled in such a way that the density of the mixture should be close to or slightly higher than its critical density. The temperature and pressure readings were made by the occurrence of strong red-glow critical opalescence and the reappearance of a meniscus on slow cooling (less than 0.3 K·min^{-1}) through the critical point. This procedure is also similar to those of Liu et al.[21] except that the liquid and gaseous substances are here charged into the view cell via a sampling tube instead of with a pump. The critical properties of the nominal reacting mixture kept stable during the period of measurement, which indicated that the change of composition due to the reactions during the measurement is negligible. The uncertainties of the critical temperature, critical pressure and mole fraction were estimated within ± 0.3 K, ± 0.03 MPa, and ± 0.003, respectively.

Results and Discussion

Pure Substances. As shown in Table 1, a comparison of the critical properties of carbon dioxide and propane measured in this work with those in the literature proved that the agreement was satisfactory.[22] The critical properties of other pure substances were not measured because they approach the endurance limit of the viewing cell; moreover, we are interested mainly in the critical properties of the reacting mixture.

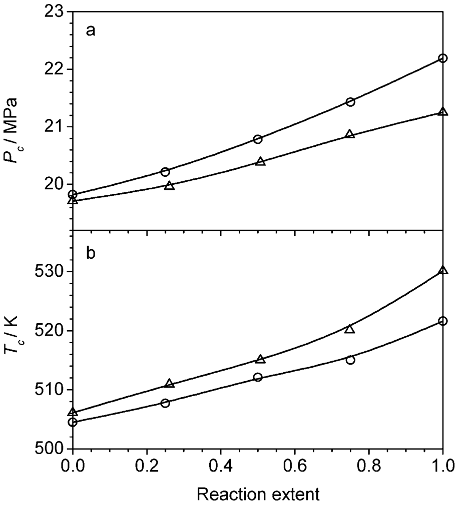

Figure 1. (a) Critical pressure and (b) temperature of the nominal reacting mixture (anisole (1) + acetic anhydride (2) + *p*-MAP (3) + acetic acid (4) + carbon dioxide (5)) along the reaction course of anisole acylation with acetic anhydride in the presence of carbon dioxide with the initial mole fraction $x_5 = 0.7$ (x_1/x_2 = ○, 5; △, 10).

Table 2. Critical Properties of the Nominal Reacting Mixture (Anisole (1) + Acetic Anhydride (2) + *p*-MAP (3) + Acetic Acid (4) + Carbon Dioxide (5)) along the Reaction Course of Anisole Acylation with Acetic Anhydride in the Presence of Carbon Dioxide

extent of reaction	x_1	x_2	x_3	x_4	x_5	T_c/K	P_c/MPa
Initial Mole Fraction $x_1/x_2 \approx 5$ and $x_5 \approx 0.7$							
0	0.253	0.052	0	0	0.695	504.5	19.82
0.250	0.238	0.038	0.013	0.013	0.699	507.7	20.21
0.500	0.227	0.025	0.025	0.025	0.697	512.1	20.78
0.750	0.213	0.012	0.038	0.038	0.699	515.0	21.43
1	0.198	0	0.050	0.050	0.702	521.6	22.19
Initial Mole Fraction $x_1/x_2 \approx 10$ and $x_5 \approx 0.7$							
0	0.268	0.028	0	0	0.704	506.1	19.71
0.261	0.257	0.020	0.007	0.007	0.708	510.9	19.96
0.507	0.258	0.014	0.014	0.014	0.700	515.0	20.38
0.748	0.250	0.007	0.020	0.020	0.702	520.1	20.86
1	0.243	0	0.027	0.027	0.703	530.1	21.25
Initial Mole Fraction $x_1/x_2 \approx 10$ and $x_5 \approx 0.9$							
0	0.090	0.009	0	0	0.901	374.8	16.15
0.264	0.086	0.007	0.002	0.002	0.903	383.6	17.46
0.487	0.087	0.005	0.005	0.005	0.900	397.3	19.21
0.750	0.083	0.002	0.007	0.007	0.901	413.6	20.36
1	0.077	0.000	0.009	0.009	0.906	441.3	22.22

