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PENTACARBONYLCHROMIUM—SOLVENT COMPLEXES

FLASH-SPECTROSCOPIC DETERMINATION OF RATE CONSTANTS OF FORMATION AND OF STABILITY CONSTANTS AND THEIR APPLICATION AS SOLVENT PARAMETERS TO CATALYTIC BUTADIENE OLIGOMERISATION*

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Summary

The rates of reaction of $\text{Cr}(\text{CO})_5$ with several solvents L (L = acetone, acetonitrile, benzene, diethyl ether, ethyl acetate and methanol) and of the decay of the $\text{Cr}(\text{CO})_5\text{L}$ in CO-saturated cyclohexane solutions have been measured by both conventional and laser flash photolysis. The rate constants for formation and the stability constants of $\text{Cr}(\text{CO})_5\text{L}$ have been deduced, and both sets of values are suggested as possible solvent parameters for organometallic reactions [e.g. for the catalytic oligomerisation of butadiene by dibutadiene-iron monocarbonyl].

Introduction

Solvent effects in organic chemistry are well known to influence both the rate and course of reactions [1,2]. A variety of solvent parameters has been developed to describe these phenomena. One of the most useful is the E_T value, which relates to the solvent dependent transition energy of *N*-phenolpyridinium betaines [2].

We have recently investigated the oligomerisation of butadiene to 1,5-cyclooctadiene (COD) and 4-vinylcyclohexene (VCH), catalysed by dibutadiene-monocarbonyliron in the presence of triphenylphosphine [3]. Besides these main products, isomers of vinylcyclohexene^{††}, and both 1,3- and 1,4-cyclooc-

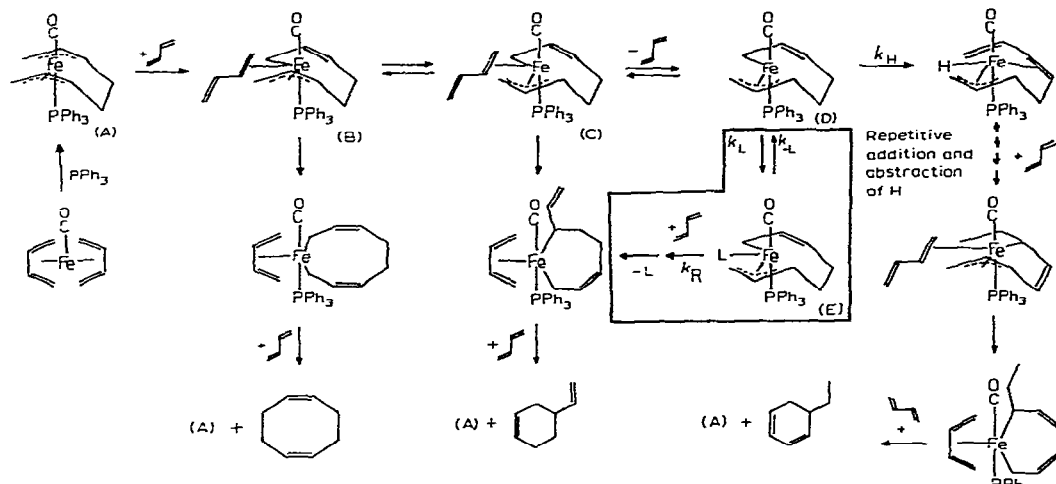
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†† These products all give ethylcyclohexane on hydrogenation.



Scheme 1. The suggested mechanism for the oligomerisation of butadiene catalysed by dibutadiene-monocarbonyliron in the presence of triphenylphosphine [3].

tadiene are formed. These side products are not produced by a secondary isomerisation of the main products but rather stem from a competing reaction of the catalytically active intermediate (see Scheme 1). The extent of formation of these side products is influenced by the solvent, although the ratio of main to side products cannot be adequately predicted by the E_T values, as is especially apparent for methanol (see Table 1). Isomerisation reactions involving β -hydrogen abstraction and transfer require the creation of a free coordination site in the closed shell complex [4]; so it is conceivable that the solvent, by its coordinating ability, may have a specific effect on these reactions by blocking such sites (see Scheme 1).

