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Role of the ligand in the cobalt(II)-catalysed decomposition of *tert*-butyl hydroperoxide. Evidence for the participation of bridged dicobalt complexes

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Abstract—In the cobalt(II)-catalysed decomposition of *t*-butyl hydroperoxide at 25°C in a 5 : 1 mixture (v/v) of chlorobenzene and dioxane, cobalt 2-ethylhexanoate is more active as a catalyst than the cobalt(II) complexes of a number of 1,3-dicarbonyl compounds. These complexes become deactivated and, in general, a decrease in the acidity of the parent 1,3-dicarbonyl compound lowers the rate of deactivation. This relationship, as well as the high activity of the 2-ethylhexanoate, is consistent with the radical chain decomposition of the hydroperoxide being initiated by a catalytic cycle which involves bridged dicobalt complexes. This cycle differs from the currently accepted Haber and Weiss cycle in that it does not directly generate an alkoxy radical. © 1997 Elsevier Science Ltd

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Cobalt(II) 2-ethylhexanoate is used extensively in the paint industry to promote the drying of those paints whose film formers contain unsaturated hydrocarbon chains that originate from naturally-occurring unsaturated fats and oils, the alkyd gloss paints for example [1]. It is generally accepted that the main function of the cobalt salt is to accelerate the polymerisation that is necessary for the paint to dry, and that it does this by catalysing the free radical decomposition of the hydroperoxides that are formed when the paint is exposed to the air [2].

Largely because of its role in certain cobalt-catalysed liquid-phase autoxidations that are of commercial importance [3], the cobalt-catalysed decomposition of hydroperoxides has been extensively studied [4–8]. In almost every book, review, and research paper which deals with this subject [3–9], eqs (1) and (2) are invariably given for the catalytic process by which the cobalt generates those radicals that are responsible for initiating the decomposition of the hydroperoxide by the radical chain mechanism represented by eqs (3) and (4). The two equations, (1) and (2), correspond to a catalytic cycle in which the cobalt oscillates between the +2 and +3 oxidation states and, in doing so, produces an alkoxy and an alkylperoxy radical from two molecules of hydroperoxide.

$$\mathrm{Co^{2+} + ROOH \rightarrow Co^{3+} + RO^{\bullet} + HO^{-}} \qquad (1)$$

$$\mathrm{Co^{3+} + ROOH \rightarrow Co^{2+} + ROO^{\bullet} + H^{+}} \qquad (2)$$

$$\mathrm{2RO^{\bullet}_{2} \rightarrow 2RO^{\bullet} + O_{2}} \qquad (3)$$

$$\mathrm{RO^{\bullet} + ROOH \rightarrow RO_{2}^{\bullet} + ROH} \qquad (4)$$

Recently it has been pointed out there is an alternative catalytic cycle by which the cobalt could act as a radical initiator [10]. This cycle is shown in the lower part of Scheme 1, and it differs from that represented by eqs (1) and (2) in a number of respects, one of which is that the overall transformation (eq (5)) does not produce an alkoxy radical.

