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The Photochemical Reaction of Iron Pentacarbonyl and 1,3-Butadiene-1,1,4,4-d_4. The Lack of Secondary Isotope Effects

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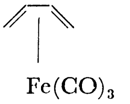
Synopsis. No significant deuterium isotope effects have been noticed in the formation of the 1,3-butadiene–iron tricarbonyl complex, in contrast to the olefin complexation of Ag^+ or Rh(I) species.

Deuterated olefins and 1,3-dienes are known to form complexes with silver nitrate more readily than their undeuterated analogs.[1] The same trend has been observed with the reaction of Rh(I) complexes.[2] In connection with a mechanistic study of the iron carbonyl-promoted reaction of 1,3-dienes and α,α'-dibromo ketones,[3] we have now examined the reaction of a deuterated butadiene and iron pentacarbonyl [$Fe(CO)_5$].

Intermolecular competition experiments were carried out using an approximate 1 : 1 mixture of 1,3-butadiene (**1**) and 1,3-butadiene-1,1,4,4-d_4 (**2**). A mixture of $Fe(CO)_5$ and a 10-fold excess of **1** and **2** was placed in a sealed Pyrex tube and exposed to a high-pressure mercury arc. The resulting iron carbonyl complexes, **3** and **4**, were isolated, and the isotopic composition was analyzed carefully on a 100 MHz NMR machine with a CAT system. The correction of the rate constant of the d_4 substrate to a per deuterium basis was done in order to determine the secondary deuterium isotope effect, k_H/k_D. The results, given in Table 1, indicate that the deuterium substitution does not exert any significant influence on the rate of butadiene–iron tricarbonyl complex formation.



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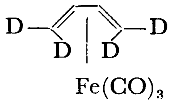

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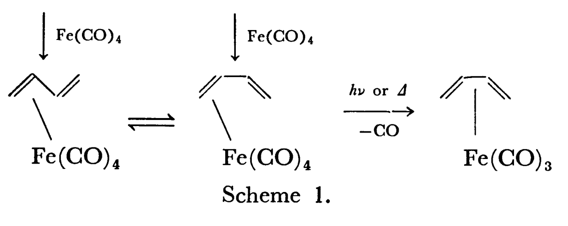
The photochemical reaction between $Fe(CO)_5$ and butadiene is considered to proceed through the pathway outlined in Scheme 1.[4] Since the butadiene ligand in **3** is not displaced by free butadiene under the present reaction conditions, the negligible deuterium isotope effect is associated with the stage of iron tetracarbonyl–butadiene (as a monoolefinic ligand) complex formation. In iron carbonyl–olefin complexes, the σ-donative ability of the olefinic ligand is less important than the π-acceptor capacity;[5] accordingly, unlike the cases of Ag^+ and Rh(I),[1,2] subtle difference in electronic properties between deuterium and protium does not affect the relative complex stabilities. In addition, this observation may imply that carbon atoms of the butadiene–iron tetracarbonyl complex are little distorted from the sp^2-hybridized structures.[6]

Table 1. Secondary deuterium isotope effect in the formation of butadiene–$Fe(CO)_3$ complex

Run	Butadiene composition, d_4/d_0[a)]	$Fe(CO)_3$ complex composition, d_4/d_0[a,b)]	$(k_H/k_D)^4$, obsd	k_H/k_D
1	0.898[c)]	0.899	0.999	1.00
2	1.19[d,e)]	1.24	0.964	0.992
3	1.19[d)]	1.21	0.983	0.996
			Av 0.982	0.996

a) Determined by NMR analysis. b) Average of 50 integrations. c) Average of 39 integrations. d) Average of 100 integrations. e) Recovered butadiene $d_4/d_0 = 1.20$.



Scheme 1.

