

## **Catalytic Esterification of Acetic Acid with Methanol; Comparison of Photocatalytic and Acid Catalysed Esterification**

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Key words: Reactive Extraction, Methyl Acetate, Photo Catalysis

Prepared for Presentation at the 2004 Annual Meeting, Austin, TX, Nov. 7-12

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November 2004, Unpublished

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### **Abstract**

Methyl acetate is produced through catalytic esterification of acetic acid with methanol. Catalytic acceleration is induced by sulfuric acid or ion exchange resins respectively. Acceptable product yield is obtained by reactive distillation. Separation and isolation of methyl acetate has to overcome two azeotropes (methyl acetate – water and methyl acetate – methanol).

Scope of this project has been the investigation of photocatalytic methyl acetate formation. The process has been compared with esterification with the catalyst sulfuric acid. In both processes methyl acetate was separated from the reaction mixture by extraction and distillation.

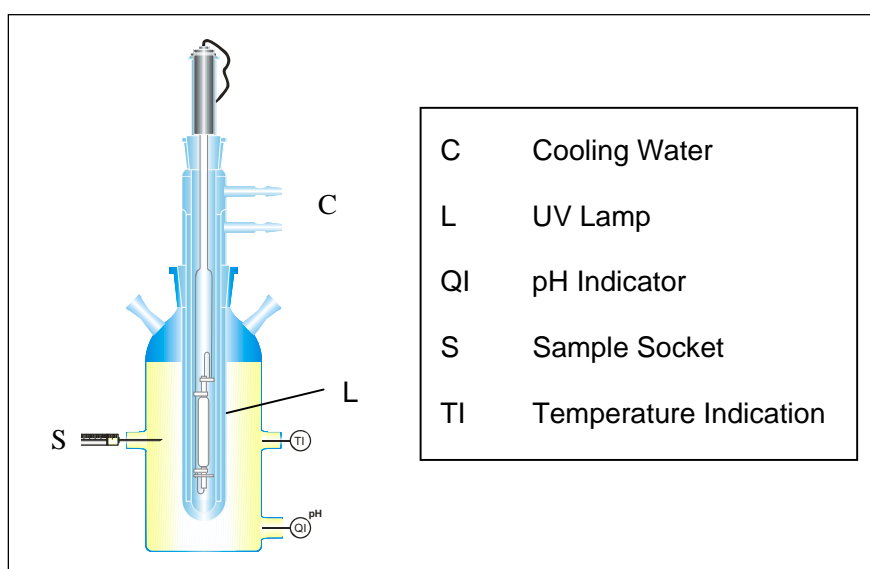
Mixed triarylsulphonium hexafluorophosphate salts (photoacid generator, PAG) are used to cure UV coatings and inks. Since PAG has the ability to generate Brönsted acids under UV irradiation it can promote esterification of acetic acid with methanol. The yield of ester formation can be controlled by extractive separation of the product. Kinetics and yield of the esterification was quantified from balances of the reaction phase and the solvent phase. For reasons of comparability with state of the art catalyst sulfuric acid the latter process was carried out following the same procedure of preparation except UV-activation.

## 1 Introduction

Simultaneous chemical reaction and separation of products in hybrid processes is advantageous over the process performance of separate unit operations. As a result of simultaneous operation capital cost and cost of operation are considerably lowered. Application of hybrid processes is possible when either one of the reaction products has a lower boiling point than the residual substances of a mixture or a higher solubility in a solvent. In latter application high solubility of the solvent for a specific reaction product is needed to decrease its concentration in the reaction mixture. Target of the present project was the investigation of an alternative process route to esterification of acetic acid with methanol by reactive distillation. Performance of methyl acetate formation by reactive extraction was investigated. Esterification was catalysed by an UV-activated photosensitizer.

