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Acrylates via Metathesis of Crotonates

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KEYWORDS: Acrylate, bio-based, crotonate, metathesis, poly-3-hydroxybutyrate (P3HB).

ABSTRACT

Crotonic acid has the potential to be produced from renewable resources at low cost, but has currently a limited market. We are investigating catalytic routes to exploit the functionalities of crotonic acid to produce a range of established industrial chemicals. Here we report our work on converting crotonates to acrylates, where a cost-competitive bio-based alternative can provide a market advantage. Our optimized cross-metathesis reaction conditions between crotonates and ethylene resulted in an increase of catalyst turn-over numbers by two orders of magnitude as compared to literature values. Control experiments showed the cross-metathesis with ethylene to be an equilibrium reaction. The turn-over number limiting factor was found to be the stability of the metathesis catalyst.

Introduction

Acrylic acid and acrylates are important industrial chemicals from which many products are manufactured.[1] Current industrial processes synthesize these molecules from fossil resources (oil, coal, natural gas),[1] which are not renewable within a human time scale.[2] Thus, pathways to provide "bio-based" acrylates starting from biological materials are being developed.[3-10] In order to access bio-based acrylates, we are pursuing two pathways. One involves the production of poly-3-hydroxypropionate (P3HP), a member of the polyhydroxyalkanoate family of bio-polymers, in a microbial organism, followed by its thermolysis/pyrolysis to provide acrylic acid[8,9] or alcoholysis to provide acrylates.[9] A related approach is the direct fermentative production of 3-hydroxypropionic acid followed by its dehydration.[5-7] Since the production of a bio-based chemical directly from plant biomass has the potential to be cost advantaged, we are investigating a second pathway. We have carried out extensive work to produce poly-3-hydroxybutyrate (P3HB) in the biomass of genetically engineered plants.[11-15] The thermolysis/pyrolysis of P3HB to provide crotonic acid is a well-known process,[16,17] which can be performed directly on P3HB-containing plant biomass.[8,18,19] Crotonic acid has the potential to be a valuable platform chemical, if it can be produced at a low cost, providing access to a range of industrial and fine chemicals such as *n*-butanol,[20] fumaric acid, maleic anhydride, propylene, and acrylic acid/acrylates.[11] As part of our efforts to develop crotonic acid as a bio-based platform chemical derived from P3HB-producing plants,[11,19,20] we investigated the production of acrylates via the olefin metathesis of crotonates. Acrylic acid/acrylates have been previously synthesized via the ethenolysis of crotonic acid, cinnamic acid, or cinnamates,[21,22] diethyl fumarate,[23] and bio-based di-*n*-butyl muconate.[24,25] However, in all of these reactions, only modest turn-over numbers (TONs) (0 to 25) were achieved, thus requiring high catalyst loadings

(2 to 12.5 mol %) to reach high yields. Herein, we report the results of our studies aimed at maximizing the TONs of metathesis catalysts and understanding the parameters influencing the cross-metathesis between ethylene/propylene and crotonates.

