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The Rate and Mechanism of Tetracyanoethylene Cycloaddition to the Tricarbonyliron Complex of 7-Methylenecycloheptatriene and some Substituted Derivatives

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Tricarbonyliron complexes of 7-methylenecycloheptatriene and some 8-substituted derivatives ($R_1R_2C{=}C_7H_6$; R_1 = H; R_2 = H, OMe, p-tolyl and Ph) form 1,8 addition products with tetracyanoethylene. The phenyl and p-tolyl derivatives undergo initial 1,3-addition followed by isomerization to the 1,8-adducts. The diphenyl derivative ($R_1 = R_2$ = Ph) undergoes 1,3-addition but does not isomerize to the 1,8-product.

Introduction

The previously reported reaction of tetracyanoethylene, tcne, with the $\eta^4Fe(CO)_3$ complexes of the 7-methylenecycloheptatrienes, (Heptafulvenes), (1b) [1, 2] and (1d) [3] provide a rare example of a cycloaddition reaction in which a coordinated ligand appears to undergo reaction by the same mechanism as the free ligand [4]. While heptafulvene provides the classic example of symmetry allowed 8 + 2π cycloaddition [5], attempts to classify the similar 1,8-dieneophile addition to the complex (1d) using the method proposed by Mingos [6] led to ambiguous results [3]. Since previous kinetic studies had suggested a concerted nature for tcne addition to related tricarbonyliron complexes, it was hoped that a detailed study of the heptafulvene reactions might resolve this ambiguity and provide more information on the role of metal coordination.

Experimental

Infra-red spectra were obtained using a Unicam SP200-G spectrometer. Ultraviolet–visible spectra were measured on a Beckmann DB-GT spectrometer.

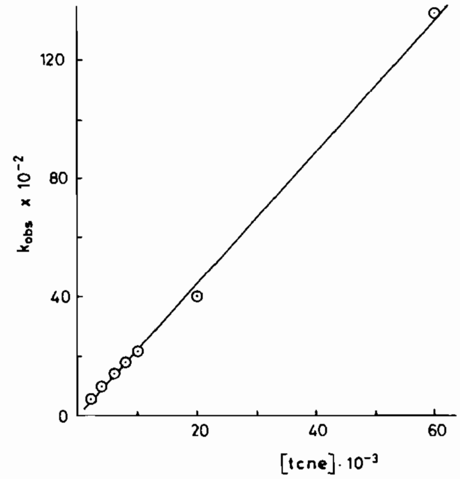

Fig. 1. Plot of k_{obs} (s^{-1}) *vs.* tcne concentration in nitromethane solution.

Reaction rate studies were carried out at 25 °C on either of the above spectrometers or on an Applied Photophysics stopped-flow device. Temperature control was ±0.1 °C. Rate constants were determined from plots of $-\ln(A - A_\infty)$ against time in all cases except k_2 which was from Guggenheim plots. The errors quoted were calculated as described by Swinbourne [14]. Solutions for the kinetic runs were freshly prepared using distilled dry solvents. Tetracyanoethylene was purified by sublimation through alumina before use. ^1H and ^{13}C n.m.r. spectra were recorded on Jeol MH-100 and FX-60 spectrometers. The rate constant k_4 was measured by monitoring the νMC–O i.r. absorption band at 2061.5 cm^{-1} of (2d), CH_2Cl_2 solution. The rate constants used to construct Fig. 1 were $k_1 = 3.0 \times 10^2\ s^{-1}$, $k_{-1} = 3.0 \times 10^2\ s^{-1}$, k_2 22.4 $dm^3\ mol^{-1}\ s^{-1}$ and $k_4 = 5.5 \times 10^{-3}\ s^{-1}$. A suitable value of k_3 was found to be 0.2 s^{-1}. The extinction coefficients

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of (1d) and (3d) in $MeNO_2$ solution at 420 nm were 167 and 29.2 mol^{-1} m^2 respectively.

Compounds (1a–e) were prepared by literature methods [1, 7, 11].