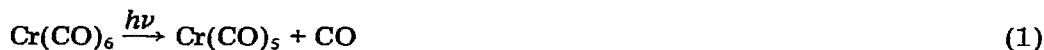
In our search for a suitable solvent parameter, it was felt that useful information might be gained by examining the reactivity of the coordinately unsaturated species $\text{Cr}(\text{CO})_5$ towards these solvents (L) as Ligands, and by examining

TABLE 1
OLIGOMERISATION OF BUTADIENE AS A FUNCTION OF THE SOLVENT

Solvent	Main products ^a (%)	Side products ^b (%)	R_{prod} (Side products/Main products)	E_T^c (kcal/mol)
n-Hexane	55.2	15.1	0.27	30.9
Benzene	59.5	14.6	0.25	34.5
Diethyl ether	64.0	14.5	0.23	34.6
Methanol	64.2	9.2	0.14	55.5
Ethyl acetate	69.4	10.0	0.14	38.1
Acetone	72.3	8.2	0.11	42.4
Acetonitrile	74.1	5.9	0.08	46.0

^a 4-Vinylcyclohexene and 1,5-cyclooctadiene. ^b 1,3- and 1,4-cyclooctadiene and isomers of 4-vinylcyclohexene. ^c See ref. 2.

the stability of the $\text{Cr}(\text{CO})_5\text{L}$ species formed*. We have recently shown [6] that flash photolysis of $\text{Cr}(\text{CO})_6$ in cyclohexane gives a highly reactive species**, suggested to be $\text{Cr}(\text{CO})_5$, which reacts rapidly with CO to reform $\text{Cr}(\text{CO})_6$. It



was further suggested [6] that the conflicting and irreproducible results in earlier studies [8,9] were caused by the exceptional reactivity of this species towards small amounts of coordinating contaminants.

We anticipated that in the presence of L, the reactions 3 and 4 would take place after the photochemical generation of $\text{Cr}(\text{CO})_5$. The $\text{Cr}(\text{CO})_6$ is reformed



by reaction 2***. If the rate constants for steps 3 and 4 are evaluated, then the equilibrium constant for the process 6 may be calculated, giving a measure of



the stability of $\text{Cr}(\text{CO})_5\text{L}$ complex. In addition, the rate constant for reaction of the uncoordinated species with L (eqn. 3) will give insight into whether a correlation exists between the chemical nature of the solvent and its speed of coordination to an unsaturated metal centre.

Experimental

Materials

Hexacarbonyl chromium (Schuchardt) was purified by sublimation. Carbon monoxide was either from Messer Griesheim (purity 99.997%), or BASF [purified by passage through columns containing BTS catalyst (BASF) and calcium chloride]. Cyclohexane (Merck p.a.) was chromatographed successively through an alumina and silver nitrate column, and then distilled from an 80 theoretical plate column. Gas chromatography showed that the material contained less than 10 ppm impurity. Methanol (Merck p.a.) was refluxed over 2,4-dinitrophenylhydrazine and distilled. Acetone (Merck p.a.) was distilled. Ethyl acetate (Merck p.a.) was distilled from tolylene-2,4-diisocyanate. Acetonitrile (Merck

* Some preliminary experiments in this area were previously carried out by Kirsch and Nasielski [5].

** Wrighton [7] has suggested that the primary species might be $\text{Cr}(\text{CO})_5\text{—OC}$. However, if this were the case, one would have to postulate that CO and L react with the species by an S_N2 type reaction, as decomposition of such a species to yield a rapidly reacting $\text{Cr}(\text{CO})_5$ is incompatible with our findings.

