

Pressure Effect on the Esterification of Phthalic Anhydride in Supercritical CO₂

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Measurements of the bimolecular rate constants for the uncatalysed esterification of phthalic anhydride with methanol in supercritical CO₂ indicate that the reaction rate is enhanced when operating in the compressible region due to increased local concentrations of the methanol around the phthalic anhydride.

Solvatochromic shift data of cosolvents (1–5.25 mol%) in supercritical (SC) CO₂ indicate that the local composition of the cosolvent around the solute probe is a strong function of pressure in the compressible region and can be as high as seven times the bulk concentration.^{1,2} In order to determine if increased local concentrations in supercritical fluids (SCFs) can enhance reaction rates, we are studying the uncatalysed esterification of phthalic anhydride with methanol in SC CO₂. The reaction involves the addition of one molecule of methanol per molecule of phthalic anhydride; addition of a second methanol would require a catalyst at the conditions under investigation.

Experiments in both liquids and SCFs confirm that the reaction is first order in both phthalic anhydride and methanol. The samples are mixed in a 750 ml high pressure vessel and then introduced into a 1.74 cm pathlength high pressure optical cell, which has been described elsewhere.³ The rate constants were determined by UV-VIS absorption spectroscopy at 50 °C and pressures from 166.5 bar to 97.5 bar (1 bar = 10⁵ Pa). The phthalic anhydride concentration was *ca.* 3 × 10⁻⁴ mol dm⁻³ (2.9 × 10⁻⁵ mol fraction) and the methanol concentration ranged from 3.6 × 10⁻² to 0.36 mol dm⁻³ (4.13 × 10⁻³ to 2.15 × 10⁻² mol fraction). All

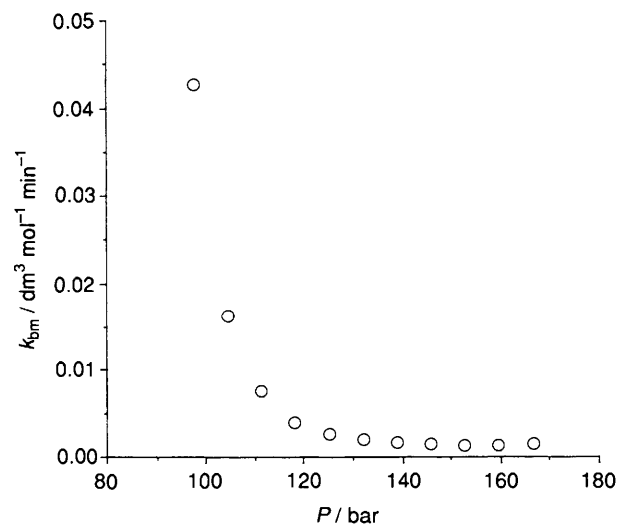
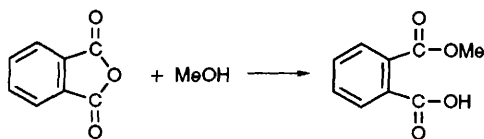


Fig. 1 Bimolecular rate constant for the uncatalysed esterification of phthalic anhydride with methanol in supercritical carbon dioxide at 50 °C as a function of pressure



experiments were performed in the one phase supercritical region.⁴ The kinetics were measured at 293 nm and the extinction coefficient of phthalic anhydride at this wavelength varied less than 5% over the pressure range of interest. The bimolecular rate constants, based on bulk concentrations, ranged from $1.42 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ at 166.5 bar to $4.27 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ at 97.5 bar (Fig. 1). This 30-fold increase in the bimolecular rate constant represents one of the most dramatic increases reported for a reaction in an SCF. Since the critical points of the mixtures were 32–35 °C and 77–78 bar,⁴ dependent on the concentration of methanol, the lower pressures are in the more compressible region nearer the critical point. These results demonstrate that reactions can be enhanced by operation in an SCF without being restricted to a very narrow window just above the critical point.

The thermodynamic pressure effect on a rate constant, as determined by transition-state theory,⁵ can be predicted from $\partial \ln k / \partial P = -\Delta v^\ddagger / RT - k_T$, where Δv^\ddagger is the activation volume of the reaction (difference in the partial molar volumes of the transition state and the reactants) and k_T is the isothermal compressibility of the solution. Estimates of Δv^\ddagger and k_T with the Peng–Robinson equation of state⁶ predict that $\partial \ln k / \partial P$ is negative; *i.e.* the rate constant should be higher at lower pressures, as observed. However, over the pressure range 166.5–97.5 bar it predicts an increase in the rate constant of *ca.* 1.2 times. Therefore, the observed results cannot be fully explained by the thermodynamic pressure effect on the rate constant. From this we conclude that the increased local concentration of the methanol around the phthalic anhydride

is, indeed, influencing the reaction. The measured bimolecular rate constants, based on bulk concentrations, are actually reflecting the increase in the concentration of methanol, which becomes more pronounced at lower pressures near the critical point,^{1,2} in addition to the thermodynamic pressure effect on the rate constant itself. It should be noted that the predicted pressure effect on the rate constant calculated from the Peng–Robinson equation is an estimate since the Peng–Robinson equation does not describe partial molar volumes in supercritical fluids exactly and one must assume a structure for the transition state. However, it should be qualitatively correct and, even when uncertainties in the calculations are taken into consideration, cannot account for the observed almost 30-fold increase in the rate constant. This ground state reaction corroborates the results of the hydrogen abstraction reaction of benzophenone triplet with propan-2-ol and cyclohexadiene.³

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