

THE REACTION OF TRICARBONYL-8-*p*-TOLYL-8-AZAHEPTAFULVENEIRON WITH TETRACYANOETHENE

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Summary

The azaheptafulvene complex adds two molecules of tetracyanoethene, TCNE, in a stepwise reversible manner. The 1 : 2 adduct was observed in solution but was not isolated. The rate of addition of both TCNE molecules was measured.

Introduction

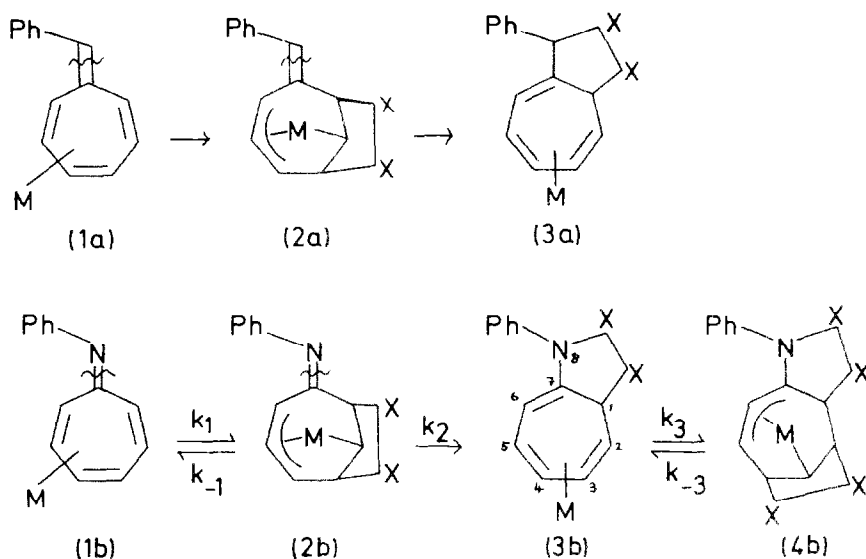
The cycloadditions of dienophiles to heptafulvenes and their η^4 -tricarbonyliron complexes were initially believed to be [8 + 2]- π -cycloadditions leading to 1,8-adducts with structures of type **3** [1,2]. A kinetic study of the addition of tetracyanoethene, TCNE, to the 8-phenylheptafulvene complex **1a** showed that the primary product was in fact a 1,3-adduct, which readily isomerised to a 1,8-adduct (Scheme 1) [3]. Since it had already been shown that 8-*p*-tolyl-8-azaheptafulvene and its tricarbonyliron complex **1b** react with the 1,3-dipolarophile DPNI to give cycloadducts [4,5], it was decided to investigate its reaction with the TCNE. It was hoped that this reaction would provide an interesting comparison with the reactions of the parent heptafulvene complexes.

Results and discussion

Complex **1b** reacts with TCNE in dichloromethane. Analytical data indicated the formation of a 1 : 1 adduct. The structure **3b** was assigned on the basis of the position of its $\nu(\text{MC}-\text{O})$ IR bands, its Mössbauer spectrum and by analogy with the reaction sequence previously established for the phenylheptafulvene complex. The solubility of **3b** was insufficient for NMR purposes.

Infrared and Mössbauer spectra

The IR spectra of almost all tricarbonyliron complexes in dichloromethane solution in the $\nu(\text{MC}-\text{O})$ region consist of two peaks. The band at higher frequency



SCHEME 1

is always sharper and is the symmetric stretching mode while the broad antisymmetric stretch absorbs approximately 60 cm^{-1} lower in frequency. Complex **1b** has IR absorptions at 2054 and 1989 cm^{-1} . On addition of TCNE to dichloromethane solutions of **1b** absorption bands due to the symmetric stretching modes of three new complexes are observed (Table 1).