$$\mathrm{3ROOH \rightarrow ROH + 2ROO^{\bullet} + H_{2}O} \qquad (5)$$

Evidence was presented that it is highly likely that

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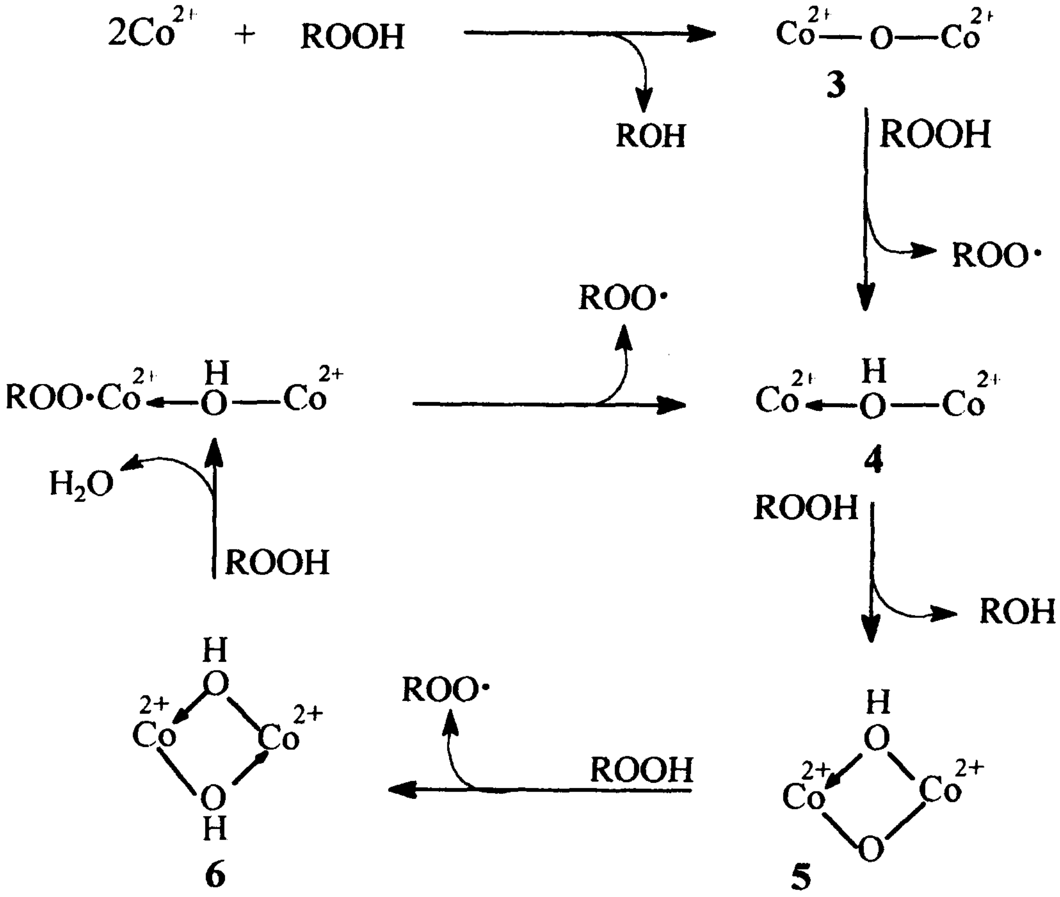
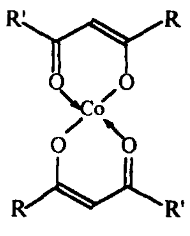


Scheme 1.

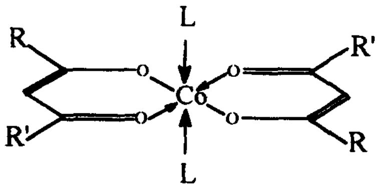
this cycle operates when the cobalt is used in the form of either the acetylacetonate or a simple carboxylate which, in fact, is usually the case. While numerous studies of the cobalt-catalysed decomposition of hydroperoxides have been carried out, the vast majority of them have been concerned largely with unravelling the highly complex kinetics of the decomposition, and relatively little attention has been given to the effect, kinetic or otherwise, of varying the ligands attached to the cobalt. One effect which has been established is that the decomposition is retarded or, in extreme cases, prevented if the cobalt is bonded to ligands which inhibit the reduction of cobalt(III) to cobalt(II) by the hydroperoxide for thermodynamic or kinetic reasons. The EDTA complex of cobalt(III) is completely inactive as a catalyst at room temperature for this reason [5].

In this paper some results obtained from a study of



1

	R	R'
a	Me	OEt
b	Me	O•CMe$_3$
c	Me	O•menthyl
d	Me	O•CH$_2$•CF$_3$
e	CF$_3$	OMe
f	CF$_3$	OEt
g	Me	Me
h	CF$_3$	Me
i	CF$_3$	CF$_3$
j	CMe$_3$	CMe$_3$



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the catalytic decomposition of *t*-butyl hydroperoxide by cobalt 2-ethylhexanoate and the cobalt(II) complexes **1**; **a–i** are described, and these results are discussed with reference to the catalytic cycle shown in Scheme 1.

