Pressure and solvent effects on the rate of the reaction of tricarbonylcycloheptatrienoneiron with tetracyanoethene

Noel Hallinan, Patrick McArdle,

Chemistry Department, University College, Galway (Ireland)

John Burgess and Pilar Guardado *

Chemistry Department, University of Leicester, Leicester LE1 7RH (Great Britain)

(Received March 23rd, 1987)

Abstract

Pressure and solvent effect studies on the reaction of tricarbonylcycloheptatrienoneiron with tetracyanoethene support a concerted mechanism for the reaction.

Introduction

The cycloaddition of tetracyanoethene (TCNE) to tricarbonylcycloheptatrienoneiron (1) has been examined by several workers. The reaction was first reported to yield a 1,5-adduct (3) [1]; this was later shown to arise by isomerisation from an initially formed 1,3-adduct (2) [2]. The rate of the 1,3-addition and the associated thermodynamic activation parameters have also been reported [3]. Very recently the reaction was reexamined in detail by high field NMR spectroscopy and a small amount (4%) of a 1,4-adduct was detected [4]. A point of considerable interest has been the true nature of the cycloaddition reaction and whether it

$$(M = Fe(CO)_3)$$
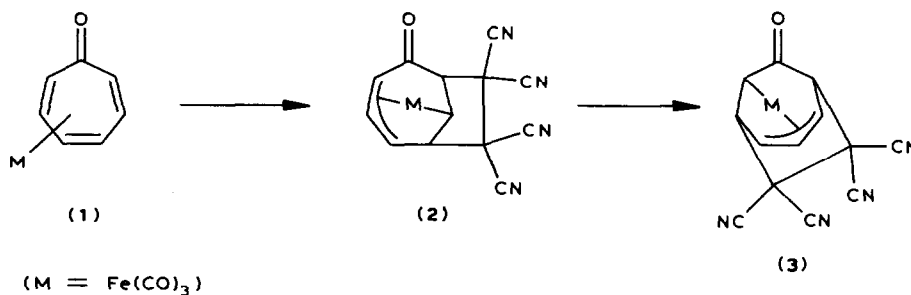
* Permanent address: Departamento de Quimica Fisica, Universidad de Sevilla, 41012 Sevilla (Espana).

proceeds via a concerted or a stepwise dipolar mechanism. It is very difficult to distinguish between these two possibilities, and the attempts that have been made have been of an indirect nature. Thus the success of frontier orbital predictions [5], and the lack of a significant solvent effect [3], together with the high dienophile dependence of the rate of addition [6], have all been cited in support of a concerted mechanism.

The present study was undertaken to try to obtain some direct information on the nature of the transition state of the reaction. It was hoped that by establishing activation volumes in solvents of widely differing polarities and by comparing solvent effects on the initial state, transition state, and final state that it might be possible to decide the nature of the reaction.

Experimental

Tricarbonylcycloheptatrienoneiron [1] and its 1,3-adduct with TCNE were prepared and characterised by published procedures [2]. The TCNE (Aldrich) was purified by sublimation through alumina before use in this preparation. All solvents were dried and distilled under nitrogen before use.

Published kinetic work [3,4] has already clearly established that the 1,3-addition is second-order (first-order in each reactant) in dichloromethane and in acetone-d_6. Preliminary experiments indicated that the reaction was also second-order in acetone and in acetonitrile. The progress of the reaction was monitored at 450 nm, the wavelength of maximum absorption of 1. Measurements at this wavelength are not affected by the isomerisation of 2 to 3 since neither absorb at this wavelength. Kinetic runs were carried out under pseudo first-order conditions (initial [1] = 2.0×10^{-3} M; initial [TCNE] = 1.6×10^{-2} M) in dichloromethane and in acetone. Second-order conditions (initial [1] = initial [TCNE] = 2.0×10^{-3} M) were necessary for the rather faster reactions in acetonitrile.