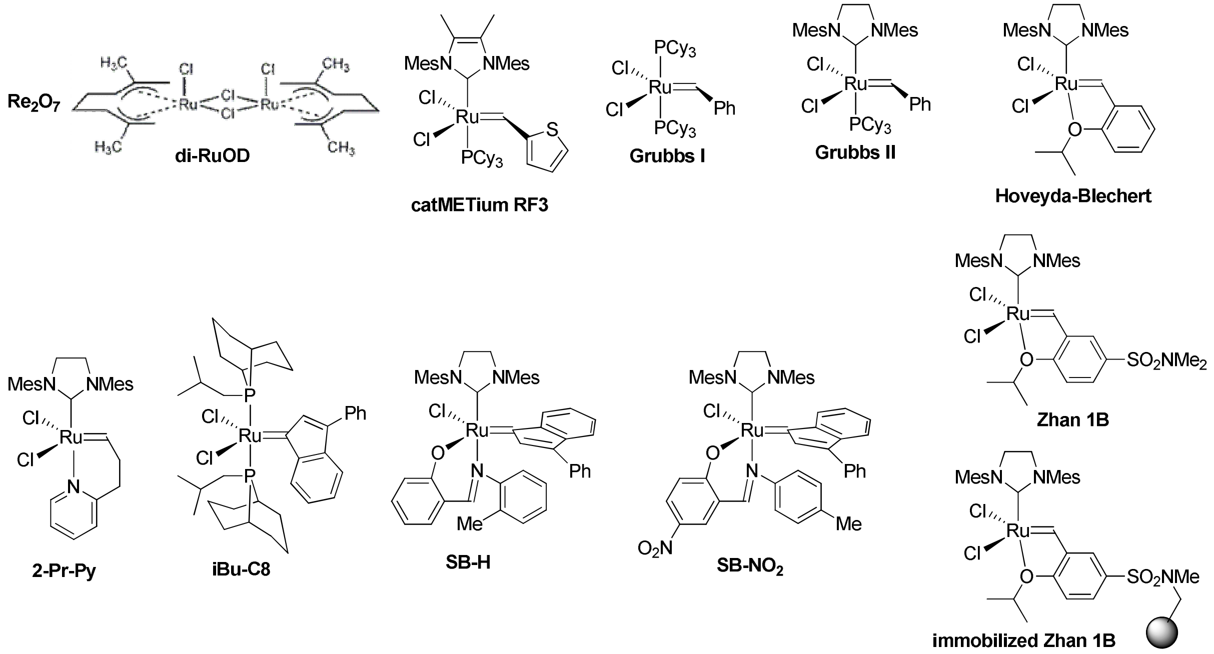


Figure 1. Catalysts evaluated in this study.

Experimental

All utilized chemicals were purchased from commercial suppliers and used as received. Specifically, the metathesis catalysts (Figure 1) were purchased from Aldrich (Grubbs I, CAS number: 172222-30-9; Grubbs II, 246047-72-3; Hoveyda-Blechert,[26] 301224-40-8; 2-Pr-Py, 802912-44-3) and Strem Chemicals (Re_2O_7, 1314-68-7; di-RuOD, 34801-97-3; catMETium RF3, 1190427-50-9; Zhan 1B, 918870-76-5; immobilized Zhan 1B; iBu-C8, 894423-99-5; SB-

H, 934538-12-2; SB-NO_2, 934538-04-2). Ethylene (Chemical Pure grade, p_{max} ~ 255 psi) and propylene (polymer-grade, p_{max} ~ 115 psi) were purchased from Airgas.

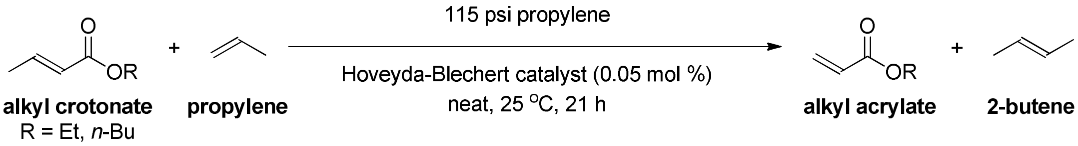
The self-metathesis experiments were performed in sealed tubes: the neat substrate (2 g, ethyl crotonate or ethyl acrylate) or a solution of the substrate in dioxane (2 g in 6 g dioxane, crotonic acid or acrylic acid) and the catalyst (~ 20 mg) were held under stirring at room temperature overnight. The reaction mixtures were analyzed using HPLC. All metathesis reactions using a gas as one of the reactants were conducted in a 5522-series Parr reactor. To the Parr reactor internal glass vessel were added the substrate (0.35 mol, ethyl crotonate, *n*-butyl crotonate, or ethyl cinnamate) followed by a weighted amount of catalyst. After assembly of the Parr reactor, under stirring, its contents were degassed 3 times with N_2 (80 to 10 psi). The internal pressure was now allowed to lower to 0 psi, at which point the metathesis partner gas (ethylene or propylene) was introduced up to the desired pressure. Following the disconnection of the gas cylinder, the contents of the Parr reactor were heated to the desired temperature for the desired amount of time. After cooling to room temperature, the Parr reactor was opened, and a sample of the reaction solution was analyzed by HPLC. Detailed HPLC methods, all numerical results, and selected chromatograms are provided in the supporting information.

