The Rate and Mechanism of Tetracyanoethylene Addition of Cycloheptatriene and Related Complexes of Tricarbonyliron

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The rate constants for the 1,3-addition of tetracyanoethylene to a range of substituted cycloheptatriene complexes have been measured. Mechanisms are proposed for the addition reactions. The results suggest that tricarbonyliron is activating and that neither ionic nor free radical intermediates are involved. The 1-formylcycloheptatriene complex was found to undergo two parallel reactions. A rapid but reversible 1,3-addition is in competition with a much slower but irreversible 4,6-addition.

THE 1,3-addition of dieneophiles to tricarbonylcycloheptatrieneiron, (1a), was first reported by Green *et al.*[1] In a subsequent paper they suggested that with certain assumptions it was possible, for the first time, to apply orbital symmetry rules to transition-metal complex cycloaddition reactions.[2] It has also been established that the addition of tetracyanoethylene, tcne, is at the *exo* surface of the ring and at the unco-ordinated double bond.[1,3] While most derivatives of (1a) undergo a 1,3-addition of tcne [3] (at the unco-ordinated double bond) the 1-formyl derivative (1f) has been reported to undergo a 4,6-addition at the co-ordinated side of the molecule.[4]

It was decided to undertake a kinetic study of these reactions to try and obtain further information on (*i*) the presumed concerted nature of the cycloaddition, (*ii*) the effect of tricarbonyliron co-ordination, and (*iii*) the role of substituents in determining the site of attack.

RESULTS AND DISCUSSION

The Concerted Nature of the Addition.—Initially Green *et al.* argued in favour of a two-step ionic mechanism. This involved initial formation of the bipolar intermediate (3), and ring closure at C^3 to give (2a). This was a reasonable mechanism for two reasons. Firstly, the cationic portion of (3) has an excellent model in the well known cation (4) and secondly, one of the products derived from nucleophilic attack by tetrahydroborate on (4) is (5).[5] However, this second point may not be valid since there have been two reports of nucleophilic attack on dienium cations which show the first point of attack may be at C^1 or C^3 but not C^2 of the dienium cation. Products thought to involve C^2 attack appear to arise by isomerization.[6,7] Subsequently Green *et al.* advocated a one-step concerted mechanism.[2] It was hoped that kinetic data might distinguish these two possibilities.

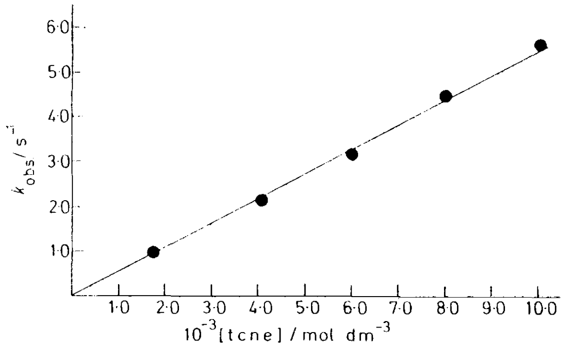
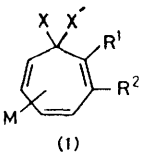


FIGURE 1 Plot of $k_{obs.}$ against [tcne] for (6) in $MeNO_2$

Pseudo-first-order rate constants are given in Table 1, tcne in excess, and second-order rate constants in Table 2.