Reactions with tcne

Tricarbonyl(7-phenylmethylenecycloheptatriene)-iron, (1d), (1.3 g) and tcne (0.6 g) were dissolved and frozen immediately with liquid nitrogen. The temperature was allowed to rise and the solvent was removed rapidly *in vacuo* to leave (2d), 15% and (3d), 60%. Separation of (2d) and (3d) was effected by fractional crystallation from CH_2Cl_2/Hexane. (2d) i.r. ν(MC–O) CH_2Cl_2 solution 2071.9 and 2009.6 cm^{-1}. (Found C, 61.3; H, 2.81; N, 12.8. $C_{23}H_{12}N_4O_3Fe$ requires C, 61.6; H, 2.7; N, 12.5%) (3d) i.r. ν(MC–O) CH_2Cl_2 solution 2061.5 and 1995.7 cm^{-1}. (Found C, 61.6; H, 2.7; N, 12.6. $C_{23}H_{12}N_4O_3Fe$ requires C, 61.6; H, 2.7; N, 12.5%). ^{13}C n.m.r. p.p.m. from TMS (3d) $(CD_3)_2CO$ solution; 48.2, C^2; 50.9, C^5; 56.8, C^1; 59.5, C^8; 90.7, C^3; 95.6, C^4; 134.8, C^6; 130.4, 129.6, Ph.

Tricarbonyl(7-methylenecycloheptatriene)iron, (1a), (0.15 g) reacted rapidly with tcne (0.80 g) in methylene chloride (0.5 h, 25 °C) to give yellow crystals of (3a) 50%. I.r. ν(MC–O) CH_2Cl_2 solution, 2060.8 and 1994.6 cm^{-1}. (Found C, 54.4; H, 2.2; N, 15.5; $C_{17}H_8N_4O_3Fe$ requires C, 54.8; H, 2.2; N, 15.1%). ^1H n.m.r. p.p.m. from TMS $(CD_3)_2CO$ solution 6.09(d), 8 Hz, 1H, H^6; 5.87(m), 2H, $H^3 + H^4$; 3.0–4.2(m), 4H, $H^1 + H^2 + H^5 + H^8$.

Tricarbonyl(7-methoxymethylenecycloheptatriene)iron, (1b) gave an adduct as reported [1]. To resolve a slight ambiguity in that report, due to a typographical error, the ^{13}C and ^1H n.m.r. spectra of (1b) were reexamined. *Cis* and *trans* isomers were present in a 3/1 ratio. The presence of a 4/5 ratio of isomers in the tcne adduct was confirmed by its ^{13}C n.m.r. spectrum p.p.m. from TMS $(CD_3)_2CO$ solution 47.9; 48.6; C^2; 50.3, 50.6, C^5; 53.86, 55.1, C^1; 57.96, 61.2, OMe; 86.1, 87.9, C^8; 90.8, 91.1, C^3; 95.9, C^4; 136.2, 138.5, C^6. I.r. ν(MC–O) CH_2Cl_2 solution 2064.0 and 1997.8 cm^{-1}.

TABLE I. Observed Rate Constants for tcne Addition at 25 °C.

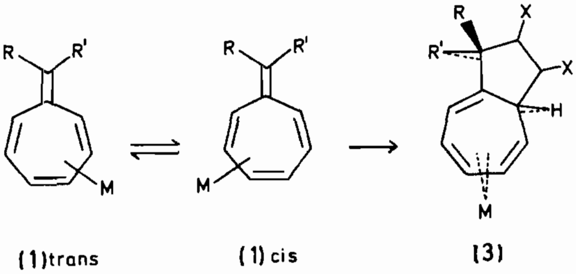
Compound	[tcne] × 10^{-3}	k_{obs} (s^{-1}) × 10^{-2}	Solvent
(1d)	2.17	5.60	$MeNO_2$
	3.96	9.5	
	6.00	13.8	
	8.02	18.0	
	10.06	22.1	
	20.00	40.0	
	60.00	135.7	
(1e)	1.93	1.09×10^{-2}	CH_2Cl_2
	4.06	2.59×10^{-2}	
	5.86	3.77×10^{-2}	
	8.13	5.18×10^{-2}	
	10.05	6.20×10^{-2}	

Results and Discussion

Final Reaction Products

The 1,8-structure previously assigned to the cycloaddition products (3b) and (3d) was based on n.m.r. data. While complex (3b) was obtained as a mixture of isomers (R′ *exo* and *endo* w.r.t. Fe), only one isomer of (3d) was isolated [1–3]. These reactions were repeated with identical results. The parent complex (1a) and the phenyl derivative (1c) also readily underwent addition of tcne to give 1,8-adducts. The ^1H n.m.r. spectrum of (3c) was almost identical to that of (3d) and again consistent with the presence of a single isomeric form with R′ *exo* w.r.t. Fe. The ^{13}C n.m.r. spectrum of (3c) also confirmed the presence of but one structural form.

