

CHARACTERISATION OF REACTIONS IN SUPERCRITICAL DIFLUOROMETHANE

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Reactions in scCO₂ are frequently limited by the low polarity of the solvent. This may result in low solute/ product solubility or low catalyst activity. The use of more polar sc fluids such as difluoromethane (HFC 32) can circumvent many of these issues and facilitate reactions that are not possible in CO₂. We demonstrate the use of HFC 32 for three types of reaction; an esterification reaction, a Friedel Crafts alkylation and the polymerisation of olefins. The extent of each reaction is monitored using a dielectrometry technique and solution dielectric constants are used to explain unusual observations in reaction rate and product distribution. It is shown that reactions can be tuned more effectively in HFC 32 than CO₂ due to the larger changes in polarisability and hydrogen bonding with pressure. It is, however, shown that in reactions where high solute solubility is observed in both fluids the reaction is unaffected by the solvent and that the clustering of reagent molecules affects the reaction dynamics.

INTRODUCTION

It has been found that reaction rates, yields and selectivity can be adjusted in a sc fluid, by varying the pressure without the need for harsh chemical changes.[1] A common observation of reactions in sc fluids is that local density and/or local composition enhancements are found to affect reaction thermodynamics and, therefore, influence reaction rates. Effects observed include local density augmentation and preferential solvation on the addition of co-solvents. Many papers have been published in this area and there have been some review papers on the topic. [2,3] These local solvation effects are in addition to the fluctuations of the properties of sc fluids normally observed near the critical point.

The majority of reactions have been studied in non-polar solvents such as scCO₂, where reagent solubility and catalyst activity can be significantly affected. To circumvent these issues, a more polar solvent can be used. It has been highlighted that some hydrofluorocarbon (HFC) fluids such as difluoromethane (HFC 32) and 1,1,1,2 tetrafluoroethane (HFC 134a) are relatively polar solvents, [4-6] even in the sc state, and this allows them to be used as efficient extraction solvents. Furthermore, these solvents are also readily available and non-toxic. They have easily accessible critical constants (HFC 134a T_c = 101.1 °C; p_c = 40.6 bar and HFC 32 T_c = 78.1 °C; p_c = 57.8 bar) and gaseous dipole moments of about 2 D. [6] HFCs have been proposed as useful solvents for synthesis in the liquid state. [7] In the current study we present data on an esterification reaction, the kinetics of a Friedel Crafts alkylation reaction and the polymerisation of methylmethacrylate in supercritical HFC32 and CO₂. Dielectrometry is used as an *in-situ* technique to follow the extent of the reaction and the rate law and rate constants of the reaction are presented as a function of pressure.

I - MATERIALS AND METHODS

The high-pressure apparatus used in this study was the same as that described previously.[8,9] HFC 32 (Ineos Fluor 99.99%) and CO₂ (BOC 99.9%) were used as received. The Friedel-Crafts alkylation of anisole (Aldrich, 99 %) and toluene (Fisher, 98 %) using 2-methyl-2-propanol (*tert*-butanol) (Aldrich, 99.5 %) or 2-chloro-2-methylpropane (*tert*-butylchloride) (BDH, 99 %) was carried out with *p*-toluenesulfonic acid monohydrate (Lancaster, 98 %) as the acid catalyst. The reactants were placed into the doser and the acid catalyst in the reaction

vessel. This was then heated to the desired temperature and subsequently pressurized pushing the reactants from the doser into the reaction vessel. The system was left to react for the desired time and where applicable capacitance measurements were taken and the conversion was calculated using the procedure described previously. [8] The products were trapped by depressurization into a larger volume autoclave, which also stopped the reaction and the products were analyzed by GC-MS (Perkin Elmer). The reagents for this reaction were chosen because they dissolve rapidly in the sc medium. Details of the polymerisation reaction are given in the literature. [9]