M = Fe(CO)$_3$, Y = (CN)$_2$
(a) X = X' = H, $R^1 = R^2 = H$
(b) X = H, X' = C_7H_7, $R^1 = R^2 = H$
(c) X = X' = H, R^1 = COMe, R^2 = H
(d) X = X' = H, R^1 = H, R^2 = COMe
(e) X + X' = O, $R^1 = R^2 = H$
(f) X = X' = H, R^1 = CHO, R^2 = H



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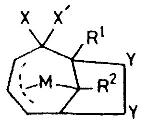

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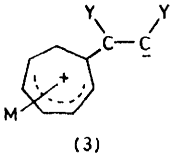

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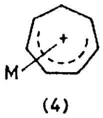

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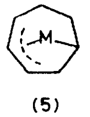

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A typical second-order plot is illustrated in Figure 1. In all cases, reactions were first order in both [tcne] and [olefin]. In Table 3 rate constants for the addition of tcne to (1a) and tricarbonylcyclo-octatetraeneiron, (6), measured in methylene chloride and nitromethane are given. The rate accelerations observed on going to the more polar solvent, 3.8 and 7.0 times respectively, are both small and not sufficient to accommodate a polar intermediate. Since a free radical mechanism has also been ruled out,[2] these reactions are probably concerted.

Effect of Tricarbonyliron Co-ordination.—Uncomplexed cycloheptatriene, cht, adds tcne *via* its norcaradiene tautomer to give the 1,4-product (7).[8] The rate of this 1,4-addition is given in Table 2. It is clear that tricarbonyliron co-ordination increased the reaction rate by a factor of at least 740. This result is in agreement with the electron releasing effect observed (by a pK_a change) when sorbic acid co-ordinates $Fe(CO)_3$.[9] It is however in conflict with the result of the intramolecular competition reaction previously described for the bicycloheptatrienyl complex (1b).[10] This complex was found to add tcne stepwise, a 1 : 1 mole ratio gave (8) and further tcne led to (9). The kinetic results show that stepwise addition does in fact take place and the rates are sufficiently different to explain the synthetic results. The increase in rate of the first step with respect to cht and the decrease in rate of the second step with respect to (1a) is surprising but could be due to a preferred eclipsed conformation in (2b) *i.e.* (10), where π interactions between the rings are possible.

TABLE 1

Observed rate constants for tcne additions *

Compound	10^{-3}[tcne]	$k_{obs.}/s^{-1}$	Solvent
cht	0.50	0.77×10^{-3}	CH_2Cl_2
	1.00	1.33×10^{-3}	
	1.50	2.26×10^{-3}	
	2.01	3.30×10^{-3}	
	2.51	3.85×10^{-3}	
(1a)	5.0	2.78×10^{-1}	
	10.0	5.68×10^{-1}	
	15.0	8.95×10^{-1}	
	20.0	11.85×10^{-1}	
	25.1	15.3×10^{-1}	
(1a)	2.16	0.46	$MeNO_2$
	4.02	0.90	
	6.12	1.44	
	7.99	1.87	
	9.99	2.27	
(1b) fast step	5.0	0.17	CH_2Cl_2
	10.0	0.32	
	15.0	0.52	
	20.0	0.72	
	25.1	0.88	
(1b) slow step	5.0	1.35×10^{-3}	
	10.0	2.48×10^{-3}	
	16.8	3.75×10^{-3}	
	20.0	4.47×10^{-3}	
	25.1	5.95×10^{-3}	
(1c)	6.7	1.26×10^{-3}	
	10.9	1.94×10^{-3}	
	15.1	2.77×10^{-3}	
	20.3	3.51×10^{-3}	
	27.0	4.63×10^{-3}	
(1d)	6.7	1.26×10^{-3}	
	10.9	1.87×10^{-3}	
	15.1	2.65×10^{-3}	
	20.3	3.28×10^{-3}	
	27.0	4.45×10^{-3}	
(1e) at 25.3 °C	10.1	0.07×10^{-3}	
	20.3	0.12×10^{-3}	
	30.1	0.19×10^{-3}	
	40.2	0.26×10^{-3}	
	45.1	0.29×10^{-3}	
(1e) at 15.6 °C	10.3	0.04×10^{-3}	
	19.8	0.08×10^{-3}	
	30.0	0.12×10^{-3}	
	39.9	0.16×10^{-3}	
(1e) at 19.9 °C	10.3	0.055×10^{-3}	
	20.7	0.11×10^{-3}	
	35.7	0.19×10^{-3}	
	40.0	0.21×10^{-3}	
(1e) at 29.4 °C	10.3	0.08×10^{-3}	
	19.8	0.17×10^{-3}	
	30.0	0.25×10^{-3}	
	39.8	0.34×10^{-3}	
(1f)	10.0	1.58×10^{-3}	
	20.0	2.05×10^{-3}	
	30.0	2.40×10^{-3}	
	4.0	2.93×10^{-3}	
(6)	1.95	0.154	
	3.97	0.317	
	5.98	0.466	
	8.05	0.644	
	9.97	0.835	
(6)	1.98	1.02	$MeNO_2$
	4.06	1.95	
	5.99	3.16	
	7.98	4.45	
	10.02	5.60	