If these results are considered together with the known fluxional nature of (1d), Scheme 1 can be used to explain the observed products. The aryl substituents with their higher steric demand could prevent tcne addition to *trans* (1c) and *trans* (1d).



M = $Fe(CO)_3$
X = $(CN)_2$
a R = R′ = H
b R = OMe; R′ = H
c R = *p*-tolyl; R′ = H
d R = Ph; R′ = H
e R = R′ = Ph

Scheme 1

(Since electrophilic attack at the uncoordinated side of the π-system is clearly preferred in a related cycloheptatriene series [11] addition to the coordinated side of these complexes is not considered likely).

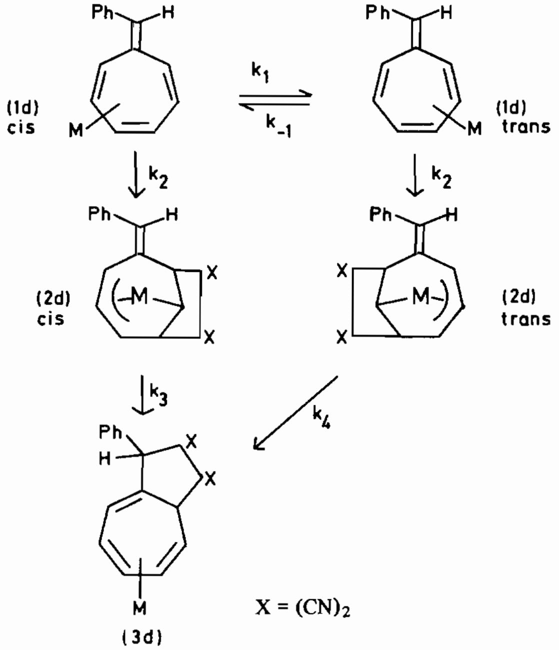
TABLE II. Rate Constants for tcne Addition and Adduct Isomerization at 25 °C.

Starting Compounds	Rate	Rate Constant	Method	Solvent
(1d) + tcne	(22.4 ± 0.45)	$k_2/dm^3\ mol^{-1}\ s^{-1}$	visible	$MeNO_2$
(1e) + tcne	(6.31 ± 0.18)	$k_2/dm^3\ mol^{-1}\ s^{-1}$	visible	CH_2Cl_2
(1d) + tcne	$(1.36 \pm 0.05) \times 10^{-4}$	k_4/s^{-1}	i.r.	CH_2Cl_2
(2d)	$(1.39 \pm 0.05) \times 10^{-4}$	k_4/s^{-1}	i.r.	CH_2Cl_2
(2d)	$(2.49 \pm 0.02) \times 10^{-3}$	k_4/s^{-1}	i.r.	$CH_2Cl_2/MeNO_2$ (1:1)
(2d)	$>5.5 \times 10^{-3}$ *	k_4/s^{-1}	i.r.	$MeNO_2$

*This rate was too fast to measure accurately by i.r. spectroscopy.