Results and Discussion

Ethylene-free Reaction

Ruthenium olefin metathesis catalysts are known to be unstable in the presence of ethylene.[27-31] If, however, steps are undertaken to remove ethylene from the reaction mixture long catalyst life times can be realized.[32] We thus decided to investigate the cross-metathesis between alkyl crotonate and propylene (Scheme 1) using the Hoveyda-Blechert catalyst (Figure 1),[33,34] which proved to be one of the more active catalysts examined herein, vide infra. Such a process provides the advantage that the initial metathesis products are alkyl acrylate and 2-butene, meaning that "the metathesis catalyst is never exposed to ethylene and is therefore" expected "to maintain the high reaction rates and high yields needed for industrial biochemical processes".[8]

Scheme 1. Cross-metathesis between alkyl crotonate and propylene



Surprisingly, only a relatively small amount of alkyl acrylate was formed in each case (R = Et: 1.6 % yield, TON = 32; R = *n*-Bu: 4.8 % yield, TON = 96). It is thus of interest to understand the parameters influencing the cross-metathesis between alkyl crotonate and ethylene/propylene.

Catalyst Screen of Self-Metathesis Reactions

In order to determine the relative catalytic ability of various metathesis catalysts (Figure 1) the self-metathesis reactions of ethyl crotonate (EtCr), ethyl acrylate (EtAc), crotonic acid (CA), and acrylic acid (AA) were chosen as test reactions (Scheme 2).

Scheme 2. Self-metathesis catalyst and substrate screening experiments

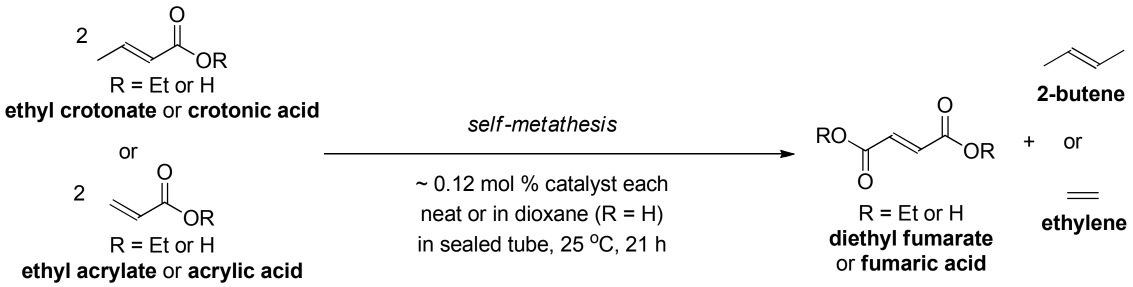


Table 1. Selected results of the self-metathesis screening experiments[a]

	Amount of Diethyl Fumarate / Fumaric Acid Self-Metathesis Product [Area %]			
	Substrate			
Catalyst	**EtCr**	**EtAc**	**CA**	**AA**
catMETium RF3	NR	4.4	NR	0.1
Grubbs II	0.2	13.5	0.1	1.3
Hoveyda-Blechert	NR	22.9	NR	7.7
Zhan 1B	0.1	24.7	0.1	4.7
2-Pr-Py	NR	7.0	NR	1.0

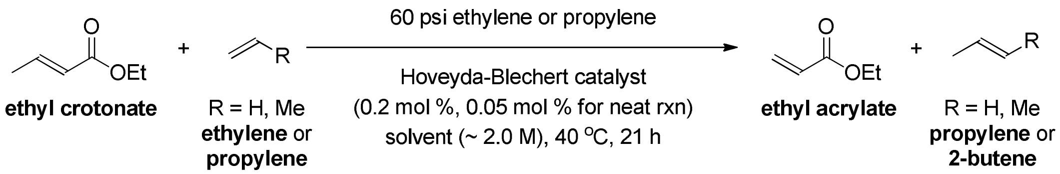
[a] Reaction conditions as denoted in Scheme 2. NR = < 0.1 area % of product present.