*All reactions were carried out at 25 °C unless otherwise stated.

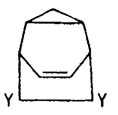
TABLE 2

Second-order rate constants for the tcne additions *

Compound		$k_2/dm^3\ mol^{-1}\ s^{-1}$	Wavelength/ nm
cht		$(1.62 \pm 0.10) \times 10^{-1}$	309
(1a)		$(6.22 \pm 0.09) \times 10^{1}$	375
(1b)	first step	$(3.63 \pm 0.11) \times 10^{1}$	340
	slow step	$(2.2 \pm 0.01) \times 10^{-1}$	340
(1c)		$(1.66 \pm 0.04) \times 10^{-1}$	340
(1d)		$(1.56 \pm 0.05) \times 10^{-1}$	340
(1e)		$(6.44 \pm 0.24) \times 10^{-3}$	450
(11)		$(>5) \times 10^{4}$	340

*All reactions were carried out at 25 °C except (1e) which was at 25.3 °C.

Substituent Effects.—It has been shown that both the 1- and 2-acetyl derivatives, (1c) and (1d), add tcne at the unco-ordinated side of the molecule.[3] Introduction of the electron withdrawing acetyl group leads to a rate decrease. The rate reduction however is almost identical for (1c) and (1d). This suggests that steric factors are not dominant and that *exo* tcne attack is from a direction normal to the unco-ordinated double bond. An even greater rate reduction is observed for the tropone complex (1e). A more efficient electron withdrawing effect is possible here because of the known planar arrangement of the unco-ordinated double bond and the C=O group.[11] Thermodynamic activation parameters were measured for this reaction at 25 °C; $\Delta G^{\ddagger}$ 85.38(±0.08) kJ mol^{-1}, $\Delta H^{\ddagger}$ 36.15(±3.13) kJ mol^{-1}, and $\Delta S^{\ddagger}$ − 165.2(±10.5) J K^{-1} mol^{-1}. These values are reasonable and the negative entropy is as expected for an associative



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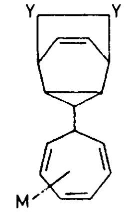

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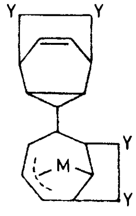

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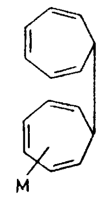

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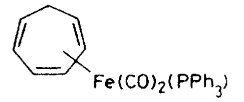

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TABLE 3

Effect of solvent on the rate of tcne addition

Compound	$k/dm^3\ mol^{-1}\ s^{-1}$	Solvent	Wavelength/ nm
(1a)	$(6.22 \pm 0.09) \times 10^{1}$	CH_2Cl_2	375
(1a)	$(2.34 \pm 0.06) \times 10^{2}$	CH_3NO_2	430
(6)	$(8.39 \pm 0.26) \times 10^{1}$	CH_2Cl_2	395
(6)	$(5.83 \pm 0.20) \times 10^{2}$	CH_3NO_2	420

reaction. When one of the CO groups in (1a) is replaced by the stronger σ donor PPh_3 the expected large rate increase is observed.