*** An S_N2 type reaction (eqn. 5) is inherently unlikely [10] and, as will be shown later, is not applicable to the systems investigated here.



p.a.) was distilled. Diethyl ether (Merck p.a.) was distilled from sodium. Benzene was distilled from sodium under an N_2 atmosphere. The purity of all liquids (GC) was $> 99.9\%$.

Sample preparation

All solutions were prepared under argon in flasks fitted with greaseless taps. All operations were carried out under diffuse red light.

For laser flash photolysis. The $Cr(CO)_6$ concentration was 0.5 to $1.0 \times 10^{-3} M$. The solutions were transferred under exclusion of air to a cell with connected degassing vessel which had previously been filled with an atmosphere of CO. The samples were shaken but were not further degassed in order to avoid loss of the ligand.

For conventional flash photolysis. The concentration of $Cr(CO)_6$ was 0.5 to $1.0 \times 10^{-4} M$. The samples were prepared by one of the following methods and then allowed to become saturated under one atmosphere of CO. The following preparation procedures were employed.

(a) 4 cycles of freezing at liquid nitrogen temperature, pumping to 10^{-3} mmHg, thawing and shaking.

(b) Sample prepared under argon and then transferred to the cell and degassing vessel, which has previously been filled with CO.

(c) As in (b), but followed by pumping on the liquid sample at room temperature. This method involves some loss of solvent ($\approx 10\%$) and a possible change in ligand concentration, in which cases a correction was made. Using the anthracene triplet as a probe, it was shown that this method was as effective as method (a) for the removal of oxygen.

Methods (a) and (b) are inadequate in removing certain reactive contaminants from cyclohexane solutions, and in these cases secondary species formed by reaction 7 are observed [6].



In samples prepared by method (c), the concentration of these secondary species was largely (though not completely) reduced. In the presence of these trace contaminants, however, eqn. 13 for the rate of decay of $Cr(CO)_5L$ will not be modified substantially so long as $k_3[L] \gg k_7[X]$ and $k_8 \gg k_4$. This is the case for acetone, ethyl acetate and diethyl ether; for benzene, which reacts more slowly with $Cr(CO)_5$, and is only weakly bonding, a secondary species is observed. In this case, therefore, only method (c) gives reliable results. Results using the various preparation methods are given in Table 3.

Apparatus

All experiments were carried out at room temperature ($23 \pm 2^\circ$).

Laser flash photolysis. The apparatus (Applied Photophysics Ltd.) employs a frequency doubled Q-switched ruby laser as the exciting source (a single pulse at 347 nm, duration 30 ns). The monitoring light (from a pulsed Xenon lamp) passes through the cell colinearly with the laser pulse. Maximum changes in optical densities measured were in the range 0.01 to 0.10.

Conventional flash photolysis was carried out on the previously described apparatus [11]. The exciting light was from a quartz argon discharge lamp (flash half-duration $\leq 3 \mu\text{s}$). The cell length was 13 cm. Spectra were measured by the point by point method at intervals of 10 nm.

Treatment of results

First order plots for decaying species were made by plotting $\log(\Delta \text{OD})$ versus time, t , where $(\Delta \text{OD}) = \log(I_0/I_t)$, I_0 being light intensity through cell before flashing and I_t the light intensity through cell at a particular time, t , after the flash. The gradient of the plot is then $-k/2.303$.

For systems where formation of a product is observed ("grow-in"), $\log \log(I_t/I_\infty)$ is plotted against t (I_∞ is light intensity through cell after product formation is complete). The gradient of the plot is $-k/2.303$.

For the competing reactions of $\text{Cr}(\text{CO})_5$ with L and with CO (eqns. 2 and 3), both the rate of decay of $\text{Cr}(\text{CO})_5$ and that of the formation of $\text{Cr}(\text{CO})_5\text{L}$ may be monitored.

$$-\frac{d[\text{Cr}(\text{CO})_5]}{dt} = (k_3 \cdot [\text{L}] + k_2 \cdot [\text{CO}]) \cdot [\text{Cr}(\text{CO})_5]_t \quad (9)$$

$$\frac{d[\text{Cr}(\text{CO})_5\text{L}]}{dt} = k_3 \cdot [\text{L}] \cdot [\text{Cr}(\text{CO})_5]_t \quad (10)$$

Clearly from eqn. 9, $\text{Cr}(\text{CO})_5$ will decay by a first order process with a rate constant k_t of $(k_3[\text{L}] + k_2[\text{CO}])$.