Critical Properties of the Nominal Reacting Mixture of Anisole Acylation with Acetic Anhydride in the Presence of Carbon Dioxide. For the acylation of anisole with acetic anhydride, one molecule of anisole is acylated by one molecule of acetic anhydride with the production of one molecule *p*-MAP and one molecule of acetic acid. Anisole is generally in excess as compared with acetic anhydride, the composition of the reacting mixture depends on the initial ratio of anisole to acetic anhydride as well as the extent of reaction (conversion of acetic anhydride). The reaction temperature is generally set in the vicinity of 373 K; a higher temperature may result in a decrease in the *p*-MAP selectivity.[9−11] However, all pure substances in the reacting mixture owns a much higher critical temperature (for example, the critical temperature of anisole is 646.5 K),[23] This suggests that the reacting mixture also owns a much higher critical temperature than what it is practical for conducting the acylation reaction. Therefore, it is essential to add a suitable solvent to the tune the critical properties of reacting mixture, and carbon dioxide, inert and easily attainable, is then considered first.

To clarify the variance of critical properties of the reacting mixture with the reaction extent and the content of carbon dioxide, the critical properties of the quinary mixture (nominal reacting mixture of anisole acylation with acetic anhydride using carbon dioxide as an additional solvent) of anisole (1) + acetic anhydride (2) + *p*-MAP (3) + acetic acid (4) + carbon dioxide (5) were determined with the composition representing the extent of acylation (conversion of acetic anhydride), with the mole fraction of carbon dioxide (x_5) being 0.7 and 0.9, and the initial mole ratio of anisole to acetic anhydride (x_1/x_2) being 5 and 10, respectively, as shown in Table 2 and Figure 1.

As shown in Figure 1, the addition of carbon dioxide changes the critical properties of reacting mixture significantly. With a fixed content of carbon dioxide in the reacting mixture, the critical temperature depends then on the extent of reaction as well as the initial ratio of anisole to acetic anhydride. Both the critical temperature and the critical pressure increase with the

Table 3. Critical Properties of the Nominal Reacting Mixture (Anisole (1) + Acetic Anhydride (2) + *p*-MAP (3) + Acetic Acid (4) + Propane (5)) along the Reaction Course of Anisole Acylation with Acetic Anhydride in the Presence of Propane