RESULTS AND DISCUSSION

Preparation and catalytic activity of the cobalt(II) complexes

While cobalt(II) 2-ethylhexanoate was readily obtained from cobalt(II) hydroxide and 2-ethylhexanoic acid as described by Hancock *et al.* [11], the preparation of pure samples of the cobalt complexes (**1**; **a–f**) presented greater difficulty than was anticipated. Of the parent *β*-keto esters associated with these complexes, only ethyl acetoacetate (eaaH) has been reported as forming a cobalt(II) complex. On two occasions Mathur *et al.* have reported the preparation of the monomeric diaquo complex **2a**; L = water, but neither report contains any experimental details or any analytical data to support the assigned structure [12]. Hay and Caughley have reported, with experimental detail and data, that treatment of an ethanolic solution of ethyl acetoacetate and sodium hydroxide with hydrated cobalt(II) nitrate affords a complex whose composition corresponds to $Co_3(eaa)_5(OH)$, and from which a complex, $Co(eaa)_2$, can be obtained by extraction (Soxhelet) with benzene [13]. We have found that a complex having the latter composition can also be obtained by the slow addition of triethylamine in methanol to a solution of ethyl acetoacetate and cobalt(II) acetate in aqueous methanol, followed by crystallisation from methanol of the resultant pink precipitate. This crystallisation has to be rapid, otherwise the hot methanol causes the formation of the complex Co(eaa)(OMe)(MeOH). A methanolysis of this type has been observed previously with cobalt acetylacetonate **1g** [13,14], as well as with a range of other transition and main group metal complexes [15].

The complexes **1**; **b–d** were obtained in a similar manner to **1a**, except that as **1c** and **1d** were formed initially as oils they removed from the reaction mixtures by extraction with ether rather than by filtration. Subsequent evaporation of the dried ether extracts afforded the complexes as pink solids. In the preparation of the trifluoromethyl complexes, **1e** and **1f**, the complexes precipitated immediately aqueous cobalt(II) acetate was added to a methanolic solution of the parent *β*-keto ester, and the use of triethylamine was not required. This was also the case in the preparations of the *β*-diketone complexes **1**; **g–i** (all of which have been reported previously) [16,17]. Presumably, this is the result of the significantly higher acidity of the parent dicarbonyl compounds.

In the solid state all the *β*-keto ester complexes **1**; **a–f** are pink in colour, suggesting that they contain octahedral cobalt(II) [13,18]. In some cases, this coordination mode could result from the presence of coordinated solvent molecules, as in the complexes of menthyl acetoacetate (**1c**. 2MeOH) and 2,2,2-trifluoroethyl acetoacetate (**1d**. $2H_2O$) respectively. In other cases, octahedral coordination could arise from the formation of oligomers in which the keto ester anions act as bridging ligands as described below for the anhydrous form of the acetylacetonate **1g**.

Initially attempts were made to compare the ability of the various cobalt complexes to catalyse the decomposition of *t*-butyl hydroperoxide using the conditions described by Hiatt [8], i.e., chlorobenzene as the solvent, a reaction temperature of 25°C, and with the hydroperoxide decomposition being followed by use of the standard iodometric titration method.

In agreement with Hiatt it was found that cobalt(II) 2-ethylhexanoate was highly active as a catalyst, and with an initial hydroperoxide concentration of 0.142 mol dm^{-3} and a catalyst concentration of 1.70×10^{-3} mol dm^{-3} the time taken for half the hydroperoxide to decompose ($t_{1/2}$) was about 1 min. The acetoacetate complexes **1**; **a–c**, however, were only slightly less active ($t_{1/2}$ values between 2 and 3 min), with the *t*-butyl ester **1b** being marginally the most active of the three. The activity of the fluorinated *β*-ketoester complexes was significantly lower, and the $t_{1/2}$ values for **1d** and **1e**, for example, were 8 and 20 min respectively. All three *β*-keto ester complexes, **1**; **a–c**, were more active than the acetylacetonate complex **1g**, which had a $t_{1/2}$ value of about 40 min.

As several of the complexes which had been prepared, e.g. **1i**, were found to be almost insoluble in chlorobenzene, the solvent was changed to a 5 : 1 (v/v) mixture of chlorobenzene and dioxane. This allowed the preparation of a 1.70×10^{-3} mol dm^{-3} solution with all the complexes. Representative data obtained from the hydroperoxide decompositions in this solvent are shown in Fig. 1, but the general features of these decompositions were as follows:

The presence of dioxane decreased the catalytic activity of all the complexes, but the inhibition was minimal with cobalt 2-ethylhexanoate. With this catalyst the $t_{1/2}$ value was only increased from about 1 min to 5 min, in contrast to that of the next active catalyst, the *t*-butyl acetoacetate complex **1b**, whose $t_{1/2}$ value was increased from about 2 min to 1 h.