## 2 Experimental Procedure

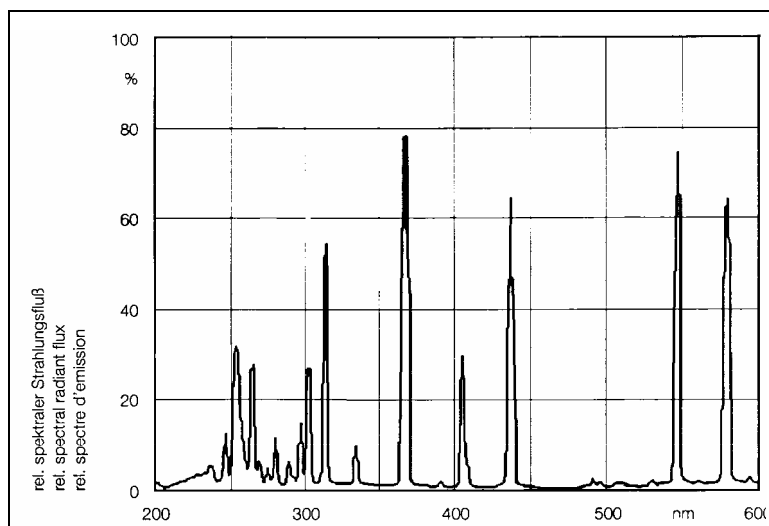
Experiments were carried out in a photochemical reactor (Heraeus company, type UV-RS-2) in lab scale (equipment: reaction vessel with a volume of 850 ml, diameter 0.1 m; water cooled mean pressure UV-lamp) as shown in Figure 1. The reaction vessel was equipped with a magnetic stirrer. Extraction of methyl acetate with n-nonane from the reaction mixture was carried out in the reaction vessel too. For that purpose equivalent amounts (2.5 mole) of methanol and acetic acid plus 500 ml of solvent were mixed in the reaction vessel under irradiation and at constant temperature of  $299\pm 2$  K. Before each experiment was started a specified amount of photo acid generator was added to the reaction mixture. Immediately afterwards the UV lamp was switched on. During each experiment several samples of both phases were taken from the reaction vessel for chemical analysis. During sampling the magnetic agitator was switched off and immediately after phase separation a sample was withdrawn from each phase. Samples were taken over a period of 180 minutes.



**Figure 1:** Experimental set-up of the esterification reactor.

The samples were analyzed with a gas chromatograph, Hewlett-Packard 5960, equipped with a J&W Scientific DBVRX column. The temperature was kept constant at 353 K for 5 min, ramped to 383 at a rate of 5 K/min and then ramped to 523K at a rate of 40 K/min. The final temperature was held constant for 10 min. The temperature of the injection port was adjusted at 523 K and the detector temperature of the FID detector was held constant at 573 K.

To ensure photocatalytic activity over a wide range of the UV spectrum irradiation was applied by a mean pressure UV lamp with an electrical power of 150 Watt (Figure 2).



**Figure 2:** Spectral radiant flux of the UV lamp versus wavelength.

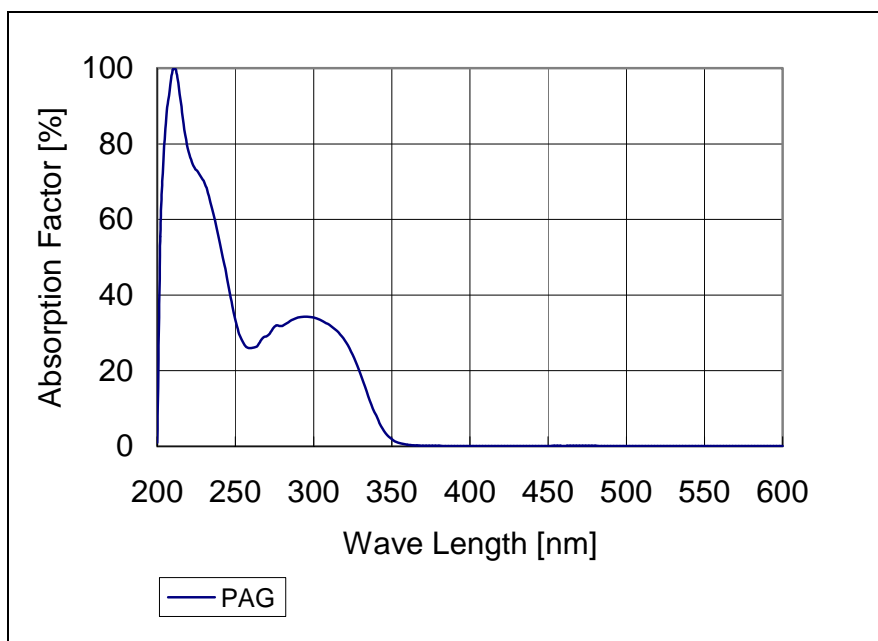
### 3 Results and Discussion

#### 3.1 Photoacid Generators (PAG)

Photoacid generators are substances which can generate acids upon irradiation with UV light. A large number of these substances has been prepared because of their promising applications in the curing technology. Photoacid generators may be divided into two classes, ionic and non-ionic substances. Ionic photoacid generators involve onium salts such as triarylsulfonium and triarylphosphonium salts that contain complex metal halides such as  $\text{AsF}_6^-$  and  $\text{PF}_6^-$ . When onium salts are irradiated at a wavelength within the range of 200-300 nm, they undergo photolysis to form a protic acid as reported by Shirai and Tsunooka (1996). Thermal stability of this class of photoacid generators paired with the possibility of modifying the chemical structure to alter their spectral absorption characteristics demonstrates the main advantages. Mixed triarylsulfonium hexafluorophosphate salts (CYRACURE<sup>®</sup> UVI-6990, Union Carbide) were selected for application in photocatalytic methyl acetate formation (Rohde et.al (2003)).