RESULTS AND DISCUSSION

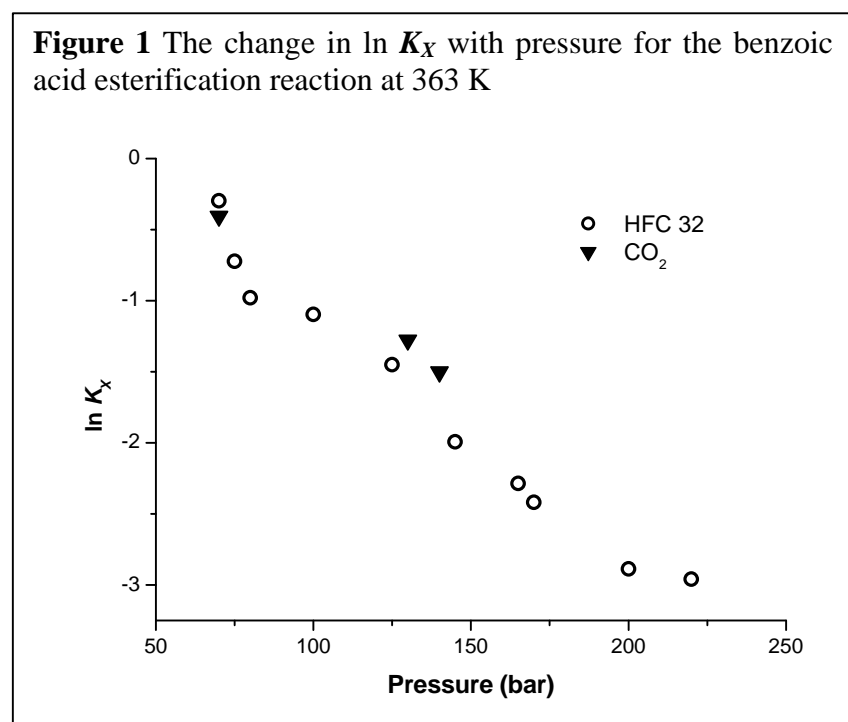
It has previously been shown that a dielectrometry technique can be employed to determine the solubility of solutes in sc fluids. [8] It is therefore logical that the same technique can be used to follow the changes in solution concentration during a reaction as it is a rapid, *in situ* method for measuring capacitance changes of reaction systems. Dielectrometry is not affected by solution concentration, high pressure and turbidity restraints that are present with spectroscopic techniques. It should, however, be noted that there are some limitations; it can only be used with reagents that are readily soluble because accurate capacitance measurements can only be obtained in homogeneous solutions and it is necessary to have a large difference in dielectric constant between the reactants and products so that product formation produces a change in the capacitance of the solution. For this to occur it is also necessary for the products to remain in solution as the reaction proceeds.

Esterification Reaction

The esterification of benzoic acid with 1-butanol was studied using *p*-toluenesulphonic (*p*Tos) acid as the catalyst. The apparent equilibrium constant, K_X expressed in terms of mole fraction was determined as a function of solvent density,

$$K_X = \frac{X_C X_D}{X_A X_B} \quad (1)$$

where X_A , X_B , X_C and X_D are the mole fractions of *A*, *B*, *C* and *D* at equilibrium conditions respectively. **Figure 1** shows 14-fold decrease in the apparent equilibrium constant is



observed when the pressure is increased from 70 to 220 bar. The increase in the K_X value with decreasing pressure was explained in terms of the activity coefficient of the reagents and products. [10] To assess whether the solution dielectric constant has this effect in a sc fluid, the esterification reaction was carried out in sc CO₂ at 363 K (CO₂, $\epsilon = 1.2$ at 363 K and 200 bar). Results obtained for K_X are also shown on **Figure 1** and it can be seen that the K_X values are similar to those