TABLE 4

Rate and equilibrium constants for the Scheme [a]

Method	k_1/dm^3 mol^{-1} s^{-1}	k_{-1}/s^{-1}	K	k_2'/dm^3 mol^{-1} s^{-1}
U.v.–visible	$(4.40 \pm 0.23) \times 10^{-2}$	$(1.14 \pm 0.06) \times 10^{-3}$	(38.2 ± 3.0)	
I.r.	$(4.72 \pm 0.18) \times 10^{-2}$	$(1.25 \pm 0.08) \times 10^{-3}$	(37.8 ± 2.9)	$(9.4) \times 10^{-4}$
Direct i.r.		$(1.32 \pm 0.07) \times 10^{-3}$	29.0	
N.m.r.			10.5 [b]	(1.06) [b] $\times 10^{-2}$

[a] All in CH_2Cl_2 unless otherwise stated. [b] In [$^2H_6$]acetone.

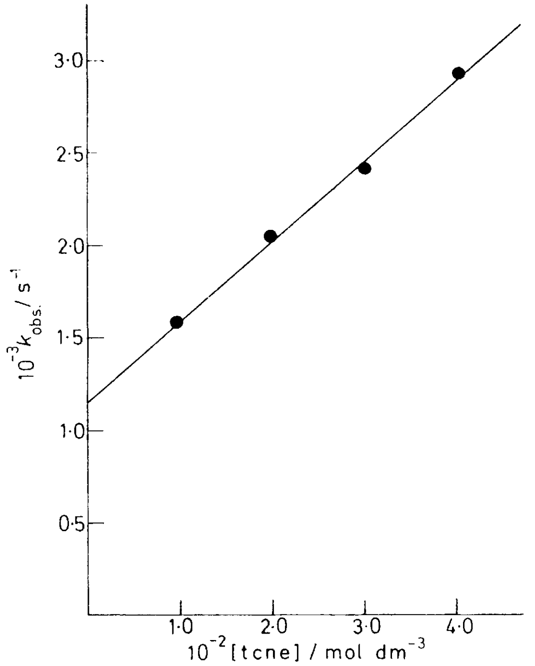
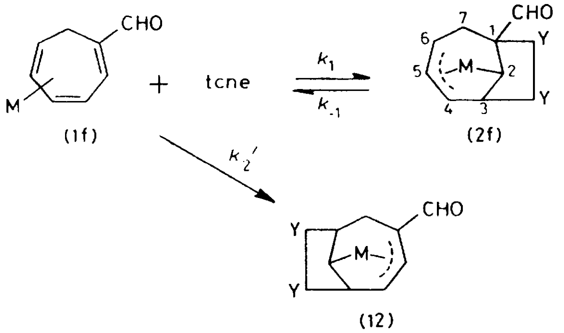