High pressure kinetic runs were carried out using the apparatus shown in Fig. 1 [7], which works on the simple principle of thermostatting a relatively large volume of reaction mixture under pressure. Samples can be ejected periodically for external monitoring, in this case spectrophotometrically, of the progress of the reaction. The high pressure apparatus and solutions of the reactants are thermostatted for some time, then a run is started by mixing appropriate volumes of reactant solutions to give a total volume of 150 cm³. Most of this solution is transferred to the cell of the high pressure apparatus, which is inserted into the bomb, pressurised, and left for several minutes to reequilibrate to bath temperature. Meanwhile an aliquot of about 3 cm³ is run into a 1 cm silica cell in the thermostatted cell compartment of a spectrophotometer. The rate constant for reaction at atmospheric pressure is obtained for this sample in the normal way, by repeat scan monitoring or recording the absorbance changes as a function of time at a given wavelength. Aliquots of the pressurised reaction solution are released at intervals through the valve indicated in Fig. 1; careful operation of the standard Aminco high pressure valve permits the ejection of about 3 cm³ of solution directly into a 1 cm spectrophotometer cell. The absorbance of each ejected aliquot is read off on a spectrophotometer as quickly as possible. The Madan Air Hydro Power Unit automatically restores the pressure to the value set at the start of the run within 2 or 3 seconds of ejecting the aliquot. Normally some 12 to 15 samples can be taken during each run; times of sampling
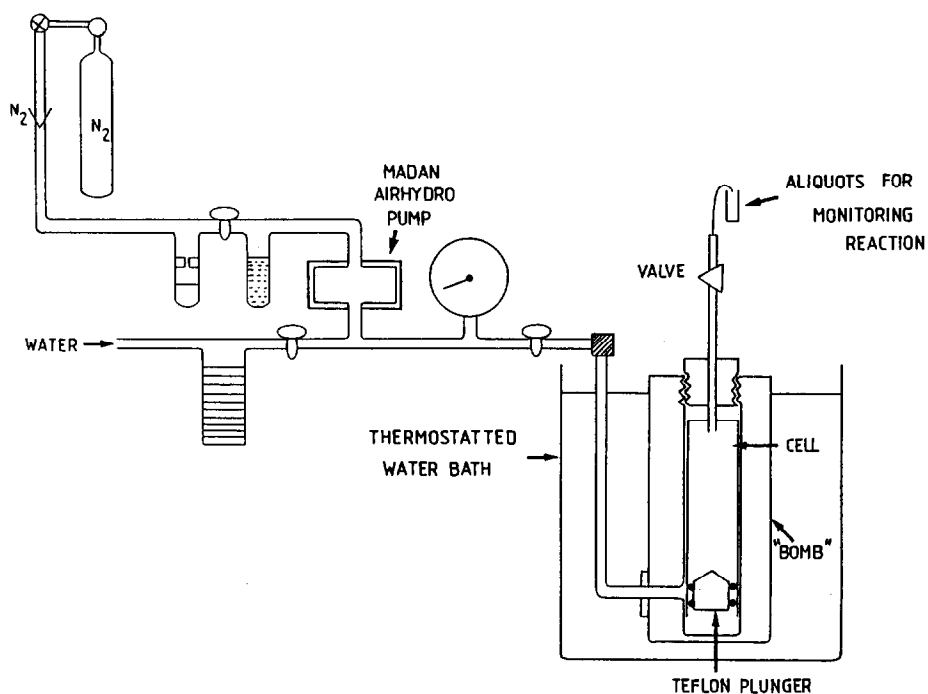
Fig. 1. Apparatus used for high pressure kinetic runs.

are chosen so that the run is monitored over between 2 and 3 half-lives at approximately equal time intervals. Rate constants are calculated in the normal way for atmospheric pressure and high pressure runs. The rate constants quoted for atmospheric pressure in the Results section are the means of all the atmospheric pressure runs in each solvent. Constancy of the atmospheric pressure rate constant was used as a check on reactant solution preparation for the various runs at different pressures.

Solubilities were determined by spectrophotometric measurements on suitably diluted aliquots of saturated solutions of 1 and of its 1,3-adduct 2. These saturated solutions were prepared by extended agitation of a generous excess of solid with the appropriate solvent in a sealed, foil-covered, sample tube thermostatted at 298.2 K.

Results and discussion

Rate constants are reported in Tables 1 and 2, which include values for activation parameters determined from the temperature and pressure dependences of reactivities. Solubilities are reported in Table 3.

It is clear from Table 2 and Fig. 2, which gives a comparative picture of the effects of pressure on reactivity in the three solvents used, that the activation volumes are equal, at -31 ± 3 cm^3 mol^{-1} in the three media examined. Thus the concerted cycloaddition mechanism seems much more likely than reaction via a dipolar species.

