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journal homepage: [www.elsevier.com/locate/jiec](http://www.elsevier.com/locate/jiec)1 One-step and *in-situ* catalytic synthesis of acrylates from acetates  
2 (or propionates) and trioxane at room temperature3 Q1 Gang Wang<sup>a,b</sup>, Hui Wang<sup>b</sup>, Chunshan Li<sup>a,b</sup>, Cuncun Zuo<sup>b</sup>, Zengxi Li<sup>a,b,\*</sup>,  
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## ABSTRACT

One-step synthesis of acrylates from acetates and trioxane *via* aldol reaction at 623 K–653 K was reported. But proceeding this process at room temperature is still a challenge due to ester activation and trioxane decomposition. Herein, series of acrylates were firstly achieved, with the one-step and *in-situ* catalytic strategy, from acetates (or propionates) and trioxane at 293 K. Selectivity of product reaches up to 94.4% with a 80.8% yield. <sup>1</sup>H NMR confirmed the soft enolization of ester, the decomposition of trioxane was catalyzed by TMSOTf, and the generated ionic liquid has catalytic performance on aldol condensation step.

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## 9 Introduction

10 Q3 Acrylates as important chemical monomers are widely used in  
11 the manufacture of polymer materials, paints and coatings,  
12 adhesives and textiles [1,2]. Traditional approach to such com-  
13 pounds are mainly acrylonitrile hydrolysis method followed by  
14 esterification process. However, it requires amounts of toxic  
15 hydrogen cyanide and produces ammonium sulfate wastes that are  
16 hard to treat with [3]. Therefore, an alternative route based on  
17 petroleum industry which includes two-step oxidation of propyl-  
18 ene (or isobutene) over mixed metal oxides of Mo–Bi and Mo–V  
19 was developed for acrylic acid production [4–8]. In recent years,  
20 with the depletion of fossil resource and increasing price of  
21 petroleum, coal-based chemicals and its downstream products  
22 such as acetates (or propionates) and formaldehyde (or trioxane)  
23 have been paid more attention to. Aldol condensation as a key and  
24 efficient reaction is universally adopted in organic synthesis for  
25 C–C bond construction [9–14]. Thus a new potential pathway for

26 fabricating acrylates from acetates (or propionates) and trioxane  
27 *via* one-step gaseous aldol reaction have been deeply investigated.  
28 And significant progress have also been achieved in one-step  
29 synthesis of methyl acrylate (MA) and methyl methacrylate (MMA)  
30 at temperatures ranging from 623 K to 653 K with the yield and  
31 selectivity of about 50% and 95% [15–18]. Although numerous  
32 catalysts have been designed for aldol reaction [19–22], a  
33 significant breakthrough, up to now, has not been made yet on  
34 one-step catalytic synthesis of acrylates from acetates (or  
35 propionates) and trioxane at room temperature due to ester  
36 activation and trioxane decomposition.

37 Typically, trioxane could be decomposed with the catalysis of  
38 protonic acid in water or alcohol solution [23–26], which are  
39 unable to activate esters. Strong bases, such as potassium *tert*-  
40 butoxide (KTB) and lithium diisopropylamide (LDA), are often used  
41 to generate active enolates that required for the formation of  
42 carbon–carbon bond. While trioxane cannot be decomposed when  
43 it is treated with such strong bases at room temperature in liquid  
44 phase. According to our previous experimental results, trioxane  
45 should be decomposed into formaldehyde firstly before occurring  
46 aldol reaction with ester [16–18]. So challenges seem to be focused  
47 on ester activation as well as trioxane decomposition at room  
48 temperature. Other than protonic acid, trioxane can also be  
49 decomposed with the catalysis of cationic initiators [23]. Silyl enol  
50 ether as an active intermediate of ester, which is widely used in

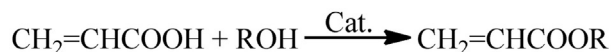
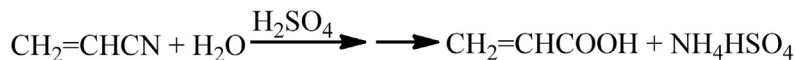
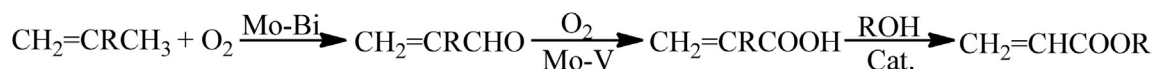
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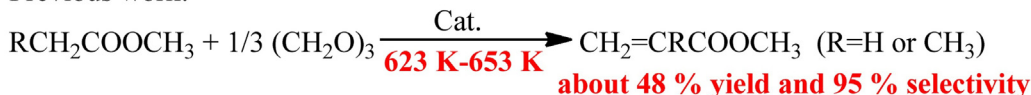
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**(1) Traditional acrylonitrile hydrolysis method****(2) Propylene oxidation route****(3) Coal-based process**