To verify if the effective spectrum of the PAG is matched with the emission spectrum of the medium pressure lamp the PAG was analyzed in a photometer (Hitachi company, type U-

2010). The comparison of Figure 3 and Figure 2 shows that the UV lamp is able to activate the PAG since it emits over the complete mercury spectrum from 160 nm to about 600 nm.

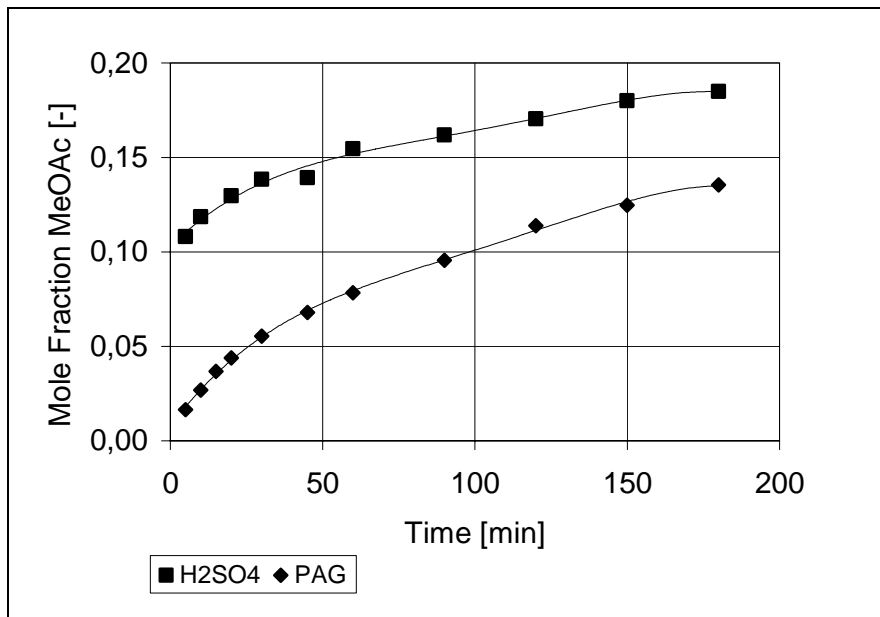


**Figure 3:** Absorption characteristic of the PAG versus wavelength.

### **3.2 Comparison of PAG - accelerated formation of methyl acetate with esterification catalyzed with sulfuric acid**

#### **3.2.1 Reaction Phase**

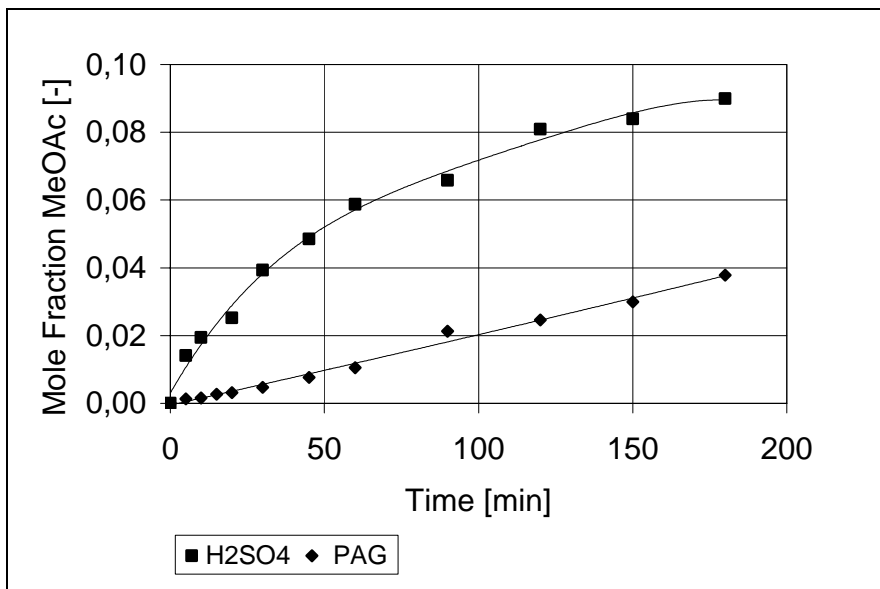
20 g/l PAG was added to the reaction mixture in a first experiment. In a further experiment esterification was carried out with an amount of 12 g/l of the catalyst sulfuric acid. Figure 4 shows that the PAG is able to accelerate esterification of acetic acid with methanol.