Experimental

The NMR spectra were recorded on a Varian Associates Model HA-100D spectrometer equipped with a Model C-1024 time-averaging computer. 1,3-Butadiene (**1**) (Tokyo Kasei) was used after distillation. 1,3-Butadiene-1,1,4,4-d_4 (**2**) was prepared by the method of Cope[9] and stored at −20 °C on Molecular sieves 3A before use. The NMR spectrum (CCl_4 solution, tetramethylsilane as the internal standard) exhibited a very small signal due to $=CH_2$ protons, indicating that the butadiene was *ca.* 96% labeled. An approximate 1 : 1 mixture of **1** and **2** was prepared, and the ratio of the d_0 substrate to the d_4 substrate was determined on the basis of integrated relative intensities for the $=CH_2$ (δ 5.10) and $=CH-$ (δ 6.25) signals in the NMR spectrum (CCl_4 solution), using factors obtained from the spectrum of undeuterated diene, **1**. The values in Table 1 are averages of 39 or 100 integrations. The isotopic composition of the iron tricarbonyl adduct was determined in the same manner; **3** (benzene-d_6 solution) showed signals at δ (benzene signal taken as δ 7.37) 0.09, 1.55 ($=CH_2$), and 4.88 ($=CH-$).

A typical experiment was executed as follows. A Pyrex tube (1 cm × 20 cm) equipped with a rubber septum was flushed with nitrogen and cooled at −78 °C. To this vessel we then introduced $Fe(CO)_5$ (Strem Chemicals, 79 mg, 0.4 mmol) and a mixture of **1** and **2** (220 mg, 4 mmol, $d_0/d_4 = 1.00/0.898$) by means of microsyringes. The tube was sealed, warmed to room temperature, and exposed to a 200 W high-pressure mercury lamp from a distance of 2 cm. After a 40-min irradiation, the tube was opened and the unreacted butadiene was removed under atmospheric pressure. The short-path distillation of the residue (20 mmHg; bath temperature, 70—100 °C) gave a mixture of **3** and **4** as a yellow oil (61 mg, 78% yield). The product was recrystallized from pentane at −90 °C under nitrogen and immediately subjected to the NMR analysis under an argon atmosphere (benzene-d_6); this analysis indicated the production of **3** and **4** in a 1 : 00 : 0.999 ratio.

References

1) R. J. Cvetanović, F. J. Duncan, and W. E. Falconer, *Can. J. Chem.*, **41**, 2095 (1963); R. J. Cvetanović, F. J. Duncan, W. E. Falconer, and R. S. Irwin, *J. Am. Chem. Soc.*, **87**, 1827 (1965).

2) V. Schurig and E. Gil-Av, *Chem. Commun.*, **1971**, 650.

3) R. Noyori, S. Makino, and H. Takaya, *J. Am. Chem. Soc.*, **93**, 1272 (1971); R. Noyori, Y. Baba, S. Makino, and H. Takaya, *Tetrahedron Lett.*, **1973**, 1741; R. Noyori, S. Makino, T. Okita, and Y. Hayakawa, *J. Org. Chem.*, **40**, 806 (1975); R. Noyori, Y. Baba, and Y. Hayakawa, *J. Am. Chem. Soc.*, **96**, 3336 (1974); R. Noyori, S. Makino, Y. Baba, and Y. Hayakawa, *Tetrahedron Lett.*, **1974**, 1049; R. Noyori, T. Souchi, and Y. Hayakawa, *J. Org. Chem.*, **40**, 2681 (1975); Y. Hayakawa, M. Sakai, and R. Noyori, *Chem. Lett.*, **1975**, 509.

4) E. Koerner von Gustorf, Z. Pfajfer, and F. -W. Grevels, *Z. Naturforsch.*, **26b**, 66 (1971).

5) Olefins bearing electron-withdrawing group(s) form the stable iron tetracarbonyl complexes; E. Koerner von Gustorf and F. -W. Gravels, *Fortschr. Chem. Forsch.*, **13**, 366 (1969).

6) The diene framework in **3** remains planar.[7] On the other hand, olefinic carbons in iron tetracarbonyl—electron-deficient olefins are considerably distorted from the sp^2 structures.[8]

7) O. S. Mills and G. Robinson, *Acta Crystallogr.*, **16**, 758 (1963); P. Crews, *J. Am. Chem. Soc.*, **95**, 636 (1973).

8) A. R. Luxmoore and M. R. Truter, *Proc. Chem. Soc. (London)*, **1961**, 466; P. Corradini, C. Pedone, and A. Sirigu, *Chem. Commun.*, **1966**, 341.

9) A. C. Cope, G. A. Berchtold, and D. L. Ross, *J. Am. Chem. Soc.*, **83**, 3859 (1961).