Reaction control and potential tuning in a supercritical fluid

Anthony A. Clifford,* Kate Pople, William J. Gaskill, Keith D. Bartle and Christopher M. Rayner

School of Chemistry, University of Leeds, Leeds, UK LS2 9JT

A maximum is found in the ratio of *endo*- to *exo*- products *vs.* density in the Diels–Alder reaction between cyclopentadiene and methyl acrylate in supercritical carbon dioxide and is explained by the adjustment of the position of the nearest-neighbour solvent molecules with respect to the transition states.

There have been a number of previous investigations of product ratio in supercritical fluids and these have been reviewed in a recently published study.[1] Many of these have concentrated on the critical region. In some cases, the lowering of diffusion coefficients in the critical region at finite concentrations can give rise to rapid changes of product ratio with density, as has been observed in the photo-Fries rearrangement of naphthyl acetate in supercritical carbon dioxide.[2] In other cases, rapid changes are seen as a function of pressure, but these largely reflect the rapid change in density with pressure, and as a function of density changes in product ratio are less dramatic. In this study we report an interesting maximum in product ratio, which occurs at a density rather higher than the critical density.

Experimental measurements on the Diels–Alder reaction between methyl acrylate and cyclopentadiene were carried out at 308 and 313 K in carbon dioxide at various pressures. A 50 ml vessel (Autoclave Engineers) with a magnetically coupled stirrer was used, which was modified in-house to improve the temperature control and pressure measurement. CO_2 was added from an HPLC pump with a cooled head and an injection valve in the supply line (Rheodyne) for adding reagents. Connecting tubes were heated to the reaction temperature to prevent condensation in them. For each experiment 200 μl of methyl acrylate was added at the beginning, the vessel pressurised with CO_2 and allowed to reach temperature equilibrium over half an hour. 100 μl of cyclopentadiene, prepared just beforehand from the dimer, was then added through the injection valve and more CO_2 added to raise the pressure another 4–5 bar. The reaction was then carried out for 4 h, after which the reaction mixture was released, trapped in HPLC grade acetone, kept at 195 K and analysed by GC. The reactions were carried out at lower dilutions than some previous experiments[3] to avoid the danger of two phases being present.

We now consider a system in which there are two competing bimolecular reactions in which the two products are stereo-isomers. The ratio of products obtained is equal to the ratio of rate coefficients, defined in terms of mole fractions, k_x'/k_x''. By manipulating the equations for transition-state theory applied to supercritical fluids[5] it can be shown that the partial derivative of the logarithm of this ratio with molar volume, V, at constant temperature and composition is given by eqn. (1).

$$RT\left(\frac{\partial \ln\left(k_x'/k_x''\right)}{\partial V}\right)_{T,x} = \left(\frac{\partial p}{\partial x_2}\right)'_{T,V} - \left(\frac{\partial p}{\partial x_2}\right)''_{T,V} \qquad (1)$$

The quantities $(\partial p/\partial x_2)_{T,V}$, which do not come under the definition of partial molar quantities, but which can be conveniently called tuning functions, are partial derivatives of the pressure with respect to the mole fraction of the appropriate transition state. Equations for the variation with V of other equilibria and individual reaction rates can also be written in terms of these functions.

Expressions for the tuning functions can be obtained in terms of an equation of state. The van der Waals equation is used below for analysing the experimental data. These tuning functions pass from negative at low density to positive at high density as the mean distance between the transition states and their nearest-neighbour solvent molecules moves from the attractive region of their mutual pair potential, through its minimum to its repulsive region. The functions therefore describe the manipulation of the transition-state solvation energy *via* the density. In the case of competing reactions, a difference in two tuning functions is important, as shown in eqn. (1). This difference is related to the change in pressure as one transition state is replaced by the other and represents the difference of the potential tuning behaviour of the two transition states.

Experimental data for the ratio of *endo*- to *exo*- product are plotted against the solution density in Fig. 1. The range of values of the ratio is no different than that which can be obtained by changing the solvent in the liquid-phase reaction.[5] However, by controlling the density, this range can be obtained in a single solvent. At the temperatures of this study, 1, 4 and 9 K above the critical temperature of carbon dioxide, inaccuracies in pressure measurement and fluctuations in pressure because of temperature instability cause large errors in the estimation of the density. Estimations of this effect are shown by horizontal error bars, which are large near the critical density, but are smaller than the point sizes at higher densities. Further errors in the measurement of the product ratio of 5%, or 0.2, are not shown.