Reaction Intermediates

When attempts were made to monitor these reactions by ^1H n.m.r. and i.r. it became clear that intermediates were involved in the case of both (1c) and (1d). Using ^1H n.m.r. the reaction could be conveniently followed in d_6-acetone by observing the two singlets assigned to H^8 in *cis* and *trans* (1d) at 6.80 and 6.52 p.p.m. respectively [12]. On addition of tcne these signals were replaced by two singlets at lower field, 6.98 and 6.65 p.p.m. respectively. The resonance at 6.98 p.p.m. disappeared in less than three minutes and the singlet at 6.65 disappeared after one hour and then only a spectrum of (3d) remained. The apparent rapid formation of two intermediates which then decayed at different but relatively slow rates to the 1,8-adduct (3d) suggested that it might be possible to isolate one of these intermediates. When the reaction was carried out on a preparative scale (*ca.* 1g of (1d)) a compound which readily isomerized to (3d) was isolated. Analytical data indicated a 1:1 adduct. Structure (2d), Scheme 2, was assigned on the basis of its Mössbauer spectrum and the position of its νMC–O i.r. bands. It has been shown that while the Mössbauer spectra of tricarbonyliron complexes of dienes exhibit a large quadrupole splitting (>1.2 mm s^{-1}) when iron is bonded η^4 to a conjugated diene, a much smaller splitting is observed when iron is bonded as in (2) [11]. The small quadrupole splitting which is characteristic of the η^3–η^1 structure (2), could be a result of octahedral coordination in (2) whereas all η^4-diene-Fe(CO)$_3$ complexes including (1d) and (3d) can only be five coordinate [13]. The Mössbauer spectrum of (2d) contains a quadrupole split doublet at 0.29 mm s^{-1} (w.r.t. sodium nitro prusside) which has a small quadrupole splitting of 0.76 mm s^{-1}. The ν(MC–O) i.r. bands of (2d) are also higher in frequency than those of (3d) and reflect the proximity of the tcne group to the Fe(CO)$_3$ moiety. Due to solubility and isomerization problems it was not possible to obtain a ^1H n.m.r. spectrum of (2d).



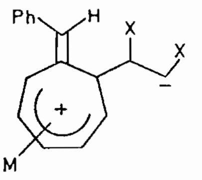
Scheme 2 includes the proposed intermediates, *cis* and *trans* (2d).

Rate Studies

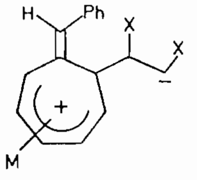
The rate of tcne addition to (1d) was measured in $MeNO_2$ solution under pseudo-first-order conditions, tcne in excess, and the results are given in Table I and Fig. 1. The second order rate constant k_2 is given in Table II. It was possible to follow the isomerization of (2d) to (3d) using the well resolved ν(MC–O) i.r. bands. The measured rates, k_4, are given in Table II. There was good agreement between the time required for complete disappearance of the (2d) i.r. bands in acetone solution, calculated using k_4 (5 × $t_{1/2}$) of 50 min and that observed by n.m.r. above in d_6-acetone (60 min). Since k_2 and k_3 were too fast for i.r. measurement it was also possible to measure k_4 starting with (1d) and tcne and both methods were in excellent agreement, Table II.

It is interesting to consider why *cis* and *trans* (2d) isomerize at different rates but yet both give the same product in contrast to tcne addition to (1b) which yields both possible isomers. Perhaps the steric requirement of the phenyl group precludes carbon–carbon bond formation at C^8 on that side of the molecule. If this were true then it would be predicted that the 8,8-diphenylmethylenecycloheptatriene complex, (1e), might undergo 1,3 addition of tcne but would be unable to isomerize to a 1,8-product. This was indeed the case. When (1e) was reacted with tcne only the 1,3-adduct, (2e), was isolated and no detectable isomerization was observed after twelve hours at 25 °C. The rate constants for tcne addition to (1e) are given in Tables I and II.

The isomerization of *cis* (2d) to (3d) could therefore proceed smoothly either directly by a concerted mechanism or via an ionic intermediate (4). Isomerization of *trans* (2d) to (3d) on the other hand is not as straightforward since it must involve rotation about the C^7–C^8 double bond. If the ionic intermediate (5) is involved then delocalization of positive charge onto C^8 could reduce the energy barrier to rotation about the C^7–C^8 bond. Support for an ionic isomerization mechanism for *trans* (2d) was sought by measuring the effect of increasing solvent polarity on k_4. There is at least a forty fold increase in rate on going from methylene chloride to nitromethane. While a much greater increase in the k_4 value would have provided strong support for an ionic intermediate, (5) cannot be ruled out since rotation about the C^7–C^8 bond rather than formation of (5) may be rate determining.



