Autoxidation of Alkyl Compounds of Zirconium and Hafnium

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Autoxidations of alkylzirconocenes of the type Cp_2ZrR_2 and $Cp_2Zr(R)X$ (Cp = π-cyclopentadienyl; R = methyl, benzyl, or substituted benzyl; X = Cl or Br) have been shown to be free-radical chain reactions involving an S_H2-type displacement of an alkyl radical from the metal centre by an alkylperoxyl radical. These autoxidations have been related to those of the tetra-alkyl compounds of the Group IVA metals. The propagation rate constants (k_p) together with the corresponding entropies and enthalpies of activation have been measured for the dibenzylzirconocenes.

In an earlier publication [1] we demonstrated that tetra-alkyl-zirconium and -titanium, as well as hexa-alkyl-dimolybdenum and -ditungsten compounds underwent rapid solution-phase reactions with molecular oxygen, even at temperatures as low as —74 °C and there were strong indications that a free-radical chain reaction was involved. Wilkinson *et al.*[2] and Lappert *et al.*[3] had discovered that homoleptic alkyl compounds of early transition metals could be isolated if structures which allowed decomposition by β-elimination of an olefin were avoided. However, the very high oxidative and hydrolytic instability of these thermally stable compounds severely hampered studies of their properties. Even our use of bulky neopentyl groups in an effort to shield the metal atom from attacking radicals did not reduce the reactivity sufficiently for our requirements, which were to study the S_H2 process at transition metals by kinetic methods. Such studies would help to provide an understanding of the role played by homogeneous, transition metal catalysts in certain industrially important reactions.[4,5] It is known that many alkyl compounds of main group elements give rise to free-radical chain reactions with molecular oxygen and the scope of homolytic alkylperoxydealkylation at main group metal atoms has been reviewed in recent years.[6] In these examples, the intermediate metal peroxides are generally unstable, so that the end products of autoxidation are metal alkoxides [reaction (i)].

$$MR_n + O_2 \longrightarrow ROOMR_{n-1} \longrightarrow (RO)_2MR_{n-2} \qquad (i)$$

Our preliminary work [1] indicated a similar sequence for early transition metals, such as tetrakis(trimethylsilylmethyl)zirconium and in the case of tetrabenzylzirconium an unstable peroxide with a half-life of 50 min at 20 °C was detected. Since autoxidations have provided a convenient method for kinetic studies of S_H2 reactions involving alkylperoxyl radicals, as has been amply demonstrated for trialkylboranes,[7] we approached the problem of the high reactivity of Group IVA organometallics by reducing the number of vacant metal orbitals available to an attacking radical. Whereas tetrabenzylzirconium has five such vacant orbitals, since three metal orbitals accommodate each η-cyclopentadienyl ligand, tribenzylcyclopentadienylzirconium has three vacant orbitals and dibenzyldicyclopentadienylzirconium has only one.

The photosensitive tribenzyl compound [8] was still too reactive for kinetic experiments around ambient temperature, but with the dialkylzirconocenes and alkylzirconocene halides it became possible to measure rates of ligand substitution at zirconium, by alkylperoxyl radicals, as we now describe, and also by thiyl, alkoxyl, and nitroxyl radicals, which will be reported elsewhere.[9]

The zirconocenes and hafnocenes with benzyl groups were particularly suitable for measurements at ordinary temperatures, partly due to the stability of displaced benzyl radicals and partly as a result of some phenyl group interactions with the metal.[10]

The moisture-sensitive crystalline solids in Table 1 were, for the most part, prepared from the interaction of a metal chloride and either a Grignard reagent (for benzyl ligands) or methyl-lithium in diethyl ether solvent. Amonst these, $Cp_2Zr(CH_2Ph)_2$,[11] $Cp_2Hf(CH_2Ph)_2$,[12] and $Cp_2Zr(CH_3)_2$[13] have already been reported in the literature. Benzylzirconocene chloride was prepared in high yield from the interaction of the dialkylzirconocene and lead(II) chloride.[13] The unsymmetric dialkyl compound $Cp_2Zr(CH_2Ph)CH_3$ was prepared by alkylation of $Cp_2Zr(CH_3)Cl$ and was found to be stable to ligand redistribution in solution.