These activation volumes are somewhat smaller, and show less variation, than would be expected by analogy with, for example, dipolar addition of TCNE to

Table 1

Second-order rate constants and activation parameters for the reaction of 1 with TCNE

T (K)	$10^2 \times k_2/$ $(dm^3 \, mol^{-1} \, s^{-1})$	Solvent
298	2.92 (± 0.05)	Acetone
309	4.87 (± 0.03)	
322	9.36 (± 0.10)	
298	1.66 (± 0.05)	Acetonitrile
309	2.70 (± 0.08)	
322	5.01 (± 0.07)	

Activation parameters			Solvent
ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	
36.15 (± 3.13)	85.38 (± 0.08)	-165 (± 10.5)	CH$_2$Cl$_2$
36.31 (± 1.79)	81.78 (± 0.12)	-152 (± 6.0)	Acetone
34.48 (± 1.19)	77.44 (± 0.06)	-144 (± 4.3)	Acetonitrile

Table 2

Rate constants and activation volumes for the reaction of 1 with TCNE

Solvent	p (kbar)	$10^4 \, k_{obs}$ (s^{-1}) [a]	ΔV^* (cm^3 mol^{-1})
Dichloromethane	0.001	0.79	-29 ± 3
	0.17	0.98	
	0.34	1.06	
	0.51	1.43	
	0.68	1.91	
Acetone	0.001	3.3	-33 ± 3
	0.24	4.5	
	0.34	5.2	
	0.51	6.9	
Acetonitrile	0.001	0.16 [b]	-31 ± 5
	0.34	0.23 [b]	
	0.68	0.41 [b]	

[a] At 298.2 K; initial concentrations as in text. [b] Second-order rate constants (dm^3 mol^{-1} s^{-1}), cf. text.

Table 3

Solubilities (mol dm^{-3} at 298 K)

Solvent	1	TCNE	2
CH$_2$Cl$_2$	1.73	0.05	0.0027
Acetone	1.40	0.017	0.095
Acetonitrile	1.38	0.12	0.225

n-butyl vinyl ether [8]. However the distinction is not really definitive, as solvent effects and positional effects (e.g., 1,3- vs. 1,4-cycloaddition) can be of comparable magnitude [9]. It was therefore decided to assess solvation effects on reactivities through initial, transition, and final states, in other words through comparison of
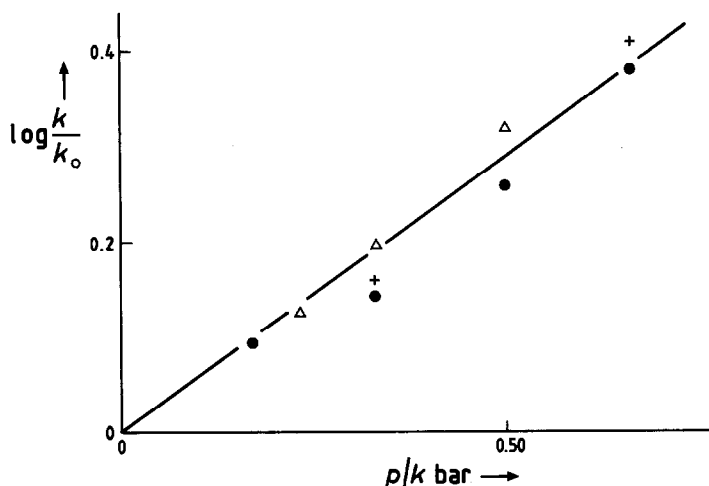
Fig. 2. Effect of increasing pressure on the rate constant for reaction of tricarbonylcyclohep-tatrienoneiron with tetracyanoethene (k_p/k_0 = ratio of rate constant at pressure p to that at atmospheric pressure; solvents: ● dichloromethane, △ acetone, + acetonitrile).

chemical potential profiles and to examine activation parameters. Table 4 shows transfer chemical potentials for the reactants and product, 2, calculated from measured solubilities (Table 3). Table 4 also shows the changes in the activation barrier ($\delta_m \Delta G^\ddagger$) calculated from rate constants in the three solvents, and the consequent transfer chemical potentials for the transition state. These results are summarised in Fig. 3, in which all transfers are from non-polar dichloromethane. It is obvious that the solvation characteristics of the transition state are intermediate between those of the reactants and the products, so there is no evidence for increased solvation of a dipolar transition state by polar solvents. It is interesting that the modest differences between rate constants in the three solvents can be attributed to transition state solvation rather than to initial state solvation changes. Transition state solvation in turn reflects product solvation differences.

Table 1 shows activation parameters in three solvents. Reactions which proceed via zwitterionic intermediates typically have $\Delta S^\ddagger$ increasing from -200 to -130 J K^{-1} mol^{-1}, over the range of solvents used [10]. The $\Delta S^\ddagger$ values in Table 3 range

Table 4

Analysis of solvent effects on reactivity into initial, transition, and final state effects for the reaction of **1** with TCNE; transfers from dichloromethane (298 K)