The reaction mixtures were analyzed by HPLC and the catalytic ability of each catalyst was judged by the observed peak area of the diethyl fumarate or fumaric acid product. Only catalysts catMETium RF3, Grubbs II, Hoveyda-Blechert, Zhan 1B, and 2-Pr-Py provided a significant amount of product (Tables 1 and S-5). Using ethyl acrylate as the starting material provided an order of magnitude larger amount of self-metathesis product than did acrylic acid, whereas ethyl crotonate provided a two orders of magnitude smaller amount of product as compared to ethyl acrylate. These results may reflect differences in the equilibrium compositions[35] resulting from these substrates and the reduced stability of metathesis catalysts in a protic environment.[21,22]

Solvent Screen of the Cross-Metathesis

Since the Hoveyda-Blechert catalyst is one of the most active catalysts of our study (Tables 1 and S-5), it was used in the investigation of the solvent dependence of the cross-metathesis between ethyl crotonate and ethylene or propylene (Scheme 3).

Scheme 3. Solvent screen of the cross-metathesis between ethyl crotonate and ethylene or propylene



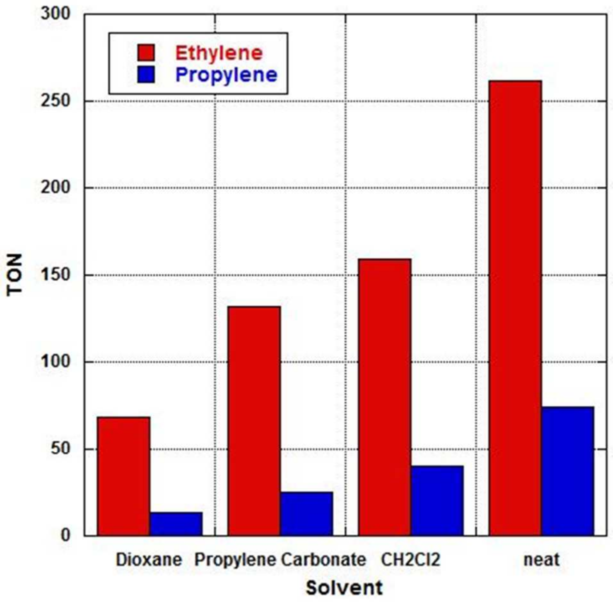


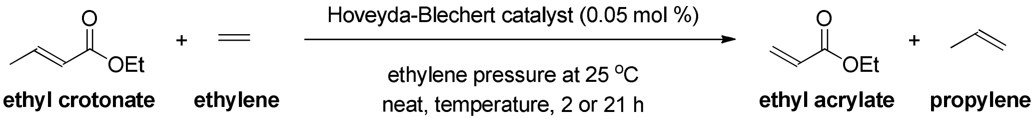
Figure 2. Results of the solvent screen of the cross-metathesis between ethyl crotonate and ethylene or propylene using the Hoveyda-Blechert catalyst (reaction conditions as denoted in Scheme 3).

Importantly, the highest TON was observed when ethyl crotonate was used without any additional solvent (Figure 2). The relative TONs observed in the four screened metathesis solvents are: neat ethyl crotonate substrate >> CH_2Cl_2 > propylene carbonate > dioxane. Notably, in all screened solvents the cross-metathesis using ethylene achieved about a 4-fold larger number of turnovers than the cross-metathesis using propylene. Potential reasons for these different observed TONs are not known, but may include (a) a difference of the ethylene versus propylene reaction rate constant, corresponding to a different amount of reaction that can occur prior to catalyst decomposition, vide infra, (b) a difference in the ethylene versus propylene reaction equilibrium composition, and (c) competing “non-productive” metathesis in the propylene reaction. Experiments to correctly identify these reason(s) are beyond the scope of our study. The results for the solvent dependence of the corresponding cross-metatheses catalyzed by SB-H and SB-NO_2 (Figure 1) are included in the SI (Table S-8). These two metathesis catalysts contain an alkoxide-Schiff-base bidentate ligand. They achieved double digit TONs at 60 °C in neat substrate as the reaction medium, but only single digit TONs at 40 °C, indicative of their higher reactivity at higher temperatures.[36,37]

Temperature and Pressure Screen of the Ethylene Cross-Metathesis

Since ethylene is a better metathesis partner than propylene (Figure 2) and the Hoveyda-Blechert catalyst is one of the most active catalysts of our study (Tables 1 and S-5), the effects of temperature and pressure on the cross-metathesis between ethyl crotonate and ethylene catalyzed by it were investigated (Scheme 4).