for HFC 32. This is a remarkable observation considering the vast differences in dielectric constant between the two solvents. In the low dielectric media such as scHex and scCO₂ it is surprising that the reaction progresses at all as the dissociation of the acid catalyst should be negligible. This suggests that either the catalyst activity is not a factor affecting the reaction rate or that the reagents affect the solution dielectric properties sufficiently to allow dissociation of the acid. The starting dielectric constant of the solution containing all the reagents in CO₂ was found to be 5.0, which is much higher than the dielectric constant for the pure solvent ($\epsilon < 2$), and significantly, it is not much lower than the value measured for the solution in HFC32 which was 5.48 (90°C and 170 bar) showing that the latter explanation is the cause of the apparent anomalous behavior. So even though the reagents are present in a small concentration (1 mol %) they have a marked effect on the dielectric constant of the solution. Hence it can be seen that the reagents themselves have a significant effect on the extent of a reaction negating, to some degree, the effect of the solvent.

Friedel-Crafts Alkylation of Anisole

The dielectrometry technique was also used to monitor the reaction kinetics of the FC alkylation of anisole with *t*-BuCl using *p*Tos as the catalyst in HFC 32 at 363 K. [11] The rate law was determined using the method of initial rates and was found to be

$$\text{rate} = k [t\text{BuCl}] [Anisole] \quad (2)$$

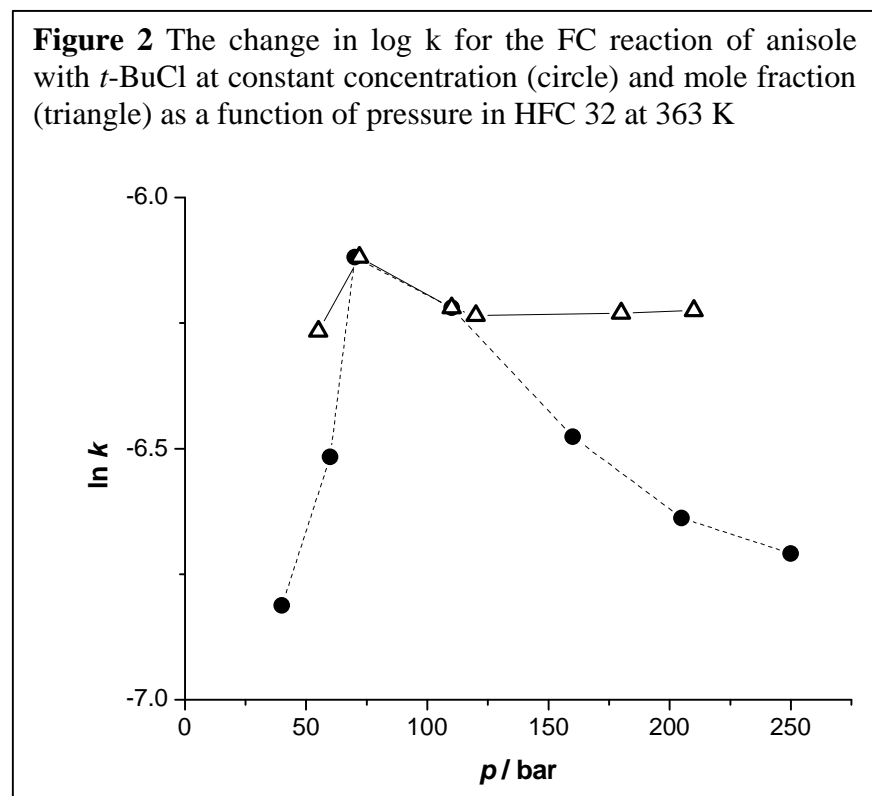


Figure 2 The change in log k for the FC reaction of anisole with *t*-BuCl at constant concentration (circle) and mole fraction (triangle) as a function of pressure in HFC 32 at 363 K

