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Computational and Experimental Probing of Product Formation and Reaction Energies for the Esterification of Maleic Anhydride Derived Surfactants using Microwave Energy.

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Abstract: The computational and experimental analyses of the esterification of maleic anhydride using straight chain alcohols were used as a model to probe product formation. It was determined that both the monoester and diester products formed under the experimental parameters for alcohols up to 1-propanol. The computational model using semi-empirical calculations found that differences greater than 50 kJ/mol produced the monoester as the sole product. However, when the energy difference was less than 50 kJ/mol, both the diester and monoester were found. This gives a good relationship between experimental data and mathematical calculations for the prediction of product formation.

Keywords: Maleic anhydride, Model, Surfactant, Microwave synthesis

Introduction

The computational analysis of organic reactions is garnering extensive attention. The mathematical understanding of molecular interactions has allowed scientist to predict product formation of novel reactions that may be very expensive or highly reactive [1]. These models also give increased insight into multiple step mechanisms by allowing for stepwise processing of the reaction [2]. Although computational models allow for greater understanding of reaction mechanisms only through experimental testing can these mathematical models be verified [3]. Creation of new models requires very simple reactions to examine product formation. One

simple reaction is that of maleic anhydride and straight chain alcohols which undergoes esterification thereby forming maleic anhydride derived surfactants [4].

Surface active agents, also called surfactants, are of great interest due to their widespread applications ranging from body cleansers to environmental remediation [5]. The synthesis of surfactants often yields various byproducts which can reduce overall manufacturing efficiency. One of the simplest reactions for the production of surfactants is the esterification of maleic anhydride with straight chained alcohols [4]. Not only is this reaction synthetically easy, but it maintains few energetic step to computational model. Additionally, this reaction produces surfactants which are easily polymerizable, called surfmers [6]. Currently, the primary application for surfmers is in the production of emulsion polymers such as latex based materials [7,8]. The coupling of the simplistic reaction mechanism and widespread applications makes them an ideal model for computational analysis of product formation [4].

Historically, the ability to directly probe the energy of reactions has been very difficult. Direct measurement of the energy input from a conventional reaction system, such as a heating mantle, was difficult to impossible due to energy loss to the external environment [9,10]. Recent microwave technology has allowed for the determination of power, pressure, and temperature during microwave syntheses [11,12]. This new computational model should allow for predictions of reaction products for the production of polymerizable surfactants.

Results and Discussion

Experimental analysis of maleic anhydride derived surfmers showed good overall product yield for most alcohols up to 1-hexanol (reaction 6) using the conditions outlined in Table 1. Alcohols containing 6 or less carbons showed yields greater than 50% with 3-pentanol having high overall product yield at 80%. Alcohols with carbon chains numbering 6 or more had reduced monoester formation and no diester formation. Monoester product yields for 1-hexanol and 1-octanol were measured to be 29% with decanol having no product under these microwave conditions.

Table 1. *Reaction products for maleic anhydride derived surfactants.*

| Reaction	Alcohol	Temp (°C)	Time (min)	Microwave Power (W)	Monoester Yield (%)[a]	Diester Yield (%)[a]
1	Methanol	60	5	1151	55	25
2	1-Ethanol	60	5	1184	56	12
3	1-Propanol	60	5	1196	66	2
4	1-Butanol	60	5	1121	77	NA
5	1-Pentanol	60	5	1300	76	NA
6	3-Pentanol	60	5	1489	80	NA
7	1-Hexanol	60	5	1639	29	NA
8	1-Octanol	60	5	1876	29	NA
9	1-Decanol	60	5	2073	NA	NA

[a] Yield determined by peak area using a Varian GC/MS.

This synthesis unexpectedly produced not only the monoester but also the diester product (Figure 1). The diester products were only found in reactions with alcohols containing fewer than 3 carbons (Table 1). The data illustrated longer alcohol chains reduced the production of the diester. An example is observed with a 50% decrease in the diester product when comparing the 1-methanol and 1-ethanol reactions.