Previous work:



This work:



Scheme 1. Method for synthesis of acrylates.

two-step Mukaiyama aldol reaction, is easier to undergo C–C coupling reaction with aldehydes [27–30]. In addition, ionic liquids regarded as efficient and potential catalysts often have been used in organic catalysis including aldol condensation [31–33].

With these in mind, one-step and *in-situ* catalytic synthesis of acrylates from acetates (or propionates) and trioxane *via* aldol reaction at 293 K (Scheme 1) was firstly developed with the yield and selectivity of 80.8% and 94.4% in present study. Herein, relatively moderate basic trialkylamine, rather than LDA or KTB, was utilized with trimethylsilyl trifluoromethanesulfonate (TMSOTf) to promote the soft enolization of esters. And the decomposition of trioxane was catalyzed with TMSOTf. The aldol condensation between enolates and decomposed formaldehyde was *in-situ* catalyzed with the generated ionic liquid. The effect of solvent, base and silicon reagent on enolization step were systematically investigated and explained. Also the catalytic mechanism of TMSOTf and generated ionic liquid was proved respectively.

**Experimental***General synthesis reaction*

All synthesis reactions were carried out in a round-bottomed flask under 1 atm and the air in flask was replaced with N<sub>2</sub> before the dehydrated reagents were added into it. The reaction mixture was kept at 293 K with a temperature-controlled water bath equipped with magnetic stirring. And typical reaction solutions consisted of about trioxane (0.08 M in solvent, 0.5 mmol), ester, solvent, amine, TMSOTf and octane that used as internal reference for determining conversion and yield. To keep molar concentrations consistent, solutions for reactions with other reagents were prepared to have the same concentration of trioxane (0.08 M, 0.5 mmol). The general molar ratio of formaldehyde (from trioxane) to ester, TMSOTf and amine was 1:3:4.5:4.5. The mixture

of solvent, trioxane, ester, amine and octane (about 5 mol.%) were added into the flask after the air was removed with N<sub>2</sub>, and the TMSOTf was carefully added with a suitable stirring speed. Product samples were periodically collected and the formed solids were removed using a Millipore PTFE syringe filter before analysis with GC–MS.

*Silyl enol ether formation studies*

The reaction solution for silyl enol ether formation study was prepared with methyl acetate (0.72 M in solvent, 4.5 mmol) and base (with the molar ratio of 1.5 to methyl acetate) in a solvent. The mixture was sealed in a flask at 293 K after the air was removed with N<sub>2</sub>, then the silicon reagent in the molar ratio of 1.5 to methyl acetate was carefully added with suitable stirring. Samples were collected and the formed solids were removed with Millipore PTFE syringe filter. And then the samples dissolved in CDCl<sub>3</sub> were analyzed with <sup>1</sup>H NMR on AVANCE 600 MHz. <sup>1</sup>H NMR of the 1-methoxy-1-trimethylsilyloxyethene (600 Hz): 0.06 ppm (9H, s, –Si(CH<sub>3</sub>)<sub>3</sub>), 3.05 ppm (1H, d, =CH<sub>2</sub>), 3.07 ppm (1H, d, =CH<sub>2</sub>), 3.58 ppm (3H, s, –OCH<sub>3</sub>), which was in accordance with the reported data [34].

*Products analysis*

Product samples were analyzed with GC–MS (6890N/5975B, Agilent Technologies) equipped with a HP-5 column (30 m, 0.32 mm, 0.25 μm). Products were identified by comparison to standards and MS information. The conversion of trioxane and yield of product based on trioxane could be calculated by using cyclohexane (about 10 wt.%) as internal standard.

$$\text{Conv. \%} = \frac{C_{\text{trioxane}-0} - C_{\text{trioxane}-t}}{C_{\text{trioxane}-0}} \times 100\% \quad (1)$$

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