Further, as $[\text{Cr}(\text{CO})_5]_t = [\text{Cr}(\text{CO})_5]_0 - [\text{Cr}(\text{CO})_5\text{L}]_t - \Delta[\text{Cr}(\text{CO})_6]_t$

$$\text{and } \Delta[\text{Cr}(\text{CO})_6]_t = \frac{k_2 \cdot [\text{CO}]}{k_3 \cdot [\text{L}]} \cdot [\text{Cr}(\text{CO})_5\text{L}]_t$$

$$\text{and } [\text{Cr}(\text{CO})_5]_0 = \frac{k_2 \cdot [\text{CO}] + k_3 \cdot [\text{L}]}{k_3 \cdot [\text{L}]} \cdot [\text{Cr}(\text{CO})_5\text{L}]_\infty$$

$$\text{then, } [\text{Cr}(\text{CO})_5]_t = \frac{k_3 \cdot [\text{L}] + k_2 \cdot [\text{CO}]}{k_3 \cdot [\text{L}]} \cdot ([\text{Cr}(\text{CO})_5\text{L}]_\infty - [\text{Cr}(\text{CO})_5\text{L}]_t)$$

and eqn. 10 transforms to:

$$\frac{d[\text{Cr}(\text{CO})_5\text{L}]}{dt} = (k_3 \cdot [\text{L}] + k_2 \cdot [\text{CO}]) \cdot ([\text{Cr}(\text{CO})_5\text{L}]_\infty - [\text{Cr}(\text{CO})_5\text{L}]_t) \quad (11)$$

i.e. the "grow-in" process takes place by a first order process with a "rate constant" k_t of $(k_3 \cdot [\text{L}] + k_2 \cdot [\text{CO}])$.

Results and discussion

As previously reported [6], flash irradiation of $\text{Cr}(\text{CO})_6$ in CO-saturated cyclohexane solution yields a species with the absorption spectrum shown in Fig. 1. This species decays by a first order process ($k_2 \cdot [\text{CO}] = 2.8 \times 10^4 \text{ s}^{-1}$),

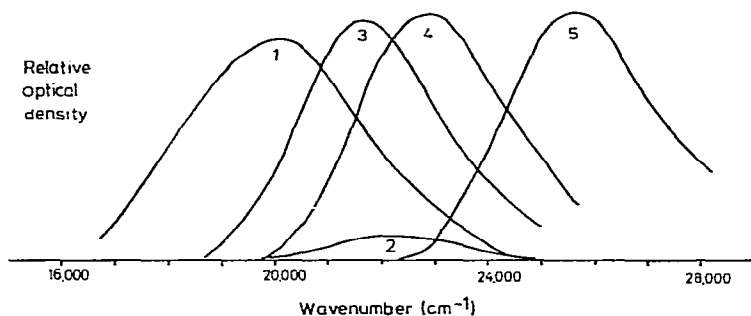


Fig. 1. Absorption spectra of transient species in cyclohexane solution: (1) $\text{Cr}(\text{CO})_5$, recorded immediately after the flash; (2) $\text{Cr}(\text{CO})_5\text{X}$, recorded 200 μs after the flash; (3) $\text{Cr}(\text{CO})_5(\text{MeOH})$; (4) $\text{Cr}(\text{CO})_5$ (acetone); (5) $\text{Cr}(\text{CO})_5$ (acetonitrile). The concentrations of the various transients are different.