Figure 1: *Schematic of mono ester and diester product of maleic anhydride and straight chain alcohol*

R= Me, Et, Prop, But, 1-Pent, 3-Pent, Hex, Oct, Dec
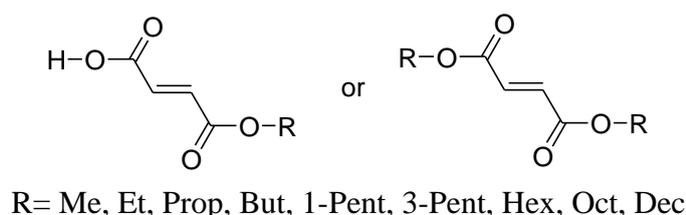
A computation analysis of the generally accepted mechanism for the esterification of maleic anhydride surfactants was conducted to determine if the formation of the diester was a thermodynamically or kinetic driven process. Three steps were proposed for our computational model of this reaction mechanism. The first step is the attachment of the alcohol to the one of the two carboxyl oxygen present in the maleic anhydride molecule to produce 5-Ethoxy-5-

hydroxy-5H-furan-2-one as a intermediate (Figure 2). A comparison of the single point energies of the maleic anhydride to the intermediate shows a net decrease of 262.64 kJ/mol (Figure 2). The second step of the reaction mechanism is the opening of the maleic anhydride ring to produce But-2-enedioic acid monoethyl ester (Figure 2) which has only a 28.85 kJ/mol difference in single point energy.

