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Preliminary communication

DIENOPHILE ADDITION TO (η^4-CYCLOHEPTA-1,3,5-TRIENE)-TRICARBONYLIRON; A CONCERTED REACTION

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Summary

Kinetic data for the addition of tetracyanoethylene (1), and tricyanoethylene (2), to (η^4-cyclohepta-1,3,5-triene)$Fe(CO)_3$ (3), suggest that the reactions are concerted.

The application of orbital symmetry rules to the cycloaddition reactions of coordinated trienes and tetraenes has been helpful in the elucidation of reaction mechanisms. It has also been possible to classify some apparent addition modes as "non-allowed" and subsequent experimental work has confirmed these predictions [1,2].

The assumption of a concerted nature for the addition of for example tetracyanoethylene (1), to (η^4-cyclohepta-1,3,5-triene)$Fe(CO)_3$ (3), to give the 1,3-adduct 4 has been justified on the basis of solvent effects on the rate of addition [1,3]. The small solvent effects observed were used to discount the dipolar intermediate 5. In the search for stronger evidence and a better test of "concertedness" the reaction between tricyanoethylene (2), and 3 has been examined. A 1/1 adduct is readily formed between 2 and 3 and satisfactory analytical data have been obtained.

It has been shown by Huisgen [4] that a typical concerted (4+2) cycloaddition reaction of the Diels—Alder type will exhibit large rate reductions of between 10^2 and 10^4 on changing dienophile from 1 to 2 whereas a (2+2) cycloaddition involving an ionic intermediate, e.g. isobutenyl methyl ether, will show only a small rate change, Table 1. The reaction rates observed for 3 clearly classify this 1,3-addition as a concerted reaction. Similar large rate reductions have been observed for other tricarbonyliron complexes which undergo 1,3-addition reactions with dienophiles 1 and 2.

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TABLE 1 [a]

	Diels—Alder type		Dipolar	
	Cyclopentadiene [b]	Dimethylanthracene [b]	Isobutenyl methyl ether [b]	(3) [c]
1	4.80×10^5	5.9×10^6	2.39	$6.22(8) \times 10^6$
2	4.30×10^7	1.3×10^{10}	3.97	$9.12(8) \times 10^3$
Rate ratio	89.5	2203	1.66	682

[a] All rates $10^5 \times k_2$ (dm^{-3} mol^{-1} s^{-1}). [b] From ref. 4. [c] CH_2Cl_2 solution at 25°C.

References

1 M. Green, S.M. Heathcock, T.W. Turney and D.M.P. Mingos, J. Chem. Soc., Dalton Trans., (1977) 204.
2 S.K. Chopra, G. Moran and P. McArdle, J. Organomet. Chem., 214 (1981) C36.
3 S.K. Chopra, M.J. Hynes and P. McArdle, J. Chem. Soc., Dalton Trans., (1981) 586.
4 R. Huisgen and R. Schug, J. Am. Chem. Soc., 98 (1976) 7819.