In toluene and at temperatures in the range 30—60 °C, the dialkylzirconocenes absorbed approximately 1 mol equiv. of oxygen and formed the corresponding dialkoxides, $Cp_2Zr(OR)_2$, in high yield. Free-radical initiators increased the rate of this reaction; thus the initial rate of oxygen consumption was increased by *ca.* 50% (corresponding to a 116% increase in the rate of initiation) when di-t-butyl hyponitrite (10 mol %) was added at 60 °C. Conversely, oxidation inhibitors and free-radical scavengers, such as galvinoxyl and phenothiazine completely suppressed the reaction (Figure) despite being present in concentrations of 1 mol % or less. Both these aspects of the autoxidation kinetics are consistent with a free-radical mechanism (ii)—(vi) similar to that previously established for alkylboron autoxidations.[7] There was no evidence that the cyclopentadienyl group was affected by autoxidation.

Initiation

$$Cp_2ZrR_2 + O_2 \xrightarrow{k_i} Cp_2Zr(R)O_2\cdot + R\cdot \qquad (ii)$$

Propagation

$$R\cdot + O_2 \xrightarrow[\text{fast}]{k_1} RO_2\cdot \qquad (iii)$$

$$RO_2\cdot + Cp_2ZrR_2 \xrightarrow[\text{slow}]{k_p} Cp_2Zr(R)O_2R + R\cdot \qquad \text{(iv)}$$

Rearrangement

$$Cp_2Zr(R)O_2R \xrightarrow{k_2} Cp_2Zr(OR)_2 \qquad \text{(v)}$$

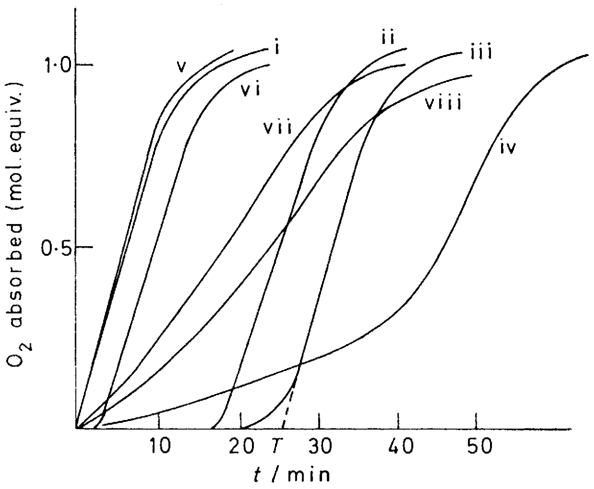
Termination

$$2RO_2\cdot \xrightarrow{k_t} \text{stable products} \qquad \text{(vi)}$$

Retardation as opposed to inhibition was achieved using a number of phenolic antioxidants (Figure), but iodine did not retard oxidation unlike alkylboranes,[14] but the zirconocene di-iodide was preferentially formed. The stoicheiometric reaction (vii) occurred rapidly at 45 °C in the absence of oxygen. When 1 mol equiv. of iodine was used the di-iodide was again produced in high yield but the intermediate $Cp_2Zr(R)I$ was not isolated.

$$Cp_2ZrR_2 + 2I_2 \longrightarrow Cp_2ZrI_2 + 2RI \qquad \text{(vii)}$$

Kinetics of Autoxidation.—The bulk of the measurements were made using dibenzylzirconocene, oxygen at atmospheric pressure, and toluene solvent over the temperature range 30—60 °C.