Figure 2: *General energetic schematic of possible reaction mechanism for mono-ester formation using Maleic Anhydride and Alcohol*
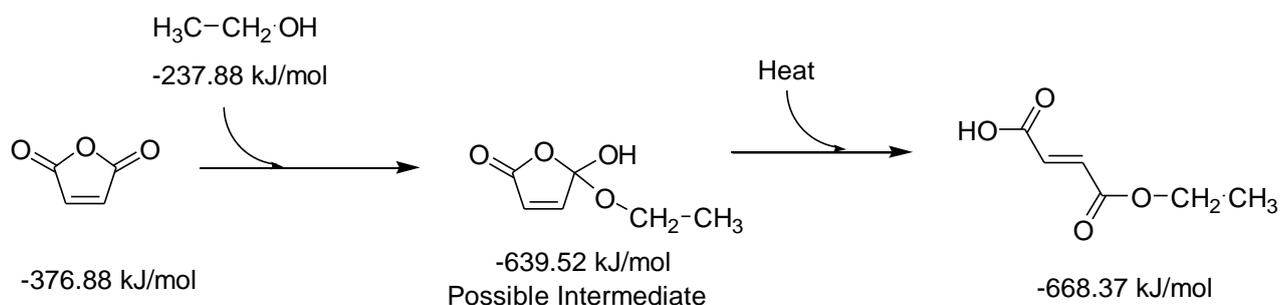
The third step in this process is the addition of an ethanol to the free acid functionality produce 4-Ethoxy-4-hydroxy-but-2-enoic acid ethyl ester as an intermediate (Figure 3). It was calculated that the intermediate had a single point energy of -702.42 kJ/mol.
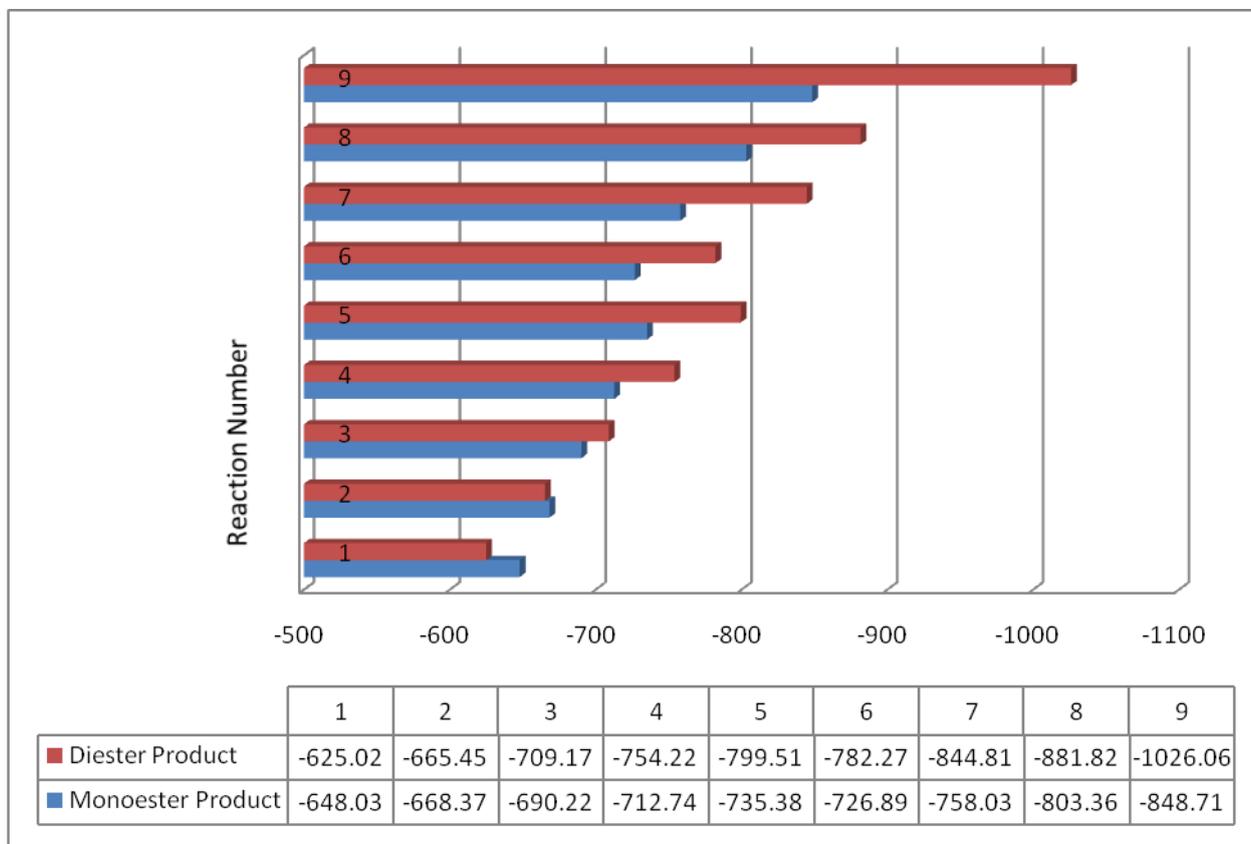
Figure 3: *General energetic schematic of possible reaction mechanism for mono-ester formation using Maleic Anhydride and Alcohol*
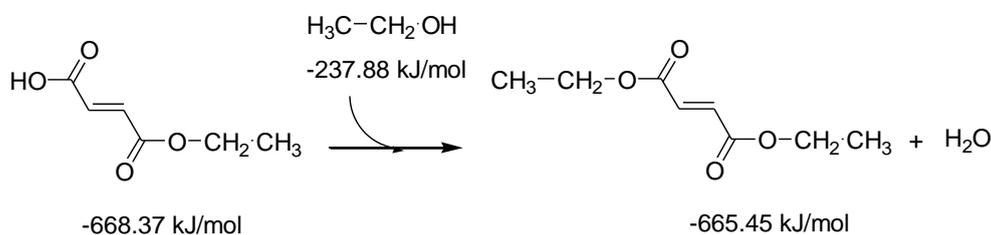