When equimolar equivalents of TCNE and **1b** are used, initially bands due to **1b** at 2054 and 1989 cm^{-1} and a new sharp peak at 2076 cm^{-1} are observed. After a few seconds the band at 2076 cm^{-1} decreases and another sharp peak appears at 2063 cm^{-1} . This peak at 2063 cm^{-1} is due to the product isolated under preparative conditions, and this is clearly not the primary addition product. Under pseudo-first order conditions, with TCNE in tenfold excess, the $\nu(\text{MC}-\text{O})$ IR bands due to **1b** were not observed at all. Initially peaks were observed at 2076 , 2063 and 2002 cm^{-1} . After 2 min the sharp peak at 2076 cm^{-1} had decreased and 2063 cm^{-1} was the

TABLE 1
INFRARED SPECTRA ($2100\text{--}1800 \text{ cm}^{-1}$)

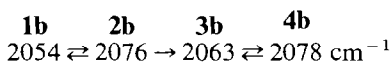
1a	2046	1983
1b	2054	1989
2a	2074	2012
2b	2076	-
3a	2063	2003
3b	2063	2002
4b	2078	-

strongest sharp band, and after 10 min, the 2063 cm^{-1} band began to decrease, and a new sharp peak at 2078 cm^{-1} increased with time.

Reversibility of adduct formation

Introduction of a simple conjugated diene which reacts rapidly and irreversibly with TCNE can be used to test the reversibility of adduct formation, and α -terpinene; 4-isopropyl-1-methylcyclohexa-1,3-diene is suitable for this purpose [6].

Addition of α -terpinene to a solution of equimolar equivalents of **1b** and TCNE which had peaks at 2076, 2063, 2054 and 1990 cm^{-1} , removed the band at 2076 cm^{-1} and enhanced the peaks due to **1b**. The peak at 2063 cm^{-1} did not change in intensity. Treatment of a solution of **1b** with a tenfold excess of TCNE, which had peaks at 2078, 2063 and 2002 cm^{-1} , removed the band at 2078 cm^{-1} and the peaks at 2063 and 2002 cm^{-1} increased. Thus a sequence of reactions represented by the frequency changes



must be present. It is also clear that at least the first and last reactions must involve TCNE.

Mössbauer spectra

It has been demonstrated that the η^4 mode of bonding in structures **1** and **3** can be distinguished from the η^3, η^1 bonding mode exhibited by structure **2** [7]. The former show broad quadrupole splittings $> 1.3\text{ mm s}^{-1}$ and the latter narrow splittings of $< 1.0\text{ mm s}^{-1}$. The isolated adduct **3b** has the expected broad quadrupole splitting ($\Delta 1.32\text{ mm s}^{-1}$, $\delta 0.30\text{ mm s}^{-1}$), and its $\nu(\text{MC-O})$ IR bands are very close to those of **3a**. Frozen acetone solutions of **3b** with a tenfold excess of TCNE showed a doublet with a small quadrupole splitting, ($\Delta 0.92\text{ mm s}^{-1}$, $\delta 0.30\text{ mm s}^{-1}$), characteristic of the η^3, η^1 bonding mode. Structure **4b** is suggested for the 1:2 adduct, that is the species formed by addition across the 2,4 positions of **3b**, since the alternative 5,7-addition seems unlikely for steric reasons.

Kinetic studies

The UV-VIS spectrum of **1b** changes on addition of TCNE. An increase in absorbance at 470 nm was observed followed by a slow decrease. The increase in absorbance was examined using a stopped flow apparatus. This increase was found to be independent of TCNE concentration (Table 2). The rate of the slow decrease was found to be dependent on TCNE concentration, as can be seen from Table 3. However, the second order plot of the Table 3 data showed a positive intercept. These results are interpreted in terms of Scheme 1.