Scheme 4. Temperature and pressure screen of the cross-metathesis between ethyl crotonate and ethylene



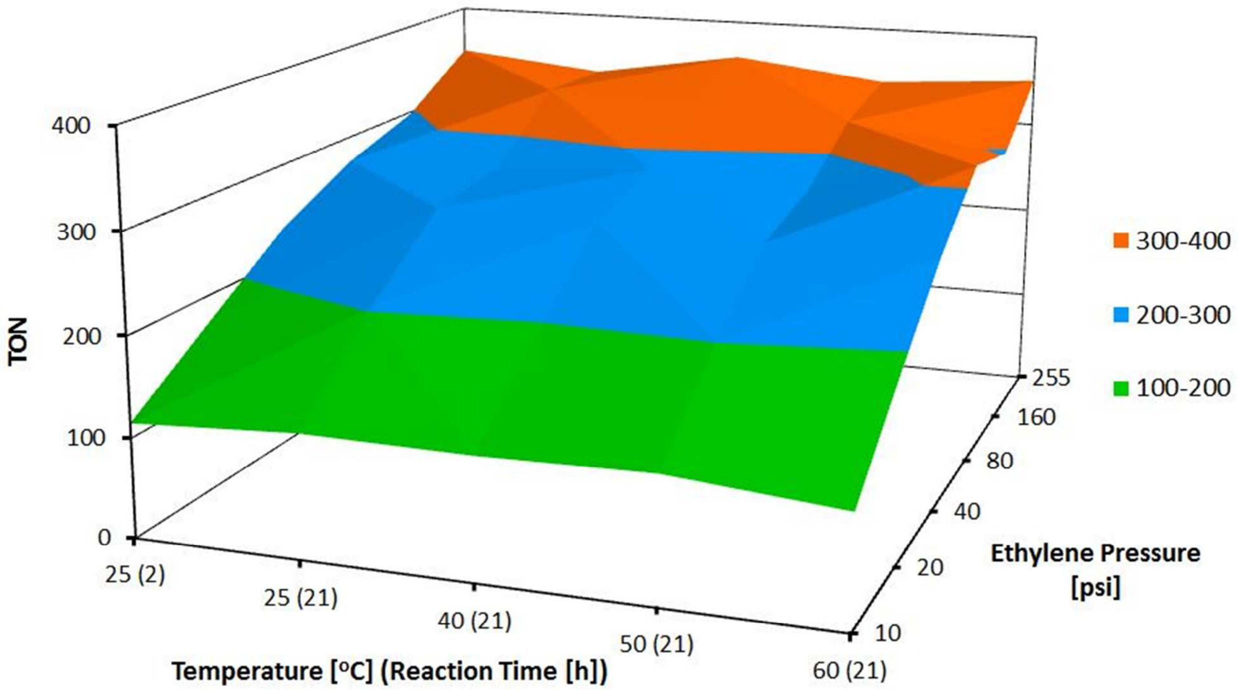


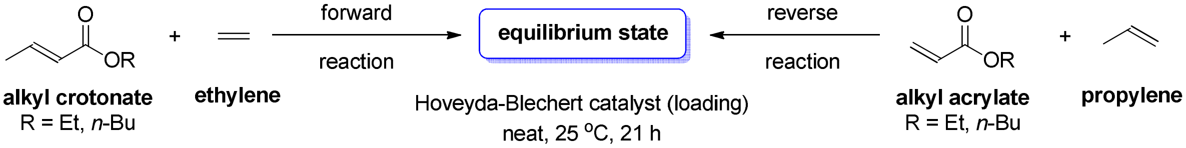
Figure 3. Contour map of the experimental results of the temperature- and pressure-dependent cross-metathesis between ethyl crotonate and ethylene using the Hoveyda-Blechert catalyst (reaction conditions as denoted in Scheme 4).