FIGURE 2 Plot of $k_{obs.}$ against [tcne] for (1f) in CH_2Cl_2



SCHEME

Tricarbonyl(1-*formylcycloheptatriene*)*iron*.—All the rates quoted in Table 2 were derived from plots of $k_{obs.}$ against [tcne]. In all cases good straight lines through the origin were obtained. The results for the 1-formyl complex (1f) however showed a large positive intercept, Figure 2 and Table 4. The presence of the intercept suggests that the system contains a rate-determining reaction which does not depend upon tcne concentration. To exclude a possible rate-determining biradical closure, the reaction was carried out in the cavity of an e.s.r. spectrometer. No e.s.r. signals were observed in the presence or absence of a free radical trap. When this reaction was carried out in an n.m.r. tube two things became clear. Firstly it was necessary to add three times the molar quantity of tcne to remove all of the absorptions due to (1f) and secondly the new absorptions did not correspond to those reported for the 4,6-adduct.[4] The new absorptions were easily assigned to (2f). The subsequent much slower formation of the 4,6-adduct was also observed. These results suggested the Scheme. The slope and intercept, Figure 2, are assigned to k_1 and k_{-1} respectively. When a large excess of tcne is used the equilibrium lies far to the right ($k_1 \gg k_{-1}$) and only k_1 is measured. It was also possible to measure k_{-1} directly as follows. After allowing sufficient time for the formation of (2f) (calculated using k_1 and the tcne concentration), an excess of α-terpinene * was added. [α-Terpinene undergoes rapid and irreversible $(2 + 4)$ π cycloaddition of tcne and reduces the tcne concentration to zero.] Following the removal of tcne the first-order conversion of (2f) back to (1f) could be monitored using the ν(M–C–O) i.r. bands. The value obtained for k_{-1} in this way is in excellent agreement with the value obtained in the forward reaction, Table 3 (direct i.r.). The equilibrium constant K was also measured using equilibrium i.r. intensity data and the result is in reasonable agreement with the more accurate kinetic data, Table 3. Due to slight decomposition over the long reaction times required k_2' was measured less accurately than all other data reported. For this reason errors are not quoted for the k_2' values obtained from either i.r. or n.m.r. data. The k_2' values are believed to be better than $\pm 20\%$. Using the kinetic results it was possible to estimate suitable reaction times for the isolation of pure samples of both (2f) and (12).

The possibility that (12) might arise by isomerization of (2f) and not by reaction of (1f) as shown in the Scheme cannot be eliminated by kinetic arguments (see Experimental section). However a 1,3 to 4,6 isomerization is unlikely since the known isomerization of this type involves the rupture of only one C–C bond.[3]

It is interesting to consider why none of the compounds in Table 2 undergoes a 4,6-addition. It has been shown that the preferred site of electrophilic attack is at the unco-ordinated side of (1a), (1c), (1d),[3] and (1e).[2] While sufficient deactivation of the unco-ordinated double

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* 4-Isopropyl-1-methylcyclohexa-1,3-diene.

bond should lead to a 4,6-addition no example in Table 2 has a rate less than k_2'. The only reason why (1f) does undergo a 4,6-addition is because its 1,3-addition is reversible. The reversibility is probably due to the labilizing effect of the strongly electron withdrawing formyl group.

EXPERIMENTAL

Ultraviolet–visible spectra were recorded on either a Cary 17 or a Beckmann DB-GT Spectrometer. Infrared spectra were obtained using a Unicam SP 200-G spectrometer. Kinetic measurements were made at 25 °C on either of the above spectrometers or on an Applied Photophysics stopped-flow device. Nuclear magnetic resonance spectra were recorded on a JEOL MH-100 spectrometer. The tcne additions, described in the Tables, which had been reported and characterized using methylene chloride as solvent were repeated using nitromethane with identical results. Rate constants were determined either from plots of $-\ln(A - A_\infty)$ against time or from Guggenheim plots. Temperature control was ±0.1 °C. The errors quoted were calculated as described by Swinbourne.[12] Thermodynamic parameters for the reaction of complex (1e) were determined from the slope of a plot of $\ln k$ against $1/T$. The rate expressions for the Scheme and the alternative isomerization possibility are $k_{\text{obs.}} = k_2'[\text{tcne}]/(1 + K[\text{tcne}])$ and $k_{\text{obs.}} = k_2''K[\text{tcne}]/(1 + K[\text{tcne}])$ respectively. In both cases a plot of $1/k_{\text{obs.}}$ against $1/[\text{tcne}]$ gives a straight line with an intercept, and in each case the slope times K equals the intercept. Kinetic results therefore cannot distinguish these two possibilities.

