The Rates of a Diels–Alder Reaction in Liquid and Supercritical Carbon Dioxide

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Kinetic measurements on the Diels–Alder reaction between *p*-benzoquinone and cyclopenta-1,3-diene have been carried out in carbon dioxide as a medium between 25 and 40 °C; the reaction effectively occurs throughout liquid and supercritical ranges with no discontinuity and rates are about 20% greater than those in diethyl ether.

Carbon dioxide, both liquid and supercritical, has received a great deal of attention as a medium for extraction, for example, of natural products.[1] As a solvent it has a number of highly desirable features such as its low cost, lack of toxicity and flammability, and low reactivity to all but very basic reagents. As a solvent it is of low polarity, generally supposed to be somewhat similar to diethyl ether but solvation parameters have yet to be measured. Equally important could be the use of carbon dioxide as a medium for reactions in place of more conventional solvents. This note details the first results of a programme designed to explore the capabilities of low boiling solvents both in their sub- and super-critical regions in which to carry out a variety of organic syntheses.[2,3]

The equipment consisted of a cylindrical stainless steel

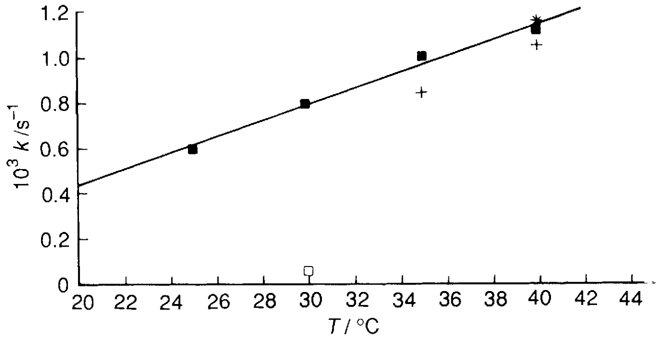

Fig. 1 Pseudo-first-order rates of reaction between *p*-benzoquinone and cyclopentadiene in carbon dioxide; ■, at density 0.8 g cm^{-3}; + at density 0.7 g cm^{-3} * at density 0.81 g cm^{-3}; □ in diethyl ether

Table 1 Rates of reaction of *p*-benzoquinone with cyclopentadiene in carbon dioxide

T/°C	p/bar	ρ/g cm^{-3}	$10^3 k/s^{-1}$
25.0	60	0.89	0.597 (±0.02)
30.0	60	0.80	0.790 (±0.02)
35.0	120	0.80	0.836 (±0.03)
35.0	180	0.83	0.993 (±0.04)
40.0	120	0.71	1.040 (±0.05)
40.0	180	0.79	1.107 (±0.05)
40.0	240	0.81	1.147 (±0.05)
In diethyl ether			
30.0	1		0.580 (±0.02)

vessel of 15 ml capacity equipped with two sapphire windows, diametrically opposed and which was thermostatted electrically. At the outlet, a valve was connected and this was connected to a second stainless steel cylinder acting as a reservoir, of the same capacity. Freshly distilled cyclopentadiene (1.5 g), a large excess, was placed in the window cell and an appropriate quantitity of *p*-benzoquinone (0.5 g) in the reservoir cylinder. Into the latter, carbon dioxide (20 g) was metered using a mass transfer valve and which, at ambient temperature, was in the liquid state and at a pressure of about 50 bar. The quinone dissolved after standing for a few minutes after which the entire solution was transferred to the window vessel and allowed to mix with the diene. The reservoir vessel was then disconnected and the amount of carbon dioxide checked by weighing the window cell and contents. This was then placed in a spectrometer and the absorbance at 320 nm monitored. The rate constant was obtained in the usual way using the Guggenheim procedure (Table 1). Duplicate measurements at temperatures between 20 and 40 °C were made.

It is interesting to note that carbon dioxide behaves as a normal solvent both in the liquid phase below 32 °C and above the critical temperature at which point the meniscus disappears yet the reactants remain homogeneously dispersed in the medium. When in the supercritical regime, the density can be continuously varied. A plot of rate against temperature at constant density shows no discontinuity at the critical temperature. Arrhenius parameters were calculated correcting for the increase in rate which can be attributed to the increase in pressure. With an activation volume of −35 cm^3 mol^{-2}, an increase of 200 bar would be accompanied by an increase in rate of 30%. To put the rate data into perspective, a comparison with diethyl ether was made. The reaction is found to proceed some 20% faster in carbon dioxide. However, since the Diels–Alder reaction is not sensitive to solvent, other more suitable reactions are being examined to assess solvation parameters for this medium.

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References

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2 Related studies have been reported by, M. E. Paulitis and G. C. Alexander, *Appl. Chem.*, 1987, **59**, 61; S. Kim and K. P. Johnston, *Chem. Eng. Commun.*, 1988, **63**, 49, who notes a slight increase in *endo*/*exo* selectivity with pressure for the reaction between cyclopentadiene and methyl acrylate in supercritical CO_2.
3 N. S. Isaacs, *Liquid Phase High Pressure Chemistry*, Wiley, Chichester, 1981, ch. 4.