Two main conclusions can be derived from the results of these experiments (Figure 3). Firstly, significant catalyst decomposition must be occurring within the first 2 h of the metathesis reaction, since the observed TON of the room temperature reaction after 2 h is not much lower than the TON of the room temperature reaction after 21 h. Secondly, the ethylene pressure utilized determines the amount of conversion of starting material occurring, as quantified by the TON achieved.[38] Our finding of a steady increase of the observed TON as a function of the ethylene pressure contradicts previously published work, wherein a maximum TON of 5.8 was observed for the cross-metathesis of cinnamic acid with ethylene at just 7.3 psi of ethylene pressure.[21,22] In comparison to the effect of ethylene pressure on the result of this metathesis reaction, temperature does not have any apparent effect. These results show that in the case of the Hoveyda-Blechert catalyst, the cross-metathesis of ethyl crotonate with ethylene proceeds best when conducted at room temperature using the maximum possible ethylene pressure (255 psi) which could be applied using the equipment available for our study. The numerical TONs for all experiments of Figure 3 are included in the SI (Table S-9).

Cross-Metathesis Equilibrium Determination

Metathesis reactions are in general equilibrium reactions.[35] Although catalyst decomposition occurs under our reaction conditions, knowledge of the equilibrium state is necessary for the design of a commercially relevant process. A commercial alkyl crotonate to alkyl acrylate process would consist of two unit operations: a cross-metathesis of the alkyl crotonate with either ethylene or propylene over an immobilized catalyst followed by a distillative separation step to isolate the desired alkyl acrylate product from the equilibrium amount of alkyl crotonate starting material.[39] In this scenario, the metathesis catalyst is not exposed to the elevated temperatures necessary for the distillation. Unreacted alkyl crotonate starting material, combined with fresh starting material, can be subjected to another round of cross-metathesis.

Scheme 5. Equilibrium determination of the cross-metathesis between ethyl or *n*-butyl crotonate and ethylene



By approaching the metathesis equilibrium from both the forward and reverse direction using increasing catalyst loadings (Scheme 5), linear relationships between the amounts of both the starting material and product as a function of the catalyst loading were obtained (Tables S-10), allowing calculation of the approximate equilibrium compositions (Table 2).

In both the ethyl and *n*-butyl system, the metathesis equilibrium state is characterized by a near 3/2 alkyl crotonate to alkyl acrylate ratio, representing the maximum achievable amount of alkyl acrylate via the reaction of alkyl crotonate with ethylene, if no product is continuously removed from the reaction mixture. Separation of the alkyl acrylate product from the reaction mixture containing an excess of alkyl crotonate is necessary as a consequence of the equilibrium state of this metathesis reaction.

Interestingly, in comparison to the equilibrium state of the ethyl ester metathesis reaction (35.8 mol % of ethyl acrylate) the equilibrium state of the *n*-butyl ester metathesis reaction (39.6 mol % of *n*-butyl acrylate) is shifted by a small amount, 3.8 mol %, towards the product side, indicative of a more hydrophobic environment in the *n*-butyl ester system. As an extension of this observation, it is expected that using an even longer alkyl crotonate ester will result in an even larger amount of alkyl acrylate ester present at equilibrium. Comparing (Table 2) the alkyl crotonate + ethylene = alkyl acrylate + propylene equilibria (Equation 1) with the methyl oleate ethenolysis equilibrium, methyl oleate + ethylene = 1-decene + methyl 9-decenoate (Equation 2),[40] whose equilibrium constant has been determined,[35,41,42] confirms this prediction in that the more hydrophobic environment of methyl oleate results in the shift of its ethenolysis equilibrium to the right side (94.6 mol % each of 1-decene and methyl 9-decenoate).

$$K_{eq} = ([\text{alkyl acrylate}][\text{propylene}])/[\text{alkyl crotonate}] \qquad [\text{Equation 1}]$$

$$K_{eq} = ([\text{1-decene}][\text{methyl 9-decenoate}])/[\text{methyl oleate}] \qquad [\text{Equation 2}]$$

Table 2. Equilibrium compositions of ethenolysis reactions

	at Equilibrium		
Ethenolysis Substrate	**mol % Substrate**	**mol % Product**	**Equilibrium Constant**
Ethyl Crotonate	64.2	35.8	0.20
n-Butyl Crotonate	60.4	39.6	0.26
Methyl Oleate[35,41,42]	5.36	94.64	16.7