Autoxidation of dibenzylzirconocene (0.1M) in toluene at 45 °C and $P(O_2)$ 1 atm: i, uninhibited; ii, galvinoxyl (1.0 mol %); iii, phenothiazine (1.0 mol %); iv, 2,6-di-t-butyl-4-methoxyphenol (1.0 mol %); v, iodine (2.0 mol %); vi, 2-t-butyl-4-methoxyphenol (2.0 mol %); vii, 2-t-butyl-4-methylphenol (2.0 mol %); viii, bis-(3,5-di-t-butyl-4-hydroxyphenyl)-methane (1.0 mol %)

The order of the reaction was found to be 1.55 with respect to dibenzylzirconocene, which is in close agreement with the rate equation required by sequence (ii)—(vi), *viz.* equation (viii). From measurements of

$$-d[O_2]/dt = k_p(k_i/2k_t)^{\frac{1}{2}}[O_2]^{\frac{1}{2}}[Cp_2ZrR_2]^{\frac{3}{2}} \qquad \text{(viii)}$$

TABLE 1

Physical, analytical, and spectral data for organometallic derivatives

Organometallic compound	Colour	Isolated yield (%)	Total reaction time (h)	Elemental analysis (%) C	Elemental analysis (%) H	^{1}H N.m.r. chemical shift τ ([$^2H_6$]C_6H_6) Ph	Cp	CH_2	Me,Bu^t
$Cp_2Zr(CH_2C_6H_5)_2$	Orange	79	3	70.8 (71.4)	6.0 (6.0)	2.6—3.2 (m)	4.45	8.16	
$Cp_2Zr(CH_2C_6H_4CH_3\text{-}o)_2$	Yellow	45	8	72.2 (72.3)	6.6 (6.5)	2.7—3.2 (m)	4.49	8.27	7.96
$Cp_2Zr(CH_2C_6H_4CH_3\text{-}m)_2$	Yellow	61	8	72.4 (72.3)	6.9 (6.5)	2.7—3.3 (m)	4.43	8.16	7.73
$Cp_2Zr(CH_2C_6H_4CH_3\text{-}p)_2$	Orange	52	8	71.9 (72.3)	6.4 (6.5)	2.8—3.3 (m)	4.42	8.15	7.70
$Cp_2Zr(CH_2C_6H_4Cl\text{-}m)_2$	Yellow-orange	26	6	61.0 (61.0)	5.0 (4.7)	2.7—3.6 (m)	4.55	8.37	
$Cp_2Zr(CH_2C_6H_4Cl\text{-}p)_2$	Orange	65	6	61.1 (61.0)	4.7 (4.7)	2.7—3.5 (m)	4.56	8.40	
$Cp_2Zr(CH_2C_6H_4F\text{-}p)_2$	Orange	67	8	66.3 (65.6)	5.3 (5.1)	2.8—3.5 (m)	4.51	8.36	
$Cp_2Zr(CH_2\text{-1-naphthyl})_2$	Orange	50	10	76.3 (76.3)	5.9 (5.6)	2.1—3.0 (m)	4.54	7.69	
$Cp_2Zr(CH_2\text{-2-naphthyl})_2$	Red-orange	62	6	76.2 (76.3)	6.0 (5.6)	2.2—3.0 (m)	4.49	8.01	
$(MeCp)_2Zr(CH_2C_6H_5)_2$	Orange	44		71.7 (72.3)	6.7 (6.5)	2.6—3.2 (m)	4.53 (m)	8.17	8.29
$Cp_2Zr(CH_2C_6H_5)CH_3$	Yellow-orange	47	4	65.3 (66.0)	6.2 (6.2)	2.6—3.3 (m)	4.42	8.33	9.99
$Cp_2Zr(CH_2C_6H_5)Cl$	Orange	82	3	59.1 (58.7)	5.1 (4.9)	2.6—3.1 (m)	4.35	7.75	
$Cp_2Zr(CH_2C_6H_5)Br$	Red-orange	67	2	51.7 (52.0)	4.3 (4.4)	2.6—3.1 (m)	4.32	7.94	
$Cp_2Zr(CH_2C_6H_5)OCH_2C_6H_5$	Pale yellow	54		68.7 (68.7)	6.0 (5.8)	2.6—3.1 (m)	4.39	5.21 7.64	
$Cp_2Zr(CH_3)Cl$ [13]	Colourless	53	2				4.23		9.56
$CpZr(CH_2C_6H_5)_3$	Yellow-orange	52	5	72.8 (72.7)	6.2 (6.1)	2.8—3.1; 3.4—3.6 (m)	4.37	8.50	
$Cp_2Hf(CH_2C_6H_5)_2$[12]	Yellow	41	8	58.7 (58.7)	5.1 (4.9)	2.6—3.2 (m)	4.51	8.46	
$Cp_2Hf(CH_2C_6H_5CH_3\text{-}p)_2$	Yellow	37	8	59.9 (60.2)	5.4 (5.4)	2.9—3.4 (m)	4.56	8.46	7.72
$Cp_2Zr(CH_3)_2$ [13]	Colourless	77					4.27		10.16