Figure 2 shows the effect of pressure on the second order rate constant for the FC alkylation of anisole (0.16 M) with *t*-BuCl (0.32 M) using *p*Tos (0.08M) in HFC 32 at 363K. It is observed that the rate constant reaches a maximum at the critical pressure and there is a significant change in the rate constant with pressure. In these experiments the reaction volume and hence the reactant concentration stays constant but as the pressure increases the number of solvent

molecules in the reaction system will increase, effectively diluting the solute. Therefore, it is necessary to see whether the observed change in rate with pressure is actually a result of a pressure effect or whether it is due to dilution. **Figure 2** also shows the same study at constant reagent mole fraction ($x_{\text{BuOH}} = 0.02$, $x_{\text{Anis}} = 0.01$). The overall effect of pressure on the rate constant at constant mole fraction is considerably smaller than that at constant concentration showing that the major effect is one of dilution. The pressure effects on rate constant can be analysed in terms of a change in the activation volume, DV^{\ddagger} , given by;

$$\frac{\partial \ln k}{\partial p} = - \frac{DV^{\ddagger}}{RT}$$

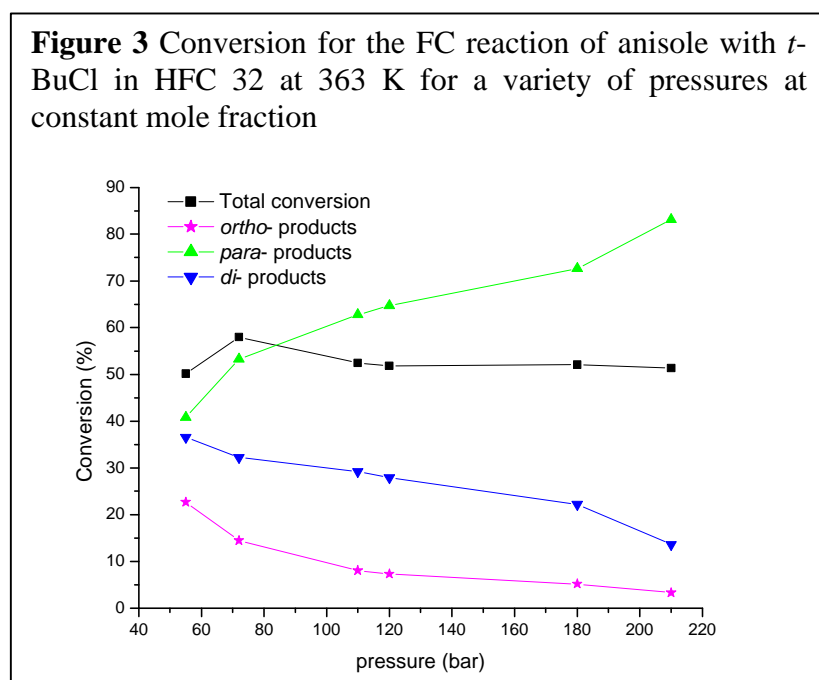
(3)

where R is the gas constant and T is the temperature.

From the gradient of the slopes at constant mole fraction in **Figure 2** at low pressures (70 to 120 bar) the volume of activation calculated for this reaction was found to be $84 \text{ cm}^3 \text{ mol}^{-1}$. At higher pressures (> 120 bar) there was negligible change in the activation volume. The positive change in the activation volume observed at low pressures suggests an expansion in the solvent as the reaction proceeds or may be brought about by changes in solvent hydrogen bonding as shown recently. [12]

While the rate constant and the yield of the FC reaction are seemingly pressure insensitive the distribution of the ortho-, para- and di- alkylated products change with pressure. **Figure 3** shows the distribution of these three products as a function of pressure at constant mole fraction. Compared to the total conversion for the reaction it is seen that the product selectivity has a large dependency on the pressure. As the pressure is increased the amount of

Figure 3 Conversion for the FC reaction of anisole with *t*-BuCl in HFC 32 at 363 K for a variety of pressures at constant mole fraction



ortho- and di- substituted products decreases and the amount of para- product increases, which is useful as it presents the opportunity to change the selectivity of the FC reaction by manipulation of the pressure.