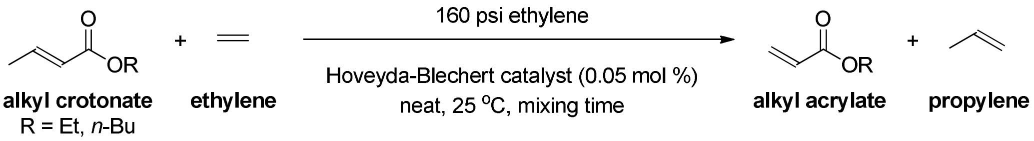
The limited catalyst stability became evident in these two equilibrium determination experiments. Although in both systems a near identical equilibrium state is approached, in the *n*-butyl ester system more conversion occurred prior to the catalyst loosing activity, i.e., the equilibrium was reached at an apparent catalyst loading of 0.34 mol % (Figure S-10-*n*-Bu), whereas in the ethyl ester system the equilibrium was reached at an apparent catalyst loading of

0.53 mol % (Figure S-10-Et). It is thus of interest to determine the time course of the ethylene metathesis, i.e., for how long conversion to product occurs before the catalyst loses activity (decomposes).

Time-Course of the Cross-Metathesis with Ethylene

To determine the stability of the Hoveyda-Blechert metathesis catalyst under the reaction conditions, the time course of the cross-metathesis of ethylene with ethyl crotonate and *n*-butyl crotonate was investigated using a series of independent experiments (Scheme 6).

Scheme 6. Time-dependent cross-metathesis between ethyl or n-butyl crotonate and ethylene



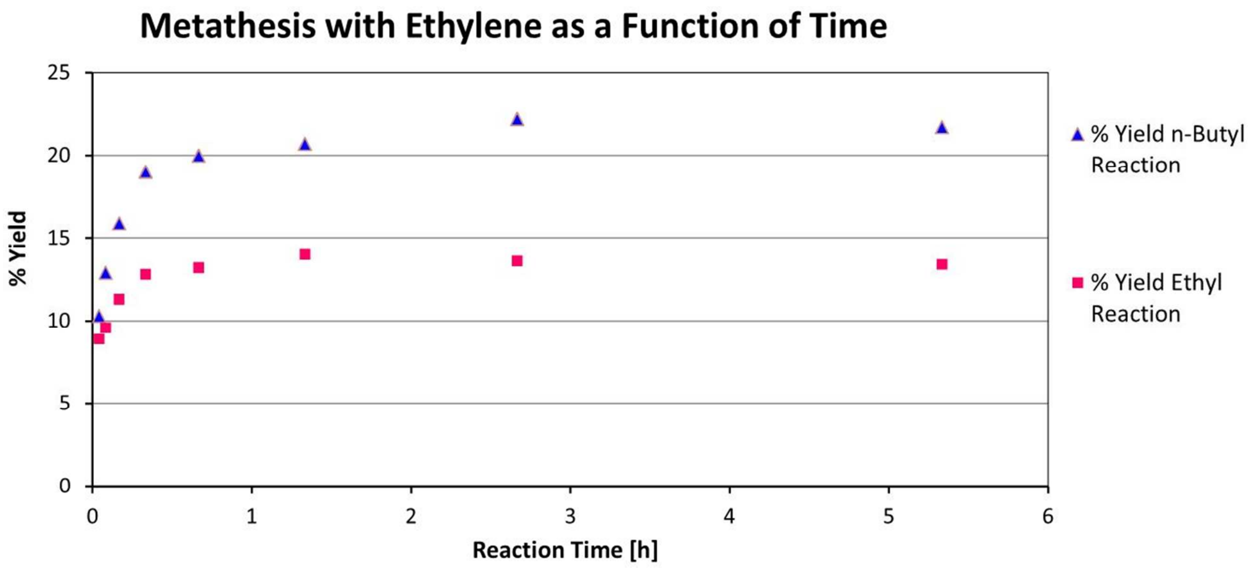


Figure 4. Results of the time-dependent cross-metathesis between ethyl or *n*-butyl crotonate and ethylene catalyzed by the Hoveyda-Blechert catalyst (reaction conditions as denoted in Scheme 6). Each data point is the end point of an experiment which was stopped at the indicated time.