Surprisingly, some of the diester products were found to lower in energy than that of the monester products. A comparison of the monoester/diester products shows that the diesters of (1-Prop, But, 1-Pent, 3-Pent, 1-Hex, 1-Oct, 1-Dec) had lower energies than that of the monoester form. Figure 4 illustrates the theoretical single point energy for both the monoester and diester products as well as the corresponding alcohol for a given reaction. This figure shows very little difference for the monoester and diester product up to 1- propanol (reaction 3) with a difference in single point energy of 19.05 (kJ/mol). With alcohol chains with four or

more carbons, the energy separation doubles becoming significantly large. This large difference seems to correlate to a decrease in diester product formation.

Figure 4: *Comparison of calculated Single Point Energy for Monoester and Diester products*

	1	2	3	4	5	6	7	8	9
■ Diester Product	-625.02	-665.45	-709.17	-754.22	-799.51	-782.27	-844.81	-881.82	-1026.06
■ Monoester Product	-648.03	-668.37	-690.22	-712.74	-735.38	-726.89	-758.03	-803.36	-848.71

The experimental data shows a decrease in diester formation as computational energy differences incresases. Figure 5 show that when experimentally tested, the 1-methanol sample (Reaction 1) had yields of 55% yield for the monoester product and 25% yield for the diester product.   This data correlates to the small difference (23 kJ/mol) in energy betwen the monoester and diester products (Figure 4).   Diester product formation was reduced by half for the 1-ethanol sample. This sample had only a 12% yield of diester while maintaining a 56% monoester yield. Reaction 3 (1-Propanol) also showed minor diester formation while increasing the monoester formation to 66%.

Figure 5: *Monoester vs Diester Product Formation*

	1	2	3	4	5	6	7	8	9
■ Monoester Product	55	56	66	77	76	80	29	29	0
■ Diester Product	25	12	2	0	0	0	0	0	0
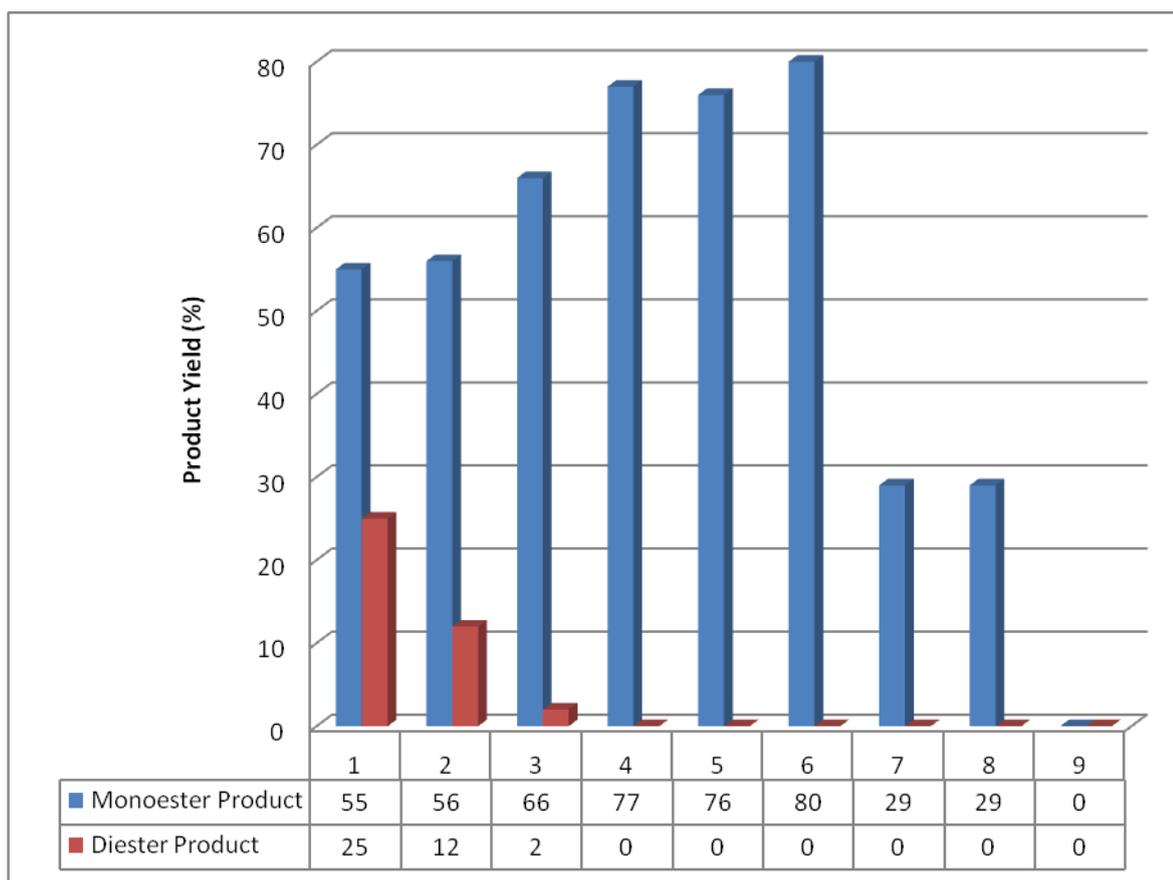
The results suggest that our computation model of the given reaction was able to predict both the monoester and diester formation. The energy difference between the monoester and diester seem to relate to the energy of activation necessary to produce the diester. It was found when minor differences in energies between the monoester and diester products were under 45 kJ/mol the diester was formed. Above 50 kJ/mol difference in single point energy produced decreased diester product formation while increasing monoester yields. Additionally, 1-hexanol showed a marked decrease in the monoester formation. It was assumed that the energy input was not sufficient to cross the threshold of the energy of activation to form high yields of the monoester. Reaction 9 (1-Decanol) showed no identifiable monoester formation. Further