presumably to reform the hexacarbonyl. Concurrently a small amount of another, more slowly decaying product [$\text{Cr}(\text{CO})_5\text{X}$] ($k = 7 \times 10^2 \text{ s}^{-1}$) is formed. The complete reversibility of the system is demonstrated by the fact that after 20 flashes no decomposition of the sample could be observed. By laser flash photolysis it has been clearly shown that in the visible region of the spectrum no further transient absorptions can be detected, indicating that the observed species is formed within 50 ns of excitation, unless there is the unlikely situation that another transient has an identical visible absorption spectrum. We have suggested [6] that these earlier observations could be explained by assuming that the species observed is $\text{Cr}(\text{CO})_5$. Turner and co-workers [12] have shown that in a methane matrix at 20 K the absorption band in the visible spectrum (λ_{max} at 490 nm) is considerably shifted compared to that observed in argon matrices (λ_{max} at 530 nm). They therefore suggested that there exists a specific interaction between $\text{Cr}(\text{CO})_5$ and methane, and, indeed, between $\text{Cr}(\text{CO})_5$ and argon. A similar interaction would be expected between $\text{Cr}(\text{CO})_5$ and cyclohexane, and therefore it is probably more correct to suggest that $\text{Cr}(\text{CO})_5$ in cyclohexane solution has a coordination site which is "readily available" rather than completely "free".

In the presence of L the conversion of $\text{Cr}(\text{CO})_5$ into a further species, which we consider to be $\text{Cr}(\text{CO})_5\text{L}$, can be monitored by laser flash spectroscopy. All species $\text{Cr}(\text{CO})_5\text{L}$ have a single absorption band in the visible or near UV region of the spectrum, and this is represented in Fig. 1. (The wavelength of maximum absorption is given in Table 5). Except in the case of acetonitrile which forms an isolable complex [13], the decay of $\text{Cr}(\text{CO})_5\text{L}$ in CO-saturated solution, to regenerate $\text{Cr}(\text{CO})_6$ and L, has been followed by conventional flash spectroscopy.

Formation of $\text{Cr}(\text{CO})_5\text{L}$

The $\text{Cr}(\text{CO})_6$ (0.5 to $1.0 \times 10^{-3} \text{ M}$) was excited at 347 nm (where L does not absorb) with the 30 ns laser pulse. The rate of decay of $\text{Cr}(\text{CO})_5$ (monitored between 500 and 540 nm) and the rate of appearance of complex (monitored at wavelengths near its maximum absorption) were measured, and in both cases conformed to first order kinetics. The rate constant (k_f) for both proc-

TABLE 2
RATE CONSTANTS FOR REACTION OF $\text{Cr}(\text{CO})_5$ WITH L

L	[L] ($\text{mol}\cdot\text{l}^{-1}$)($\times 10^{-2}$)	k_f (s^{-1})($\times 10^6$)	k_3 ($\text{l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)($\times 10^8$)
Acetone	0.50	0.5	1.0
	0.70	1.2	1.7
	0.75	1.0	1.3
	1.00	1.0	1.0
	1.00	1.6	1.6
	1.25	1.4	1.1
	1.40	2.3	1.6
	1.50	1.5	1.0
	1.75	2.2	1.2
	2.00	2.90	1.4
Acetonitrile	0.50	0.85	1.7
	0.80	1.25	1.6
	1.00	1.60	1.6
	1.60	2.61	1.6
Benzene	11.2	0.86	0.074
	20.2	1.37	0.066
Diethyl ether	7.0	0.83	0.11
	10.0	0.90	0.09
	14.0	1.65	0.12
Ethyl acetate	0.50	0.49	0.92
	1.00	0.98	0.95
	1.02	1.07	1.02
	1.50	1.20	0.78
Methanol	3.1	1.0	0.32
	5.0	1.9	0.38
	6.2	2.1	0.33
	10.0	2.7	0.27
	15.0	3.9	0.26

esses was the same within experimental error and as derived in the experimental section (eqns. 9 - 11).

$$k_f = k_3 \cdot [\text{L}] + k_2 \cdot [\text{CO}] \quad (12)$$

Values of k_f , determined at various [L] are shown in Table 2. It may be seen that the derived value of k_3 is substantially independent of [L], in agreement with eqn. 12. The average values of k_3 for each L are collected in Table 5.