It was found that the ethylene metathesis with ethyl crotonate reached maximum yield within 1.3 h, whereas the corresponding reaction with *n*-butyl crotonate occurred for up to 3 h (Figure 4). Ceasing of product formation, while the equilibrium has not yet been reached, is indicative of the catalyst having undergone decomposition. These results show that the Hoveyda-Blechert catalyst is more stable in *n*-butyl crotonate than in ethyl crotonate. It can catalyze more reaction cycles in *n*-butyl crotonate, TON = 444 under our reaction conditions (t = 2.67 h experiment), than in ethyl crotonate, TON = 280 (t = 1.33 h experiment), before it decomposes. The higher catalyst stability in *n*-butyl crotonate as the solvent, as compared to ethyl crotonate, is also evident in the equilibrium determination experiments previously discussed. In comparison, since methyl oleate is more hydrophobic than *n*-butyl crotonate, even longer catalyst life times are realized in it, allowing the achievement of one order of magnitude higher ethylene metathesis

TONs.[41,43-45] The numerical TONs for all time-dependent cross-metathesis experiments are included in the SI (Table S-11).

Reaction Pathway Control Experiments

An alternative mechanistic pathway for the formation of alkyl acrylate from alkyl crotonate could occur via dialkyl fumarate as an intermediate: a self-metathesis of alkyl crotonate to form butylene and dialkyl fumarate followed by its cross-metathesis/cleavage with ethylene to provide two equivalents of alkyl acrylate (Scheme S-12). To test this hypothesis, neat ethyl crotonate was exposed to metathesis catalyst without any metathesis partner gas being present (0.1 % yield, TON 1) and neat diethyl fumarate was exposed to the maximum possible pressure of ethylene (255 psi), which was available for our study, in the presence of metathesis catalyst (1.0 % yield, TON 20).[23] The results of these two control experiments demonstrate that, while some reaction products were detected, the pathway via dialkyl fumarate as an intermediate does not significantly contribute to the formation of alkyl acrylate from alkyl crotonate in the presence of ethylene.

Optimal Reaction Temperature of Metathesis Catalysts

The temperature- and pressure-dependent experiments presented above for the Hoveyda-Blechert catalyst show that it catalyzes the cross-metathesis of ethyl crotonate with ethylene best when the reaction is conducted at room temperature under the maximum possible ethylene pressure (255 psi) available for our study. Using the ethenolysis of *n*-butyl crotonate under 255 psi ethylene pressure as the test reaction, the optimal reaction temperature of selected other metathesis catalysts was determined. For comparison, the ethenolyses of ethyl crotonate and ethyl cinnamate[21,22] were then performed at these optimized temperatures. Maximum TONs in the 500s were observed for the ethenolysis of *n*-butyl crotonate (HB and Z1B at 25 °C, 2-Pr-Py at 60 °C), in the 300s for ethyl crotonate (HB and Z1B at 25 °C, SB-H at 120 °C), and in the 100s for ethyl cinnamate (HB and Z1B at 25 °C) (Tables 3 and S-13).

Table 3. Selected results showing the optimal reaction temperature of various ethenolyses[a]

		TON		
		Substrate		
Catalyst	**T [°C]**	***n*-Butyl Crotonate**	**Ethyl Crotonate**	**Ethyl Cinnamate**
Hoveyda-Blechert	25	492	332	125
Zhan 1B	25	537	350	125
2-Pr-Py	60	537	210	73
SB-H	120	356	340	48

[a] 0.05 mol % catalyst, 255 psi ethylene, 21 h.

Conclusions

Our optimized cross-metathesis reaction conditions (neat crotonate substrate, 25 °C, 255 psi ethylene, Hoveyda-Blechert or Zhan 1B catalyst) resulted in an increase of the observed TONs by two orders of magnitude as compared to previously reported values.[21-23,25] Maximum TONs in the 500s were achieved for the ethenolysis of *n*-butyl crotonate, in the 300s for ethyl crotonate, and in the 100s for ethyl cinnamate. Control experiments showed the cross-metathesis with ethylene to be an equilibrium reaction. Thus, a commercially relevant process must include a separation step of the formed product from the equilibrium reaction mixture. The TON limiting factor was found to be the stability of the metathesis catalyst.

Acknowledgements

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Supporting Information. Detailed experimental methods, all numerical results, and selected chromatograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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