Experimental Section

General: The monomode microwave reactions were carried out in a CEM Discover Microwave. All Gas Chromatograph Mass Spectrometry (GC-MS) were performed using a Varian GC/MS system. All reagents were purchased from Fisher Scientific Company and were used without further purification. The synthesis of the remaining esters uses the general synthesis with the corresponding alcohol.

General Synthesis of But-2-enedioic acid monomethyl and diemethyl ester: Maleic anhydride (1.0 g, 10.0 mmol), methanol (0.33g, 10 mmol) were thoroughly placed in a CEM vial with a magnetic stirrer. The mixture was capped and heated in a CEM Discover microwave for 5 minutes at 60 °C. The sample was rapidly cooled to room temperature yielding a clear liquid and white crystalline solid. The sample was dissolved in 4 ml of acetone and tested using a Varian GC/MS.

Computational Analysis: The single point energy was calculated using SPARTAN® Semi-Empirical Single Point Energy Calculations (PM3).

Acknowledgements

Supplemental Information

Table 1. *Single point energy calculations for the esterification of Maleic Anhydride Derived Surfactants.*

Reaction	Alcohol (substrate)	Alcohol (kJ/mol)	Monoester product (kJ/mol)[a]	Diester Product (kJ/mol)[a]
1	Methanol	-217.05	-648.03	-625.02
2	1-Ethanol	-237.88	-668.37	-665.45
3	1-Propanol	-260.23	-690.22	-709.17
4	1-Butanol	-282.73	-712.74	-754.22
5	1-Pentanol	-305.42	-735.38	-799.51
6	3-Pentanol	-315.96	-726.89	-782.27
7	1-Hexanol	-328.08	-758.03	-844.81
8	1-Octanol	-378.43	-803.36	-881.82
9	1-Decanol	-418.80	-848.71	-1026.06

[a] Energy for Maleic anhydride was calculated to be -376.88.

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