The curves shown in Fig. 1 are theoretical curves obtained from eqn. (1) using tuning functions calculated from the van der Waals equation of state, with simple combination rules for the parameters, to give a ratio of the rate constants, eqn. (2),

$$\frac{k_x'}{k_x''} = \left(\frac{k_x'}{k_x''}\right)_0 \exp\left(-\frac{b_2' - b_2''}{V - b_1} - \frac{2\sqrt{a_1}\left(\sqrt{a_2'} - \sqrt{a_2''}\right)}{RTV}\right) \qquad (2)$$

where a_1 and b_1 are the van der Waals parameters for the solvent, a_2', b_2', a_2'' and b_2'' are those for the two transition states and $(k_x'/k_x'')_0$ is the rate coefficient ratio in ideal gas conditions as $V \rightarrow \infty$. Thus the equation has three unknown parameters: $(k_x'/k_x'')_0$, $(b_2' - b_2'')$ and $[\sqrt{a_1}(\sqrt{a_2'} - \sqrt{a_2''})]$, which were obtained by fitting the data at 313 K. A value for b_1 for CO_2 of 31.33×10^{-6} m^3 mol^{-1}, obtained from its critical volume, was used. The same three parameters obtained were then used to produce curves for both temperatures in Fig. 1, on the assumption that $(k_x'/k_x'')_0$ will not change significantly between the two temperatures, as is expected from reaction behaviour in the liquid phase.[5]

The rising part of the curve at lower densities is associated with the difference between the attractive forces of the two transition states and the steeper falling part with repulsion differences. A more physically transparent investigation can be made using the virial theorem of Clausius, which leads to the same relationship between tuning functions and the inter-molecular pair potential, as will be reported later. The interpretations can be summarised as follows. In a compressible medium such as a supercritical fluid it may often be possible, by controlling the density, to vary the mean distance between a

solute species and its nearest-neighbour solvent molecules within a range where their mutual pair potential energy is changing significantly. This statement is substantiated by calculations of the naphthalene–carbon dioxide pair correlation function in a supercritical fluid.[6] The solvation energy of the solute can therefore be controlled by the density of the medium and this will cause variations in a physical or chemical equilibrium or, if the species is a transition state, the rate of a chemical reaction. We suggest that the present study demonstrates that the effect of this 'potential tuning' is significant and observable for two competing reactions under accessible conditions. Recent results on absolute rate constants, which show a minimum in the reaction rate *vs.* density,[7] can also be explained by this effect, which is not particularly associated with the region around a critical point or line or with the critical density.

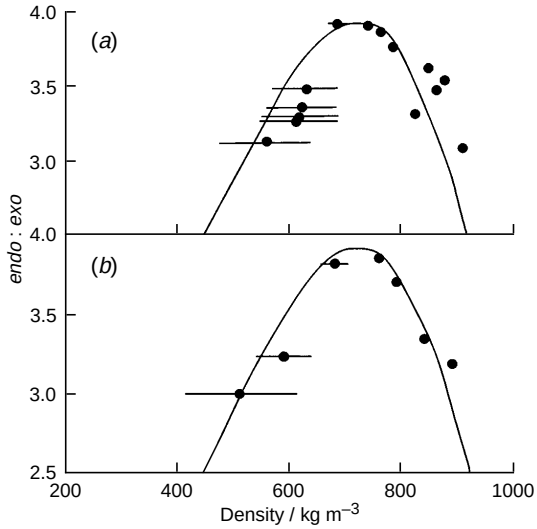

Fig. 1 Experimental data (points) for the ratio of *endo*- to *exo*- product from the reaction of methyl acrylate and cyclopentadiene in carbon dioxide at (*a*) 308 and (*b*) 313 K. The curve shows predictions from the van der Waals equation, fitted to the experimental points at 313 K. Horizontal bars show errors in the calculated density, which are large near the critical density of 466 kg m^{-3}.

The authors would like to acknowledge discussions with Professor J. S. Rowlinson and financial support from EPSRC (UK)

References

1 B. L. Knutson, A. K. Dillow, C. L. Liotta and C. A. Eckert, in *Innovations in supercritical fluids*, ACS Symposium Series 608, ed. K. W. Hutchenson and N. R. Foster, American Chemical Society, Washington, 1995, p. 166.
2 D. Andrew, B. T. Des Islet, A. Margaritis and A. C. Weedon, *J. Am. Chem. Soc*., 1995, **117**, 6132.
3 S. Kim and K. P. Johnston, *Chem. Eng. Commun*., 1988, **63**, 49.
4 A. A. Clifford, in *Supercritical fluids*, ed. E. Kiran and J. M. H. Levelt Sengers, Kluwer, Amsterdam, 1994, 449.
5 J. A. Berson, Z. Hamlet and W. A. Mueller, *J. Am. Chem. Soc*., 1962, **84**, 297.
6 H. D. Cochran and L. L. Lee, in *Supercritical fluid science and technology*, ACS Symposium Series 406, ed. K. P. Johnston and J. M. L. Penninger, American Chemical Society, Washington, 1988, p. 27.
7 R. D. Weinstein, A. R. Renslow, R. L. Danheiser, J. G. Harris and J. W. Tester, *J. Phys. Chem*., 1996, **100**, 12337.

Received, 26th November 1996; Com. 6/08066I