$-d[O_2]/dt$ and the rate of initiation in these systems, the 'oxidisability' $k_p/(2k_t)^{\frac{1}{2}}$ was determined at various temperatures and Arrhenius graphs were drawn. The oxygen absorption curve showed no natural induction period, indicating that secondary initiation effects due to homolytic decomposition of the zirconocene peroxide intermediate were negligible. Attempts to isolate the peroxide or to detect it spectroscopically were unsuccessful.

Examination of the autoxidation mixture after 40% of reaction at 45 °C showed that the alkoxides $Cp_2Zr(OR)_2$ and $Cp_2Zr(R)OR$ were present in the mol ratio of *ca.* 13 : 1. The intermolecular decomposition route has been demonstrated by Schwartz *et al.*[15a] for $Cp_2Zr(Cl)O_2R$, but reaction (ix) is only of minor importance in the autoxidation of dibenzylzirconocene.

$$Cp_2Zr(R)O_2R + Cp_2ZrR_2 \longrightarrow 2\,Cp_2Zr(R)OR \qquad (ix)$$

The alkoxide $Cp_2Zr(R)OR$ as prepared by the interaction of dibenzylzirconocene and benzyl alcohol, was stable to ligand redistribution and autoxidation in solution (for at least 1 h at 50 °C). The deactivating effect of alkoxide ligands in autoxidations of organometallics has been previously noted.[7a] Further evidence for the intramolecular peroxide decomposition was the formation of the unsymmetric dialkoxide $Cp_2Zr(OR)OBu^t$ in 70% yield when t-butyl hydroperoxide was added to dibenzylzirconocene. This rearrangement is analogous to those previously reported for boron peroxides [7c] and the transition state is envisaged as involving the vacant orbital on the metal.

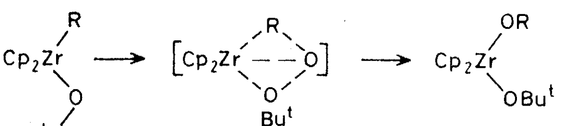
TABLE 2

Bimolecular rate constants for homolytic alkylperoxyl dealkylation at zirconium

Compound (toluene solution)	k_p (40°)/ l mol^{-1} s^{-1}	$10^{-7}A$/ l mol^{-1} s^{-1}	E_a/ kJ mol^{-1}	ΔH‡ (40°)/ kJ mol^{-1}	ΔS‡ (40°)/ J K^{-1} mol^{-1}
$Cp_2Zr(CH_3)_2$	9.2×10^3 *				
$Cp_2Zr(CH_2Ph)_2$	2.8×10^4	5.71	19.9	17.3	−106
$Cp_2Zr(CH_2C_6H_4CH_3\text{-}m)_2$	2.3×10^4	5.41	20.3	17.7	−106
$Cp_2Zr(CH_2C_6H_4CH_3\text{-}p)_2$	2.9×10^4	7.00	20.3	17.7	−104
$Cp_2Zr(CH_2C_6H_4Cl\text{-}m)_2$	4.5×10^4	5.74	18.6	16.0	−105
$Cp_2Zr(CH_2C_{10}H_7\text{-}1)_2$	2.2×10^4	1.59	17.2	14.6	−116
$Cp_2Zr(CH_2Ph)Cl$	5.7×10^4				
$Cp_2Zr(CH_2Ph)Br$	4.9×10^4				