extent of reaction	x_1	x_2	x_3	x_4	x_5	T_c/K	P_c/MPa
Initial Mole Fraction $x_1/x_2 \approx 2$ and $x_5 \approx 0.6$							
0	0.270	0.135	0	0	0.595	528.7	8.35
0.251	0.232	0.100	0.033	0.033	0.601	542.8	8.85
0.503	0.201	0.067	0.068	0.068	0.598	559.7	9.45
0.737	0.162	0.035	0.097	0.097	0.609	581.1	10.58
1	0.135	0	0.134	0.134	0.596	596.7	11.86
Initial Mole Fraction $x_1/x_2 \approx 2$ and $x_5 \approx 0.7$							
0	0.201	0.101	0	0	0.698	510.1	8.42
0.250	0.176	0.076	0.025	0.025	0.697	514.5	9.03
0.501	0.150	0.050	0.050	0.050	0.701	522.9	9.75
0.750	0.126	0.025	0.076	0.076	0.698	534.3	10.38
1	0.100	0	0.099	0.099	0.701	549.9	11.01
Initial Mole Fraction $x_1/x_2 \approx 2$ and $x_5 \approx 0.8$							
0	0.136	0.068	0	0	0.796	471.0	7.41
0.250	0.118	0.050	0.017	0.017	0.798	475.7	8.06
0.499	0.101	0.034	0.034	0.034	0.797	482.1	8.62
0.749	0.084	0.017	0.050	0.050	0.799	493.3	9.35
1	0.067	0	0.067	0.067	0.798	507.8	10.16
Initial Mole Fraction $x_1/x_2 \approx 2$ and $x_5 \approx 0.9$							
0	0.068	0.034	0	0	0.898	416.6	5.74
0.250	0.058	0.025	0.008	0.008	0.900	417.4	5.90
0.501	0.050	0.017	0.017	0.017	0.899	419.1	6.15
0.751	0.042	0.008	0.025	0.025	0.899	421.5	6.38
1	0.033	0	0.034	0.034	0.900	424.9	6.62
Initial Mole Fraction $x_1/x_2 \approx 5$ and $x_5 \approx 0.6$							
0	0.327	0.066	0	0	0.608	530.9	7.61
0.251	0.312	0.049	0.016	0.016	0.605	535.1	8.15
0.501	0.301	0.033	0.033	0.033	0.598	542.5	8.46
0.751	0.289	0.017	0.051	0.051	0.592	554.8	9.04
1	0.261	0	0.065	0.065	0.608	569.8	9.45
Initial Mole Fraction $x_1/x_2 \approx 5$ and $x_5 \approx 0.7$							
0	0.248	0.049	0	0	0.702	512.0	7.79
0.249	0.234	0.037	0.012	0.012	0.704	515.5	8.03
0.502	0.224	0.025	0.025	0.025	0.701	520.5	8.41
0.749	0.210	0.012	0.037	0.037	0.704	529.9	8.69
1	0.198	0	0.050	0.050	0.701	542.4	9.23
Initial Mole Fraction $x_1/x_2 \approx 5$ and $x_5 \approx 0.8$							
0	0.164	0.034	0	0	0.802	472.0	6.83
0.250	0.158	0.025	0.008	0.008	0.800	475.6	7.22
0.499	0.150	0.017	0.017	0.017	0.800	480.8	7.69
0.743	0.143	0.009	0.025	0.025	0.798	488.3	8.03
1	0.136	0	0.033	0.033	0.798	498.1	8.46
Initial Mole Fraction $x_1/x_2 \approx 5$ and $x_5 \approx 0.9$							
0	0.083	0.016	0	0	0.900	417.3	5.41
0.250	0.080	0.013	0.004	0.004	0.899	418.4	5.54
0.498	0.075	0.008	0.008	0.008	0.899	419.3	5.71
0.750	0.071	0.004	0.013	0.013	0.899	421.1	5.85
1	0.067	0	0.017	0.017	0.899	423.5	5.97
Initial Mole Fraction $x_1/x_2 \approx 10$ and $x_5 \approx 0.6$							
0	0.361	0.036	0	0	0.603	537.6	7.69
0.252	0.357	0.028	0.009	0.009	0.596	541.1	7.87
0.494	0.347	0.019	0.018	0.018	0.597	547.8	8.11
0.752	0.340	0.009	0.028	0.028	0.596	555.6	8.32
1	0.328	0	0.036	0.036	0.600	566.7	8.62
Initial Mole Fraction $x_1/x_2 \approx 10$ and $x_5 \approx 0.7$							
0	0.265	0.026	0	0	0.709	515.2	7.70
0.250	0.263	0.020	0.007	0.007	0.703	516.8	7.91
0.499	0.260	0.014	0.014	0.014	0.699	519.9	8.13
0.754	0.254	0.007	0.021	0.021	0.697	525.1	8.37
1	0.241	0	0.027	0.027	0.705	530.3	8.56
Initial Mole Fraction $x_1/x_2 \approx 10$ and $x_5 \approx 0.8$							
0	0.184	0.019	0	0	0.797	474.2	7.41
0.250	0.178	0.014	0.004	0.004	0.799	474.8	7.63
0.497	0.174	0.009	0.009	0.009	0.798	479.3	7.81
0.744	0.167	0.005	0.014	0.014	0.801	483.5	8.08
1	0.170	0	0.019	0.019	0.793	488.4	8.29
Initial Mole Fraction $x_1/x_2 \approx 10$ and $x_5 \approx 0.9$							
0	0.089	0.009	0	0	0.902	422.3	5.84
0.254	0.090	0.007	0.002	0.002	0.899	423.1	5.91
0.505	0.084	0.004	0.004	0.004	0.902	424.3	6.05
0.766	0.084	0.002	0.007	0.007	0.899	425.8	6.12
1	0.083	0	0.010	0.010	0.898	427.4	6.24