Decay of $\text{Cr}(\text{CO})_5\text{L}$

For purposes of discussion, the observed reactions may be grouped as follows.

Acetonitrile. On flashing a CO-saturated solution of $\text{Cr}(\text{CO})_6$ in cyclohexane in the presence of $10^{-2}M$ acetonitrile, a species having the absorption spectrum shown in Fig. 1 was formed. The concentration of this species remained unchanged within 20 min. Further flashing of the solution produced small quantities of a further species (half-life ≈ 1 s) presumably caused by excitation of $\text{Cr}(\text{CO})_5(\text{CH}_3\text{CN})$.

Acetone, diethyl ether and ethyl acetate. In each of these cases, only one species was observed after reaction of $\text{Cr}(\text{CO})_5$ with L was complete. The complex decayed by first order kinetics and the decay process was unchanged even

TABLE 3
RATE CONSTANTS FOR DECAY OF Cr(CO)₅L COMPLEXES

L	[I] (mol·l ⁻¹)(X 10 ⁻²)	k _{expt} ^a (s ⁻¹)	k ₃ /k ₄ = K ₆ (l·mol ⁻¹)	k ₄ (s ⁻¹)	De-gassing method ^b
Acetone	0.17	1.64	8.9 × 10 ⁶	1.5 × 10 ¹	c
	0.24	1.06	10.1 × 10 ⁶	1.3 × 10 ¹	c
	0.61	0.49	9.0 × 10 ⁶	1.4 × 10 ¹	c
	0.68	0.40	9.9 × 10 ⁶	1.3 × 10 ¹	b
	1.36	0.22	9.0 × 10 ⁶	1.4 × 10 ¹	b
	1.42	0.22	8.7 × 10 ⁶	1.5 × 10 ¹	c
Benzene	10.6	7.6 × 10 ³	3.4 × 10 ¹	2.1 × 10 ⁵	c
	18.6	4.6 × 10 ³	3.2 × 10 ¹	2.2 × 10 ⁵	c
	23.5	3.2 × 10 ³	3.6 × 10 ¹	1.9 × 10 ⁵	c
Diethyl ether	5.1	7.70	6.8 × 10 ⁴	1.6 × 10 ²	b
	9.6	3.56	8.0 × 10 ⁴	1.4 × 10 ²	b
	9.6	3.46	8.1 × 10 ⁴	1.4 × 10 ²	a
	14.7	2.34	7.7 × 10 ⁴	1.4 × 10 ²	b
	14.7	2.60	7.2 × 10 ⁴	1.5 × 10 ²	a
	21.1	1.73	8.3 × 10 ⁴	1.3 × 10 ²	b
Ethyl acetate	1.02	2.50	1.1 × 10 ⁶	8.2 × 10 ¹	a
	2.04	1.21	1.1 × 10 ⁶	8.3 × 10 ¹	c
	3.06	0.77	1.2 × 10 ⁶	7.9 × 10 ¹	c
	4.08	0.63	1.1 × 10 ⁶	8.5 × 10 ¹	b
	4.08	0.57	1.2 × 10 ⁶	7.7 × 10 ¹	a

^a All values contain a possible experimental error of ± 20%. ^b See experimental section.

after 20 flashes. The rate constant was also unaffected by a four-fold variation in flash energy. As can be seen from Table 3, the experimental first order rate constant for decay of the complex (k_{expt}) varies with [L].

$$-\frac{d[\text{Cr}(\text{CO})_5\text{L}]}{dt} = k_{\text{expt}} \cdot [\text{Cr}(\text{CO})_5\text{L}] \quad (13)$$