* Calculated using k_t 1.5×10^8 l mol^{-1} s^{-1} and therefore an overestimate. Using k_t 2.0×10^7 l mol^{-1} s^{-1} for n-butylperoxyl, (J. A. Howard and K. U. Ingold, *J. Am. Chem. Soc.*, 1968, **90**, 1058.) k_p for $Cp_2Zr(CH_3)_2$ becomes 2.5×10^4 l mol^{-1} s^{-1}.

$$Cp_2ZrR_2 + Bu^tO_2H \longrightarrow Cp_2Zr(R)O_2Bu^t + RH \qquad (x)$$



(xi)

Calculation of the benzyl alcohol to be expected as a result of the termination reaction (xii) suggests that by

$$2\,PhCH_2O_2\cdot \longrightarrow PhCH_2OH + PhCHO + O_2 \qquad (xii)$$

itself it cannot account for all of the $Cp_2Zr(CH_2Ph)OCH_2Ph$ observed in the autoxidation mixture.

The propagation rate constants in Table 2 were obtained from the oxidisabilities by substitution of k_t 1.5×10^8 l mol^{-1} s^{-1} (the literature [16] value for the *p*-methylbenzylperoxyl radical), into equation (viii) and can be compared with the value for tribenzylborane found by Ingold *et al.*,[16b] k_p 5×10^6 l mol^{-1} s^{-1} at 30°. Table 2 indicates that *meta*- and *para*-substituents attached to the phenyl groups in dibenzylzirconocene do not greatly influence free-radical substitution by alkylperoxyl radicals at the metal centre. The bulk of the naphthylmethyl group may, however, be reflected in the somewhat greater negative entropy of activation.

The rate of initiation, R_i, was determined from the relationship $T = n\,(\text{inhibitor})/R_i$ where T is the induction period and n is the number of free radicals removed by an inhibitor molecule. The value $n = 1.5$ for the number of radicals scavenged by phenothiazine was assigned by measuring the induction period it produced and then comparing it with that produced by galvinoxyl.* R_i Showed a first-order dependence on both organometallic and oxygen concentrations and the deactivating effect of electron-withdrawing substituents and halide ligands (Table 3) can be attributed to destabilisation of charge separation in the transition state for reaction (ii), recombination of radicals being spin forbidden. The resonance stabilisation of the benzyl radical would appear to account for the greater reactivity of dibenzylzirconocene, as compared to dimethylzirconocene, towards ligand substitution by the O_2 molecule.

TABLE 3

Rates of autoxidation–initiation of dibenzylzirconocenes

Compound (0.1M in toluene)	R_i[50 °C; $P(O_2)$ 1 atm]/ mol l^{-1} s^{-1}	Relative reactivity
$Cp_2Zr(CH_2C_6H_4CH_3\text{-}p)_2$	2.6×10^{-6}	1.8
$Cp_2Zr(CH_2C_6H_4CH_3\text{-}m)_2$	1.6×10^{-6}	1.1
$Cp_2Zr(CH_2Ph)_2$	1.5×10^{-6}	1.0
$Cp_2Zr(CH_2C_6H_4F\text{-}p)_2$	9.3×10^{-7}	0.62
$Cp_2Zr(CH_2C_6H_4Cl\text{-}m)_2$	6.3×10^{-7}	0.43
$Cp_2Zr(CH_2C_{10}H_7\text{-}1)_2$	5.2×10^{-7}	0.36
$Cp_2Zr(CH_2Ph)Cl$	6.2×10^{-8} at 40 °C	
$Cp_2Zr(CH_2Ph)Br$	9.6×10^{-8} at 40 °C	
$Cp_2Zr(CH_3)_2$	1.2×10^{-7} at 40 °C	

* Bartlett and Funahashi [16c] demonstrated a radical trapping stoicheiometry of unity for galvinoxyl.[17] The relative rates of trapping of alkyl and alkylperoxyl radicals by galvinoxyl [7c] suggests that benzylperoxyl radical trapping predominates in the case of the difunctional phenothiazine [18] although benzyl radicals are also trapped.