acylation extent. The critical temperature of reacting mixture also increases with the initial ratio x_1/x_2; however, the reacting mixture with $x_1/x_2 = 10$ exhibits a lower critical pressure than that with $x_1/x_2 = 5$.

With carbon dioxide as a solvent ($x_5 = 0.7$), the critical temperature of reacting mixture lies between 504 K and 530 K, and the critical pressure is between 19.5 MPa and 22.2 MPa, which indicated that high temperature and pressure were still necessary to conduct the anisole acylation with acetic anhydride under supercritical condition. Although the critical temperature of the reacting mixture can be reduced to below 443 K through increasing the content of carbon dioxide (x_5) to 0.9 (Table 2), the critical pressures are still at a high level. Moreover, the critical properties of the reacting mixture change violently with the reaction extent and initial composition; this is unfavorable for regulating the reaction under supercritical conditions near the critical point of reacting system in the course of reaction.

Critical Properties of the Nominal Reacting Mixture of Anisole Acylation with Acetic Anhydride in the Presence of Propane. With propane as an additional solvent, the critical properties of the nominal reacting mixture of anisole acylation with acetic anhydride (quinary mixture) of anisole (1) + acetic anhydride (2) + *p*-MAP (3) + acetic acid (4) + propane (5) were determined with the composition representing the extent of acylation (conversion of acetic anhydride), with the mole fraction of propane (x_5) being 0.6 to 0.9 and the initial mole ratio of anisole to acetic anhydride (x_1/x_2) being 2 to 10, respectively, as shown in Table 3 and Figures 2 and 3.

Similar to using carbon dioxide as a solvent, the critical properties of the reacting mixture here depend also on the reaction extent, initial x_1/x_2, and the content of propane. Both the critical temperature and the pressure increase with acylation extent but decrease with the increase of propane content in the mixture. The influence of initial x_1/x_2 on the critical properties is not so evident except for the reacting mixture with low propane content.

With propane as the solvent (Figures 2 and 3), the critical temperature and pressure of the reacting mixture can be reduced considerably by adjusting the propane content, for example, they are about 423 K and 6 MPa with $x_5 = 0.9$, which is more easily attainable for conducting the reaction under supercritical conditions than using carbon dioxide as the solvent.

Moreover, with propane as the solvent, the span of critical properties along the reaction course decreases with increase of the initial ratio of anisole to acetic anhydride and the content of propane in the mixture. These suggest that a flat critical temperature and pressure of the reacting mixture along the reaction course can be obtained by adjusting the propane content and the ratio of anisole to acetic anhydride. This is helpful to regulate the reaction condition in the vicinity of the critical point of the reacting mixture in the course of reaction, which is often desirable to make the most of the unique characteristics of supercritical fluid.