If the mechanism for reaction is a combination of steps 2, 3, and 4, then:

$$k_{\text{expt}} = k_2 \cdot k_4 [\text{CO}] / (k_2 \cdot [\text{CO}] + k_3 \cdot [\text{L}]) \quad (14)$$

$$\text{and } 1/k_{\text{expt}} = 1/k_4 + k_3 \cdot [\text{L}] / k_2 \cdot k_4 \cdot [\text{CO}] \quad (15)$$

In Fig. 2 the $1/k_{\text{expt}}$ is plotted against both [acetone] and [ethyl acetate], and it may be seen that the experimental results are in agreement with the relationship 15. Values of k_3/k_4 and k_4 at various [L], calculated using eqn. 15, are shown in Table 3. k_3/k_4 gives the equilibrium constant for the process 6.

Benzene. After reaction of Cr(CO)₅ with benzene, two species were found. The first, assigned as Cr(CO)₅ (benzene), has an absorption maximum at 475 nm. The other (weakly absorbing) species is Cr(CO)₅X, having an absorption spectrum similar to the secondary species observed in cyclohexane (Fig. 1) and decaying with a similar rate constant ($k = 7 \times 10^2 \text{ s}^{-1}$). In this case, as described in the experimental section, $k_4 > k_3$ and $k_3[\text{L}] \neq k_7[\text{X}]$, allowing observation of Cr(CO)₅X.

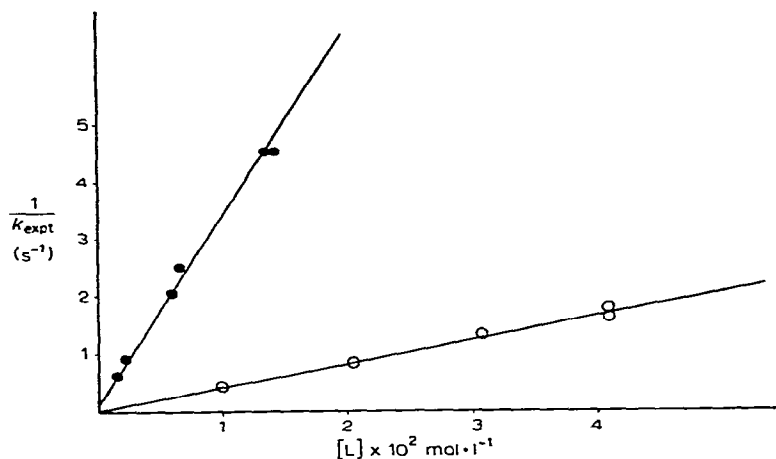


Fig. 2. Plot of $1/k_{\text{expt}}$ versus $[L]$. • Acetone; ○ ethyl acetate.

The first order rate constant for decay of the $\text{Cr}(\text{CO})_5$ (benzene) complex at various concentrations of benzene is shown in Table 3 and the results are in agreement with the mechanism involving the processes in eqns. 2, 3 and 4.

Methanol. Also in this case, only one species is observed after reaction of $\text{Cr}(\text{CO})_5$. This species decayed obeying first order kinetics and the value of k_{expt} decreased with increasing methanol concentration. However the values of " k_4 " and " k_3/k_4 " are markedly dependent on the [methanol] in contrast to the behaviour of the other L (Table 4). A plot of " k_4 "* against $1/[\text{methanol}]$ is linear within experimental error, suggesting that a mechanism involving two methanol molecules is applicable. Two possible schemes are proposed.