Autoxidation of benzylzirconocene chloride and bromide led, in each case, to a mixture of the alkoxide $Cp_2Zr(OR)X$ and the oxygen-bridged species $(Cp_2ZrX)_2O$ the mol ratios of these two being 4 : 1 and 1 : 1, respectively. By comparison with the dibenzyl compound, propagation rates were higher (Table 2) and initiation rates were lower (Table 3) and the kinetic chain lengths that were measured were in the range 1—2 × 10^3 at 40 °C. Consequently, the autoxidation mechanisms for alkylzirconocene chloride suggested by Schwartz *et al.*[15a] must be revised in favour of a free-radical chain reaction.

The autoxidation of dibenzylhafnocene at 50 °C in toluene differed significantly from that of the zirconium analogue in the following ways: a natural induction period was observed; 2 mol equiv. of oxygen were absorbed relatively slowly; and an orange precipitate, possibly an oxygen-bridged, polymeric species [19] was formed.

The autoxidation of tetrabenzylhafnium was briefly studied for a comparison with tetrabenzylzirconium.[1] At −78 °C, a 0.05M solution of tetrabenzylhafnium in toluene absorbed 2 mol equiv. of oxygen very rapidly, so that the reaction was 90% complete within 3 mins. Unlike the zirconium compound, excess pyridine significantly reduced the initial rate of reaction at dry ice temperature and only 1 mol equiv. of oxygen was absorbed. This is consistent with the known greater stability of the hafnium-pyridine bond.[20]

$$HfR_4{\cdot}py + O_2 \longrightarrow RO_2HfR_3{\cdot}py \longrightarrow (RO)_2HfR_2{\cdot}py \qquad \text{(xiii)}$$

At low temperature π-donation from the alkoxy-oxygens to vacant metal orbitals prevents further attack by free radicals. On warming to room temperature, another mol equiv. of oxygen was absorbed; thus dissociation of the pyridine complex of the dialkoxide in (xiii) is indicated.

EXPERIMENTAL

All manipulations were carried out under nitrogen and solvents were rigorously dried and degassed before use. The compounds in Table 1 were stored below 0 °C in the absence of light. The yields quoted are minimum values since losses occurred during low temperature crystallisation.

Preparation of Alkylzirconium Compounds.—(i) *Dialkylzirconocenes with substituted benzyl ligands.* These were prepared from zirconocene dichloride and the appropriate Grignard reagent, after the method for $Cp_2Zr(CH_2Ph)_2$.[11] The Grignard reagent was added dropwise over a number of hours to a stirred suspension of zirconocene dichloride in diethyl ether at 0 °C. The solvent was removed under vacuum and sufficient toluene to give a 0.2M solution of the product (assuming 100% yield) was added. After filtration from magnesium chloride and the addition of an equal volume of hexane, cooling to −74 °C afforded crystalline dialkylzirconocenes which were washed in hexane and dried under vacuum. In some cases, *e.g.* $Cp_2Zr(CH_2C_6H_4Cl\text{-}p)_2$, the ring-substituted benzyl compounds tended to occlude toluene; this difficulty was overcome by use of methylene chloride as solvent.

(ii) *Benzylzirconocene chloride.* Dibenzylzirconocene (4.84 g, 12.0 mmol) in toluene (80 cm^3) was added to lead(II) chloride (1.67 g, 6.0 mmol) with stirring at 20° (3 h). After filtration and dilution with hexane (100 cm^3) the solution was cooled to −74 °C to give the orange crystals (yield 82%). The alternative preparation using equivalent amounts of Grignard reagent and zirconocene dichloride after the method of Lappert *et al.*[21] gave a lower yield, 57%, after careful recrystallisation to remove zirconocene dichloride. Dibenzylhafnocene did not appear to undergo transmetallation with lead chloride and was recovered in high yield. Bis-(*p*-methylbenzyl)hafnocene was prepared in an analogous manner to the unsubstituted compound.[12]

(iii) *Benzylzirconocene bromide.* Benzylmagnesium chloride in ether was added to a stirred solution of an equivalent amount of zirconocene dibromide at 0 °C. After 2 h the mixture was worked-up as for the dibenzylzirconocene (yield 67%).