The observed decrease in the ortho- and di- products with increasing pressure may be related to the decrease in hydrogen bonding ability of the HFC 32 solvent. [12] At low pressures where hydrogen bonding is prevalent, the local density of the alkylating agent in close

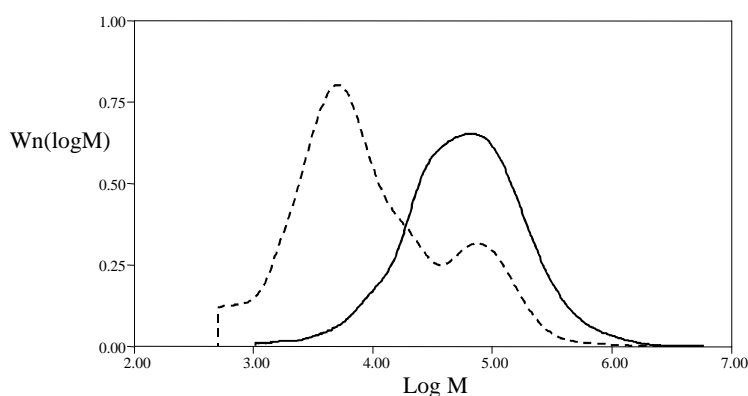
proximity to the methoxy group on the anisole should be higher than that around the rest of the molecule. [12]

Polymerisation

Free radical polymerisation of methylmethacrylate (MMA) was carried out in scHFC 32 using AIBN as the initiator. [9] The high-pressure reactions were carried out in a stirred, windowed reactor in order to view the progress of the reaction and to ascertain any changes in phase behaviour. In scHFC 32, at reaction temperature and pressure, the supercritical solution of monomer and initiator exhibited a single-phase, which was milky in appearance showing that all of the monomer is soluble and polymerisation begins as a homogeneous process. As polymerisation proceeded, the solution darkened, eventually appearing black to transmitted light. As the reaction proceeded further, the solution became paler and, in most cases, was transparent after 30 minutes to 1 hour, the exact time being dependent upon the conditions employed. In scCO_2 the phase behaviour is somewhat different, in that the monomer is not totally soluble in the solvent under the reaction conditions (two distinct phases are observable at all times) and the sc-phase does not darken as the reaction proceeds (consistent with no monomer dispersion/colloid formation). The polymerisation process can occur in either phase, but the lack of optical transmission attenuation suggests that the polymer does not grow to a significant molecular weight in the sc-phase before precipitation into the gas-expanded liquid phase. Reactions carried out in scHFC 32 formed significantly greater amounts of higher

molecular weight fractions of PMMA compared to similar conditions in scCO₂. [9] **Figure 4** shows a comparison between the molecular weight distributions in both CO₂ and HFC 32 at comparable conditions. Clearly, scCO₂ and scHFC 32 support significantly different polymer growth mechanisms. In scCO₂ at 200 bar most of the polymer has a molecular weight distributed around 5000 g mol⁻¹. Since the dielectric constant of this solution is relatively low, it is probable that the polymer phase separates at a low molecular weight. The proliferation of low molecular weight polymer suggests that phase separation may encourage chain termination. The smaller distribution around 10⁵ g mol⁻¹ probably results from a second stage

Figure 4 Distribution of molecular weights for PMMA produced in CO₂ (dashed) and HFC 32 (solid) at 363K and 200 bar



growth mechanism, *i.e.* once the polymer precipitates from the solution. This phase separation may have other ramifications as the monomer may also phase separate, being preferentially soluble in the PMMA rather than the CO₂ phase. The dielectric constant of the HFC 32 solutions is considerably higher than that for the scCO₂ solutions permitting the polymer to grow to

higher molecular weights before precipitation, something reflected by the narrower molecular weight distribution (**Figure 4**). Here the monomer should reside predominantly in the scHFC 32 phase meaning that the growth rate may change significantly if the process is mass transport limited.

CONCLUSION

This work has shown that sc HFC32 is a useful polar solvent for a variety of synthetic applications.

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