(η-Bicycloheptatrienyl)tricarbonyliron, (1b).—A suspension of $[C_7H_7][BF_4]$ (4.0 g) in CH_2Cl_2 (50 cm^3) was treated with (1a) (6 g). After stirring for 5 h dropwise addition of OEt_2 precipitated tricarbonyl(η-6-cycloheptatrienylcycloheptadienium)iron tetrafluoroborate, 8.2 g (Found: C, 49.5; H, 3.5. $C_{17}H_{15}BF_4FeO_3$ requires C, 49.8; H, 3.7%). Treatment with sodium methoxide and silica gel, by the method previously used for other cycloheptatriene complexes,[13] converted this salt into (1b), a yellow oil, 60% (Found: C, 63.4; H, 4.4. $C_{17}H_{14}FeO_3$ requires C, 63.4; H, 4.4%).

Reactions with tcne.—Complex (1b) reacted rapidly with tcne in methylene chloride (0.5 h, 20 °C) to give white crystals of (8) (Found: C, 61.1; H, 3.3; N, 12.2. $C_{23}H_{14}FeN_4O_3$ requires C, 61.3; H, 3.1; N, 12.4%). Compound (8) reacted with further tcne to yield (9) (Found: C, 60.45; H, 2.5; N, 19.1. $C_{29}H_{14}FeN_8O_3$ requires C, 60.2; H, 2.4; N, 19.4%). The i.r. spectra support the structures assigned to these compounds. The 1,3-adducts having similar ν(MC–O) frequencies. I.r.: ν(MC–O), $CHCl_3$ solution, (1b), 2 048 and 1 978 cm^{-1}; (8), 2 054 and 1 983 cm^{-1}; (2a), 2 076 and 2 012 cm^{-1}; and (9), 2 080 and 2 013 cm^{-1}. Dicarbonyl(η-cycloheptatriene)(triphenylphosphine)iron reacted with tcne to give an adduct (Found: C, 66.5; H, 4.0; N, 9.3. $C_{33}H_{23}FeN_4O_3P$ requires C, 66.7; H, 3.9; N, 9.4%).

Tricarbonyl(η-formylcycloheptatriene)iron.—In an n.m.r. tube (1f) (35 mg) in [$^2H_6$]acetone (0.4 cm^3) was treated with tcne (36 mg, three-fold excess). The n.m.r. spectrum of (1f) was immediately replaced by the following new absorptions, (2f), Scheme: 1.82(d), 9 Hz, 1 H, H^2; 2.6(d), 16 Hz, 1 H + 3.5 (dd), 16 and 6 Hz, 1 H, H^7; 4.64(m), 1 H, H^3; 5.0(m), 1 H, H^6; 5.24(m), 2 H, H^4 + H^5; 9.74 (s) p.p.m., 1 H, CHO. The observation of a doublet at 1.82 p.p.m. strongly supports structure (2f). Spin decoupling experiments also supported this assignment. After *ca.* 0.5 h new absorptions appeared. The new absorptions eventually replaced those assigned to (2f) and corresponded exactly to those reported by Goldsmidt and Bakal for (12).[4] It is also possible to monitor these reactions in methylene chloride solution using the ν(MC–O) i.r. absorption bands. In CH_2Cl_2 i.r. bands are observed for (1f) at 2 054 and 1 987 cm^{-1}; for (2f) at 2 076 and 2 014 cm^{-1}; and for (12) at 2 082 and 2 021 cm^{-1}. Using the kinetic data as a guide it was possible to obtain a pure sample of (2f). Compound (1f) (0.18 g) and tcne (0.39 g) in CH_2Cl_2 (50 cm^3) were allowed to react for 0.5 h. The solution was frozen with liquid nitrogen and the solvent was removed rapidly under vacuum when the temperature was allowed to rise. Excess of tcne and a trace of (1f) were removed in an efficient sublimation apparatus (liquid nitrogen cold finger, 10^{-3} Torr) * at 40 °C, to leave (2f), 80% (Found: 52.0; H, 2.4; N, 14.3. $C_{17}H_8FeN_4O_4$ requires C, 52.6; H, 2.1; N, 14.1%).

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* Throughout this paper: 1 Torr = (101 325/760) Pa.

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