The increase in absorbance which is independent of TCNE concentration is the 1,3- to 1,8-isomerization, with rate constant k_2 . The TCNE-dependent decrease in absorbance is the addition of the second TCNE, with rate constant k_3 , and the positive intercept represents the reversible loss of this second TCNE, with rate constant k_{-3} . An increase in absorbance in the visible region would be expected for the 1,3- to 1,8-isomerization process, k_2 , since complexes with structure **2** are usually colourless while η^4 -diene complexes are usually light yellow in colour and absorb at 470 nm. A decrease in absorbance is thus also reasonable for the addition

TABLE 2
FIRST ORDER RATE CONSTANTS

[TCNE] ($\times 10^{-3}$)	k_2 ($\times 10^{-2}$) (s^{-1})
9.93	1.81 (± 0.03)
19.89	1.82 (± 0.04)
30.11	1.79 (± 0.04)
40.05	1.78 (± 0.06)
44.93	1.80 (± 0.03)

TABLE 3
FIRST ORDER RATE CONSTANTS^a

[TCNE] ($\times 10^{-3}$)	k_{obs} ($\times 10^{-2}$) (s^{-1})
1.97	4.00 (± 0.07)
3.96	6.20 (± 0.07)
5.99	7.80 (± 0.11)
8.04	9.40 (± 0.20)
10.09	10.80 (± 0.20)

^a Slope, k_3 13.8 (± 0.6) ($\times 10^{-2}$) $dm^3 mol^{-1} s^{-1}$. Intercept, k_1 4.45 (± 0.6) ($\times 10^{-4}$) s^{-1} .

of the second TCNE to **3b**. The value of the observed first order rate constant, k_1 $1.8 \times 10^{-4} s^{-1}$ is larger than that of k_3 $4.45 \times 10^{-4} s^{-1}$, and that for pseudo-first order rate constant for the second order reaction at the highest concentration used, $1.38 \times 10^{-3} s^{-1}$. This rate difference is sufficient to allow time differentiation between the 1,3- to 1,8-isomerisation and the addition of the second TCNE.

The failure to observe the addition of the first TCNE, k_1 , in dichloromethane with the stopped flow apparatus is not unprecedented. The addition of TCNE to the electron-rich (η^4 -cycloheptatriene)Fe(CO)₂PPh₃ is also too fast to measure on the same apparatus [6]. Complex **1b** is not the first tricarbonyliron complex that was found to undergo addition of two dienophiles: tricarbonylditropylium also adds two molar equivalents of TCNE in a stepwise manner, the first to the uncoordinated ring and the second to the coordinated ring. However in the ditropyl system the two ring π -systems are not conjugated with one another [8]. Since **1b** is the first complex reported to undergo the addition of two molecules of TCNE to the same complexed conjugated π -system, (a reaction which is not observed for **1a**), it is reasonable that the first TCNE addition to **1b** should be fast.

Experimental

Infra-red spectra were obtained on a Unicam SP 200G spectrometer. Rate studies were carried out with either a Beckman DB-GT Ultraviolet-visible spectrometer or on an Applied Photophysics stopped-flow device. Stopped flow kinetic data were recorded on a transient recorder and transferred to a BBC microcomputer for computation of the rate constants. The temperature on the Beckmann and the Stopped flow device was maintained constant to $\pm 0.1^\circ C$. The errors quoted were

calculated as described by Swinbourne [9]. Mössbauer spectra were obtained on a J & P Engineering Spectrometer with the sample at liquid nitrogen temperature and the source at room temperature. The spectrometer was calibrated with sodium nitroprusside and the values quoted are accurate to $\pm 0.003 \text{ mm s}^{-1}$. The Mössbauer spectra of frozen acetone solutions were obtained by plunging a small aluminum foil packet of the solution into liquid nitrogen. The foil packets were formed on a suitable coin (an Irish penny) which was removed before the solution was injected from a syringe.

Reaction with TCNE

Complex **1b** (0.15 g) and TCNE (0.07 g) were stirred for 1 h with dichloromethane (25 ml). The solvent was removed and the product **3b** crystallized (70%). (**3b**), IR $\nu(\text{MC-O})(\text{CH}_2\text{Cl}_2)$ 2002 and 2063 cm^{-1} . Found: C, 59.8; H, 3.0; N, 14.8%, $\text{C}_{23}\text{H}_{13}\text{N}_5\text{O}_3\text{Fe}$ calcd.: C, 59.6; H, 2.8; N, 15.1%.

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