With cobalt(II) 2-ethylhexanoate, the hydroperoxide decomposition proceeded to completion. If more hydroperoxide was then added, further decomposition occurred. With all the other complexes there was an initial rapid reaction, but this was followed by deactivation of the catalyst and after a while the addition of more complex was required for hydroperoxide decomposition to proceed further. As indicated by Fig. 1, there was a striking variation in the rates at which the various complexes underwent deactivation. With both the acetoacetic ester and the 1,3-diketone series of complexes the replacement of a methyl group by a trifluoromethyl group increased

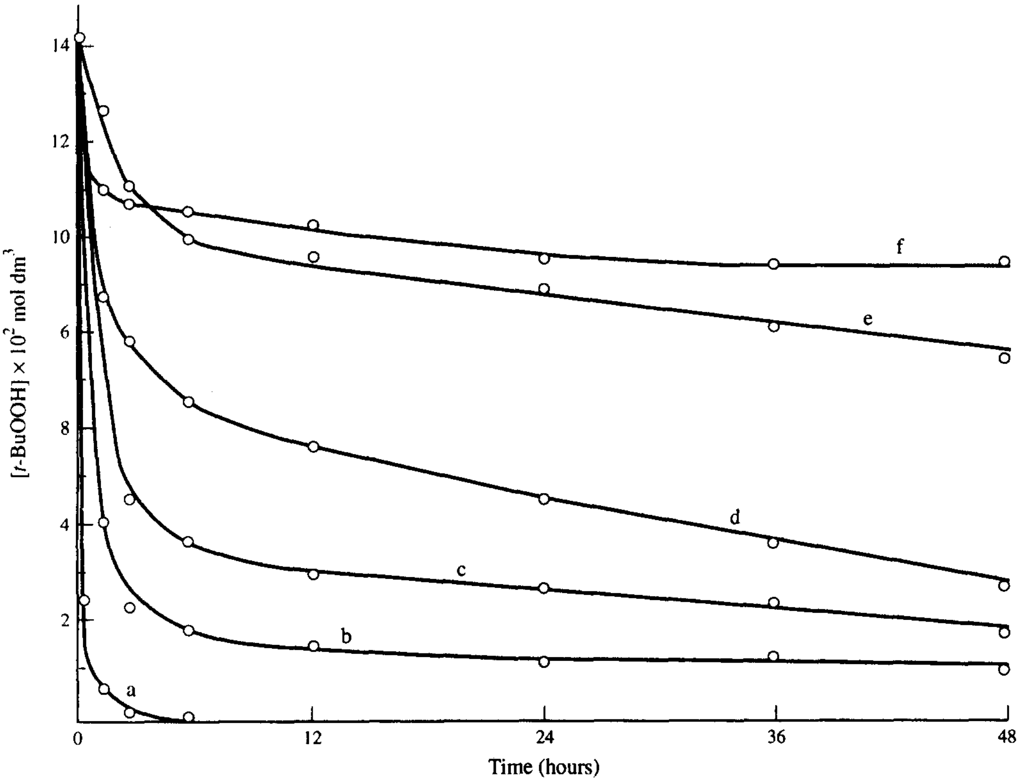


Fig. 1. Concentration of *t*-butyl hydroperoxide in cobalt(II)-catalysed decompositions at 25°C in 5 : 1 (v/v) chlorobenzene/dioxane with a catalyst concentration of 1.70×10^{-3} mol dm^{-3} and an initial hydroperoxide concentration of 0.142 mol dm^{-3}: (a), cobalt 2-ethylhexanoate; (b), **1b**; (c), **1a**; (d), **1g**; (e), **1e**; (f), **1i**.

the rate of deactivation. With the three β-diketone complexes, for example, this rate increased in the order **1g** < **1h** < **1i**, with only about 30% of the hydroperoxide having been decomposed by the time the last complex was completely deactivated. Of the three acetoacetic ester complexes **1**; **a–c**, the *t*-butyl complex **1b** had the lowest rate of deactivation, but all three complexes were deactivated at a much lower rate than the acetylacetonate **1g**.