(iv) *Benzylmethylzirconocene.* Benzylmagnesium chloride (15.7 mmol) in ether was added dropwise with stirring to methylzirconocene chloride [13] (4.3 g, 15.7 mmol) in ether (65 cm^3) at 0 °C and then worked-up as in the previous case.

(v) *Benzyloxybenzylzirconocene.* Benzyl alcohol (1.87 g, 17.5 mmol) was added dropwise to a stirred solution of dibenzylzirconocene (7.07 g, 17.5 mmol) in toluene (88 cm^3) at 0 °C. The solution rapidly changed from orange to yellow. After 1 h the solution was diluted with hexane (100 cm^3) and then cooled to −74 °C when the benzyloxybenzylzirconocene was filtered off. The isolated yield was 54%, but when the reaction was repeated at 35 °C in [$^2H_6$]benzene, the ^1H n.m.r. spectrum indicated an almost quantitative yield within 1 min. When the experiment was repeated using 2 equiv. of benzyl alcohol at 35 °C the dibenzyloxyzirconocene was formed *ca.* 100 times slower having ^1H n.m.r. signals at τ 4.01 (s, Cp) and 5.01 (s, CH_2).

(vi) *Bis(methylcyclopentadienyl)dibenzylzirconium.* Bis-(methylcyclopentadienyl)zirconium dichloride was prepared by the method of Samuel.[22] Benzylmagnesium chloride (0.1 mol) in ether was added dropwise to a stirred suspension of bis(methylcyclopentadienyl)zirconium dichloride (16.4 g, 0.05 mol) in ether (160 cm^3) at 0 °C (0.5 h). After 3.5 h at 0 °C it was worked-up as for dibenzylzirconocene.

(vii) *(Cyclopentadienyl)tribenzylzirconium.* Cyclopentadienylzirconium trichloride was prepared by the method of Krebs *et al.*[23] To the trichloride (23.1 g, 88.0 mmol) in ether (215 cm^3) at 0 °C was added dropwise benzylmagnesium chloride (0.264 mol) in ether (1 h). After a further 5 h at 0 °C the solvent was removed under vacuum and the mixture worked up as for dibenzylzirconocene.

Interaction of Dibenzylzirconocene and t-Butyl Hydroperoxide.—To a vigorously stirred solution of dibenzylzirconocene (1.0 mmol) in [$^2H_6$]benzene (5 cm^3), under nitrogen, at 20 °C was added dropwise over 5 min t-butyl hydroperoxide (0.5 mmol), b.p. 41° at 23 mmHg. After 0.5 h the ^1H n.m.r. spectrum indicated a 70% yield of the unsymmetric dialkoxide $Cp_2Zr(OCH_2Ph)OBu^t$, τ 3.95 (s, Cp), 4.97 (s, CH_2), and 8.86 (s, Bu^t). The other products were toluene (0.54 mmol), $Cp_2Zr(CH_2Ph)OBu^t$, (0.07 mmol), and $Cp_2Zr(CH_2Ph)OCH_2Ph$ (0.16 mmol). The compound $Cp_2Zr(CH_2Ph)OBu^t$ was identified by comparison with its ^1H n.m.r. spectrum prepared by alcoholysis of $Cp_2Zr(CH_2Ph)_2$ with t-butyl alcohol, τ 4.30 (s, Cp), 7.62 (s, CH_2), and 8.94 (s, Bu^t). This alcoholysis reaction was more than a 100 times slower than with benzyl alcohol or t-butyl hydroperoxide. Interaction of benzyloxybenzyl zirconocene (1 mmol) with t-butyl hydroperoxide (1 mmol) yielded bis-benzyloxyzirconocene, the unsymmetric dialkoxide, and $Cp_2Zr(CH_2Ph)OBu^t$ in the mol ratio *ca.* 4 : 2 : 1 at 35 °C.