**Figure 4:** Comparison of methyl acetate formation in the reaction phase with the catalysts PAG and sulfuric acid; temperature: 299 K; PAG: 20 g/l, sulfuric acid: 12 g/l.

### 3.2.2 Solvent phase

Expectedly the amount of methyl acetate in the solvent phase increased within each experiment. Since less PAG is fed to the reaction mixture than sulfuric acid the amount of methyl acetate in the solvent phase has to be less as well. The solvent composition of both experiments is shown in Figure 5.



**Figure 5:** Comparison of the concentration of methyl acetate in the solvent phase catalyzed by 20 g/l PAG and 12 g/l sulfuric acid respectively.

### 3.2.3 Rate constants

The rate constants for depletion of methanol and acetic acid depending on the amount of PAG-catalyst were calculated. The results were compared with the rate constants of esterification with sulfuric acid. PAG-catalyzed esterification follows a second order reaction according to Equation 10.

$$r_A = k \cdot c_{0,A}^2 \cdot (1 - X_A) \quad (10)$$

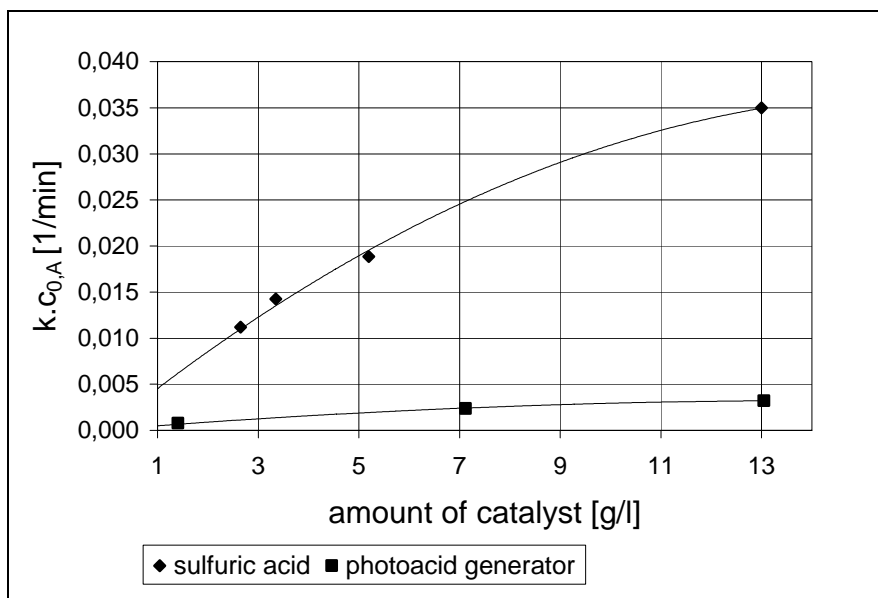
with the feed concentration  $c_{0,A}$  of either methanol or acetic acid based on equimolecular mixture of both substances.

Integration of Equation 10 yields Equation 11:

$$\frac{X_A}{1 - X_A} = k \cdot c_{0,A} \cdot t \quad (11)$$

$$\text{With: } X_A = \frac{X_{0,A} - X_A}{X_{0,A}} = (c_{0,A} - c_A)/c_{0,A} \quad (12)$$

The concentration of the photoacid generator was varied between 1.41 g/l and 13.05 g/l to observe the rate constant while changing the amount of catalyst. The different values for  $k \cdot c_{0,A}$  indicate the dependency of the rate constant on the mass of catalyst. The results were compared with the rate constants obtained with the catalyst sulfuric acid. Data of esterification with the catalyst sulfuric acid are reported elsewhere (Rohde et al. (2002)).



**Figure 6:** Effect of the catalyst concentration of PAG and sulfuric acid on the rate constant of esterification.

## 4 Summary

Target of the present project was to investigate whether indirect photo catalysis is able to accelerate esterification of acetic acid with methanol. The following results have been obtained:

- Esterification of acetic acid with methanol can be catalyzed by indirect photocatalysis with homogeneous catalyst.
- When irradiated with a UV source mixed triarylsulfonium hexafluorophosphate salts generate Brønsted acids which can promote esterification.

## 5 Abbreviations and Symbols Used

$c$	concentration [mol/l]
$c_0$	start concentration [mol/l]
$k$	second order rate constant [l/mol·min]
$r_A$	reaction rate of the educt [mol/l·min]
$t$	reaction time [min]
$T$	temperature [K]
$x$	mole fraction [-]
AcOH	acetic acid
H <sub>2</sub> SO <sub>4</sub>	sulfuric acid
MeOAc	methyl acetate
MeOH	methanol

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