TABLE 4
RATE OF DECAY OF METHANOL COMPLEX IN CO-SATURATED SOLUTION

[MeOH] ($\text{mol}\cdot\text{l}^{-1}$)($\times 10^{-2}$)	k_{expt}	" k_4 " (s^{-1})	" k_3/k_4 " ($\text{l}\cdot\text{mol}^{-1}$)($\times 10^6$)	Degassing method
0.6	5.30	40	0.77	b
1.2	1.73	25	1.3	b
1.2	1.82	26	1.2	a
1.8	1.09	23	1.4	b
1.8	1.25	26	1.2	a
2.0	0.77	18	1.8	b
2.4	0.53	15	2.1	b
4.0	0.24	11	3.0	b
7.9	0.074	6.5	5.0	b

$$* \text{ " } k_4 \text{ " } = \frac{k_{\text{expt}} \cdot (k_3 \cdot [L] + k_2 \cdot [\text{CO}])}{k_2 \cdot [\text{CO}]}$$

TABLE 5
RATE CONSTANTS AND STABILITY CONSTANTS FOR REACTION OF $\text{Cr}(\text{CO})_5$ WITH L

L	k_3 ($\text{l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)	k_4 (s^{-1})	K_6 ($\text{l}\cdot\text{mol}^{-1}$)	λ_{max}^a (nm) for $\text{Cr}(\text{CO})_5\text{L}$
Benzene	7.0×10^6	2.1×10^5	3.4×10^1	475
Diethyl ether	1.1×10^7	1.4×10^2	7.6×10^4	455
Methanol	3.1×10^7			460
Ethyl acetate	9.2×10^7	8.1×10^1	1.1×10^6	445
Acetone	1.3×10^8	1.4×10^1	9.3×10^6	438
Acetonitrile	1.6×10^8	$< 1 \times 10^{-2}$	$> 1 \times 10^{10}$	391

^a ± 5 nm.

or



Further experiments will be required to clarify this matter.

Conclusion

Reaction rate constants of $\text{Cr}(\text{CO})_5$ with L (Tables 2 and 5) range from $1.6 \times 10^8 \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (for acetonitrile) to $7.0 \times 10^6 \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (for benzene) and are therefore not insignificant compared to the diffusion controlled rate constant in cyclohexane of $6.6 \times 10^9 \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ [14]. While no general prediction can be made from the few results presented here, it may be seen that the compounds with a polar π -system, e.g. acetonitrile, acetone and ethyl acetate, react more rapidly than do simple n-donors (methanol and diethyl ether). There is however no simple dependence of k_3 on the ionisation potential of L, which is often taken as a measure for the donor properties of the ligand (see Table 6). The stability of the complex $\text{Cr}(\text{CO})_5\text{L}$ (given by equilibrium constant K_6) also increases in the sequence: benzene, diethyl ether, ethyl acetate, acetone and acetonitrile.

TABLE 6
PRODUCT DISTRIBUTION FROM THE CATALYSED OLIGOMERISATION OF BUTADIENE AS A FUNCTION OF SOLVENT PARAMETERS

Solvent	Ionisation Potential ^a (eV)	Dipole moment ^b (D)	$\log k_3$	$\log K_6$	R_{prod}^c
n-Hexane	10.2	0.0			0.27
Benzene	9.2	0.0	6.85	1.53	0.25
Diethyl ether	9.6	1.25	7.04	4.88	0.23
Methanol	10.8	1.65	7.49		0.14
Ethyl acetate	10.1	1.85	7.98	6.05	0.14
Acetone	9.7	2.7	8.11	6.97	0.11
Acetonitrile	12.2	3.5	8.20	10.0	0.08

^a Ref. 16. ^b Ref. 2. ^c See Table 1.

As seen from Table 6, $\log K_6$ and $\log k_3$ both correlate qualitatively with the effect of L on the ratio R_{prod} of side products to main products in the catalysed butadiene oligomerisation. In particular $\log k_3$ correlates well with R_{prod} , which is to be expected (see Scheme 1), provided that $k_{\text{R}} \cdot [\text{butadiene}] \gg k_{\text{-L}}$.

Further studies will indicate whether other coordinatively unsaturated species [e.g. $\text{Fe}(\text{CO})_4$] [15] show the same order of reactivity as $\text{Cr}(\text{CO})_5$ towards coordination of L. Such data should be of use to the organometallic chemist interested in solvent effects on reactions involving unsaturated intermediates as generated during photochemical reactions or catalytic processes.

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