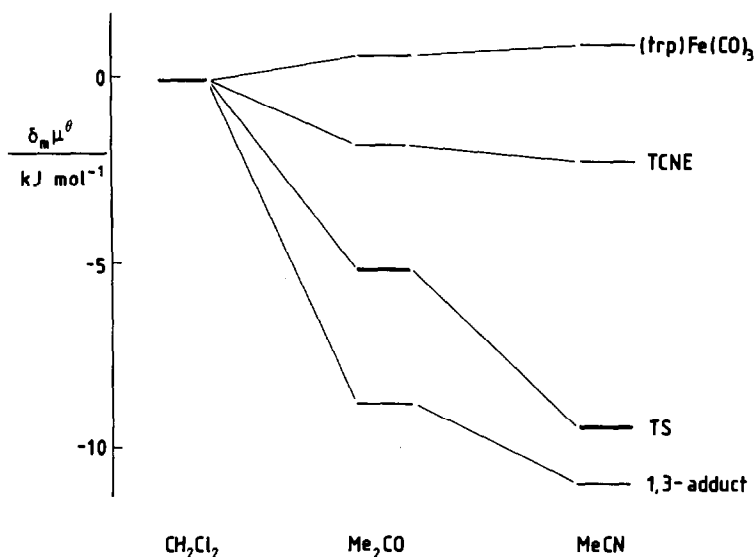| kJ mol^{-1}	Acetone	Acetonitrile
$\delta_m \mu$ (**1**)	+ 0.52	+ 0.56
$\delta_m \mu$ (TCNE)	− 1.88	− 2.17
$\delta_m \mu$ (initial state)	− 1.36	− 1.61
$\delta_m \mu$ (**2**)	− 8.81	− 10.95
$\delta_m \Delta G^{\ddagger}$	− 3.78	− 7.98
$\delta_m \mu^{\ddagger}$	− 5.14	− 9.59

Fig. 3. Solvent effects on the initial, transition, and final states for reaction of tricarbonylcycloheptatrienoneiron with tetracyanoethane to form the 1,3-adduct.

from -165 to -145 J K^{-1} mol^{-1}, and are similar to those encountered in Diels–Alder reactions [11,12] and indicate a highly ordered transition state with concerted bond formation.

The relative invariance of $\Delta H^{\ddagger}$ with solvent polarity would also indicate that there are no dramatic changes in transition state solvation in the different solvents. A typical reaction proceeding via a zwitterionic intermediate would be expected to show a range of approximately 12 kJ mol^{-1} for $\Delta H^{\ddagger}$ whereas only 1.5 kJ mol^{-1} is observed.

An indication of the extent of bond formation in the transition state comes from the relative sizes of $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$. In the present case $\Delta H^{\ddagger}$ is approximately 44% of $\Delta G^{\ddagger}$ indicating appreciable bond formation in the transition state. This clearly supports the transfer chemical potential data, which showed that the transition state was intermediate in character between initial and final states.

A combination of the evidence from pressure and solvent effects thus provides very strong support for a concerted cycloaddition mechanism for the reaction of tricarbonylcycloheptatrienoneiron (1) with tetracyanoethene.

Acknowledgements

References

1 D.F. Hunt, G.C. Farrant, and G.T. Rodeheaver, J. Organomet. Chem., 38 (1972) 349; and refs. therein.

2 Z. Goldschmidt and Y. Bakal, Tetrahedron Lett., (1976) 1229; M. Green, S.M. Heathcock, T.W. Turney, and D.M.P. Mingos, J. Chem. Soc., Dalton Trans., (1977) 204.

3 S.K. Chopra, M.J. Hynes, and P. McArdle, J. Chem. Soc., Dalton Trans., (1981) 586.

4 Z. Goldschmidt, H.E. Gottlieb, and D. Cohen, J. Organomet. Chem., 294 (1985) 219.

5 S.K. Chopra, G. Moran, and P. McArdle, J. Organomet. Chem., 214 (1981) C36.

6 P. McArdle and S. Kavanagh, J. Organomet. Chem., 282 (1985) C1.

7 F.M. Mikhail, P. Askalani, J. Burgess, and R. Sherry, Transition Met. Chem., 6 (1981) 51; J. Burgess and C.D. Hubbard, J. Am. Chem. Soc., 106 (1984) 1717.

8 F.K. Fleischmann and H. Kelm, Tetrahedron Lett., (1973) 3773; J. Sauer and R. Sustmann, Angew. Chem. Int. Ed. Engl., 19 (1980) 779.

9 Y. Yoshimura, J. Osugi, and M. Nakahara, J. Am. Chem. Soc., 105 (1983) 5414.

10 G. Steiner and R. Huisgen, Tetrahedron Lett., (1973) 3769.

11 A. Wasserman, Diels–Alder Reactions, Elsevier, New York, 1965.

12 P. Brown and R.C. Cookson, Tetrahedron, 21 (1965) 1977.