Because the critical properties change with the reaction extent, the reaction conditions should be tuned up according to the critical properties of the reacting media along the reaction course to ensure that the reaction was carried out under supercritical conditions near the critical point. The reaction conditions should be a compromise of both initial reactants and final products

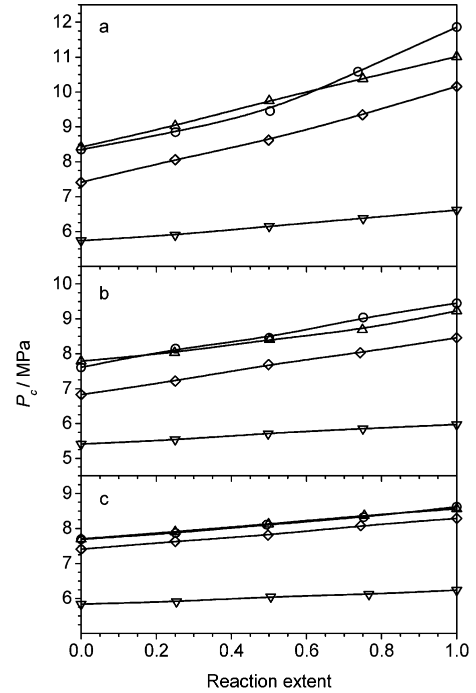

Figure 2. Critical pressure of the nominal reacting mixture (anisole (1) + acetic anhydride (2) + *p*-MAP (3) + acetic acid (4) + propane (5)) along the reaction course of anisole acylation with acetic anhydride in the presence of propane with the initial mole fraction x_5 = ○, 0.6; △, 0.7; ◇, 0.8; ▽, 0.9 and x_1/x_2 = a, 2; b, 5; c, 10.

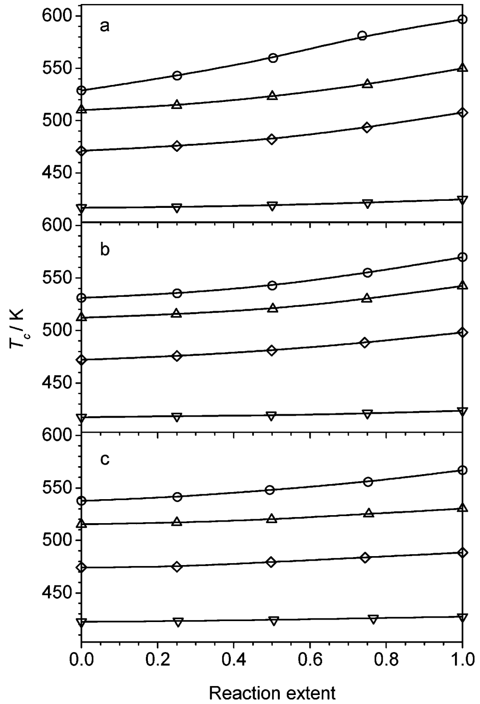

Figure 3. Critical temperature of the nominal reacting mixture (anisole (1) + acetic anhydride (2) + *p*-MAP (3) + acetic acid (4) + propane (5)) along the reaction course of anisole acylation with acetic anhydride in the presence of propane with the initial mole fraction x_5 = ○, 0.6; △, 0.7; ◇, 0.8; ▽, 0.9 and x_1/x_2 = a, 2; b, 5; c, 10.

when the reaction is carried out at a fixed temperature and pressure.

It should be noted that some side reactions such as di- or triacylation of anisole may occur along with the acylation of anisole. The critical properties of the actual reacting mixture should then be reevaluated with considering these factors.

Conclusions

The critical properties of the nominal reacting mixture of anisole acylation with acetic anhydride using propane or carbon dioxide as solvent were determined by using a high-pressure viewing cell with visual observation.

The critical properties of the reacting mixture depend on the reaction extent, initial ratio of anisole to acetic anhydride, and content of solvent. The addition of a solvent is an effective way to tune the critical properties of the reacting mixture.

Propane is a more compatible solvent than carbon dioxide in anisole acylation with acetic anhydride under supercritical conditions. The critical temperature and pressure of the reacting mixture can be reduced considerably through the addition of proper content of propane. Moreover, a flat critical temperature and pressure along the reaction course can be obtained by adjusting the propane content and the ratio of anisole to acetic anhydride, which is favorable for regulating the reaction under supercritical conditions near the critical point of reacting system in the course of reaction.

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