(4)



(5)

In view of the complexity of Scheme 2 it might appear unlikely that pseudo-first-order behaviour could be observed. To obtain further support for Scheme 2 the reaction scheme was simulated using two computer programs RMCHSS [14] and CAKE [15] and both gave the same results. The measured rate constants k_1, k_{-1}, k_2 and k_4 were used together with trial values of k_3. It was assumed that *cis* and *trans* (1d) both reacted at the same rate with tcne. The expected variation of optical density with time was calculated using the extinction coefficients of (1d) and (3d) and the fact that (2d) did not absorb at the wavelength chosen for the kinetic measurements. It was easy to find a value of k_3, 0.2 s^{-1}, which gave a pseudo-first-order plot, and using different tcne concentrations a linear second order plot with a slope close to that observed experimentally was obtained [13]. Pseudo-first-order behaviour is exhibited because the extinction coefficient of (3d) is lower than that of (1d) and because the concentration of (3d) is low until late in the reaction, Fig. 2.

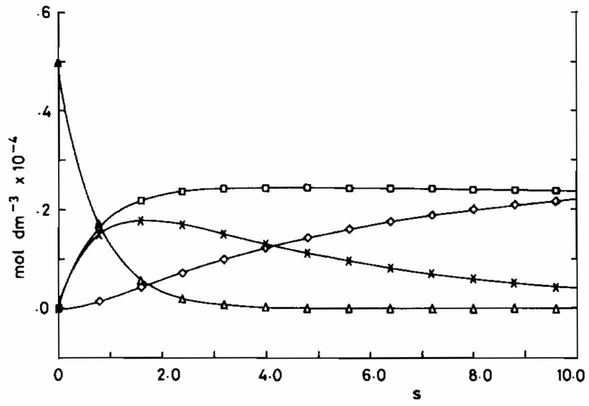


Fig. 2. Calculated concentration profiles for the reaction of (1d) with a pseudo-first-order excess of tcne (6.0×10^{-2} mol dm^3). △ = (1d), × = *cis*(2d), □ = *trans*(2d), ◇ = (3d).

No direct evidence could be obtained for initial 1,3-addition and subsequent isomerization for (1a) and (1b) and thus it is not possible experimentally to rule out direct 1,8-addition in these cases. However in all related cases where the addition rate is slow enough to detect intermediates, 1,3-addition is the initial mode of attack. Thus a postulated 1,5-addition to η^4-troponeFe(CO)$_3$ was shown to involve initial 1,3-addition [6] and the 1,6-adduct of an η^4-azepineFe(CO)$_3$ complex was also shown to involve initial 1,3-attack [16].

References

1 Z. Goldschmidt and Y. Bakal, *J. Organometal. Chem.*, *168*, 215 (1979).
2 Z. Goldschmidt and Y. Bakal, *J. Organometal. Chem.*, *179*, 197 (1979).
3 P. McArdle, *J. Organometal. Chem.*, *144*, C31 (1978).
4 W. von E. Doering and D. W. Wiley, *Tetrahedron*, *11*, 183 (1960).
5 R. B. Woodward and R. Hoffman, 'The Conservation of Orbital Symmetry', Verlag Chemie–Academie Press, New York, p. 82 (1969).
6 M. Green, S. M. Heathcock, T. W. Turney and D. M. P. Mingos, *J. Chem. Soc. Dalton*, 204 (1977).
7 E. S. Swinbourne, 'Analysis of Kinetic Data', Nelson (1971).
8 G. T. Rodehaver, G. C. Farrant and D. F. Hunt, *J. Organometal. Chem.*, *30*, C22 (1971).
9 Z. Goldschmidt and S. Antebi, *Tetrahedron Letters*, *14*, 1225 (1978).

10 K. Karel Johnson, *Ph.D. Thesis,* Princeton University (1978).
11 D. Cunningham, P. McArdle, H. Sherlock, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. Dalton,* 2340 (1977).
12 B. F. G. Johnson, J. Lewis, P. McArdle and G. L. P. Randall, *J. Chem. Soc. Dalton,* 2076 (1972).
13 G. Moran, *Ph.D. Thesis,* National University of Ireland (1981).
14 D. F. DeTar, *J. Chem. Ed., 44,* 193 (1967).
15 P. F. Ridler, *J. Phys. Chem., 81,* 2419 (1977).
16 S. K. Chopra, G. Moran and P. McArdle, *J. Organometal. Chem., 214,* C36 (1981).