Autoxidation of Benzylzirconocenes.—Dibenzylzirconocene. Autoxidation of a 0.2M solution of $[^2H_6]$benzene at 45 °C for a period corresponding to *ca.* 40% reaction gave the following stable composition as determined by ^1H n.m.r., $Cp_2Zr(CH_2Ph)_2$, 58%; $Cp_2Zr(OCH_2Ph)_2$, 39%; $Cp_2Zr(CH_2Ph)(OCH_2Ph)$, 3%. There were no signals attributable to a peroxidic compound. The dialkoxide had τ 4.01 (s, Cp), and 5.01 (s, CH_2).

Kinetic Measurements.—Oxygen absorption was measured at constant volume using the previously described apparatus;[7c] thermostatting was accurate to ±0.2 °C and the apparatus was shielded from light. Experiments were carried out in duplicate in order to ensure reproducibility, and measurements were on freshly prepared toluene solutions since it was found that solutions a few hours old showed signs of slow thermal decomposition. The effect of antioxidants is shown in the Figure, and the phenothiazine was selected for induction period (T) measurements since it could be made up as a stable stock solution.

The order with respect to dibenzylzirconocene was determined using the logarithmic form of equation (viii) at constant oxygen pressure, *viz.* equation (xiv) where $r_i = k_i\,[O_2]^y$.

$$\log\left(\frac{d[O_2]}{dt}\right)_0 = \log\left[k_p\left(\frac{r_i}{2k_t}\right)^{0.5}\right] + 1.5\log[Cp_2Zr(CH_2Ph)_2]_0 \qquad \text{(xiv)}$$

A plot of log $(d[O_2]/dt)_0$ against $\log[Cp_2Zr(CH_2Ph)_2]$ at 45 °C gave a good straight line plot of slope 1.55. The method ignores effects such as evolution of oxygen due to initiation and termination reactions involving alkyl radical combinations since they are believed to be small.

From relationship (xv) a plot of log T against log $[Cp_2Zr(CH_2Ph)_2]_0$ at 45 °C with constant $[O_2]$, gave a straight line of slope 0.95. The order with respect to oxygen (y) was not

$$\log T = \frac{\log 1.5\,[\text{pheno}]_0}{r_i} - x\log[Cp_2Zr(CH_2Ph)_2]_0 \qquad \text{(xv)}$$

measured over a range of oxygen concentrations although induction period measurements using pure oxygen or dry air indicated a value close to unity. At low spontaneous initiation rates the degree of solvent participation R_i^s needs consideration; hence $R_i + R_i^s = 1.5[\text{pheno}]_0/r_iT$, whence $[Cp_2Zr(CH_2Ph)_2]_0 = 1.5[\text{pheno}]_0/r_iT - R_i^s/r_i$ and from a graphical intercept R_i^s/R_i was found to be <0.1 and R_i^s was discounted. From measurements of oxygen consumption of uninhibited and inhibited solutions the ' oxidisabilities ' $k_t/(2k_i)^{\frac{1}{2}}$ were calculated [equation (viii)] as well ask inetic chain lengths or the mean chain lifetime $l_0 = (2\,k_tR_i)^{-\frac{1}{2}}$.

Chain lengths measured for the listed dibenzylzirconocenes were in the range 107—481; and the chain lifetimes were 3—13 × 10^{-2} s.

The temperature dependence of the propagation rate constant k_p[16a] over the range 30—65 °C for the compounds in Table 2 provided least-squares Arrhenius graphs from whence the enthalpies and entropies of activation were derived.

The oxidation measurements on dimethylzirconocene were carried out at one temperature (40 °C) using a 0.1M solution in toluene, O_2 at 1 atm, and $[\text{pheno}]_0$ 5 × 10^{-4}M. In the case of benzylzirconocene chloride and bromide the induction periods were >3 h at 40 °C and gave the values in Table 3, the initiation process was assumed to produce benzyl radicals similar to equation (ii) because of the other similarities with the autoxidation of dibenzylzirconocene.

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