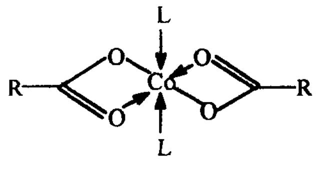
Deactivation was also observed with those decompositions carried out in neat chlorobenzene, but to a smaller extent than observed when chlorobenzene/dioxane was used as the solvent. In chlorobenzene, for example, the acetylacetonate **1g** ultimately decomposed about 95% of the hydroperoxide before reaction ceased, in contrast to about 80% in the chlorobenzene/dioxane mixture. In all cases, regardless of solvent, catalyst deactivation was accompanied by the precipitation of a dark coloured solid. Solids of this type have often been observed with cobalt-catalysed reactions that involve the decomposition of hydroperoxides [19].

Mechanistic considerations

In a recent Communication [10] mechanistic reasons were presented to show that when the acetylacetonate **1g** or a simple cobalt(II) carboxylate is oxidised by a hydroperoxide or peracid the very first product is the short-lived oxo-bridged species **3** (see Scheme 1), first suggested by Jones [20]. The thin-layer chromatographic and EXAFS studies by Chipperfield [21] indicate that in the case of cobalt(II) acetate the bridging oxygen in this species rapidly coordinates with unchanged cobalt(II) to give mixed valence oxo-centred trimers. We suggest that when a species of type **3** is generated in the presence of a large excess of a hydroperoxide, the alternative pathway in which the bridging oxygen abstracts a hydrogen atom from the hydroperoxide is followed. The resultant hydroxy-bridged complex **4** then initiates the catalytic cycle shown in Scheme 1, thereby inducing the radical-chain decomposition of the remaining hydroperoxide.

If the concentrations of the dinuclear species that are involved in this catalytic cycle are not maintained, one would expect an associated decrease in the rate of hydroperoxide decomposition. This decrease would normally be explained (as above) in terms of "catalyst deactivation". With the cobalt-catalysed hydroperoxide decompositions described here, we suggest that catalyst deactivation is the result of one or more of the dinuclear species involved in the catalytic cycle partly dissociating. The resultant monomeric species then coordinates with an undissociated dinuclear one to give an oxo-centred trimer which, catalytically, is relatively unreactive. An example of an equilibrium between a (cationic) hydroxy-bridged dicobalt complex of type **6** and an oxo-centred trimer has been reported by Sumner [22], while the relatively low catalytic activity of the trimer obtained from the *m*-chloroperoxobenzoic acid oxidation of cobalt(II) acetate is evident from the work described by Jones [20] and Chipperfield [21(a)].

relatively large quantities of dioxane there is little tendency for the solvated monomeric complex, **7**; L = dioxane, to be formed. Several cobalt(II) carboxylates have been shown by X-ray crystallography to have a dimeric structure of type **8** in the solid state [24], and the relatively high stability of this structure in non-aqueous solvents has been deduced for a number of cobalt(II) carboxylates by the data obtained from solvent extraction studies [25].



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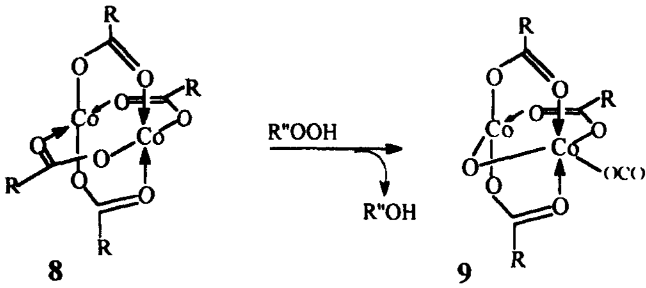

8 **9**

R = CH(Et)Bu

As shown in the following discussion, the relative tendency of the cobalt catalysts **1**; **a–i** to undergo deactivation correlates extremely well with the relative ease with which the dinuclear species involved in their respective catalytic cycles would be expected to dissociate into monomeric units.

While solutions of cobalt(II) 2-ethylhexanoate in water are the pink colour expected for the monomeric octahedral structure **7**; L = water, solutions in non-coordinating solvents are deep blue and in benzene show λ_{max} 528 and 572 nm (ε 39.5 and 45.8 respectively). These absorption characteristics result from the dimeric structure **8** [23], which has been shown by cryoscopic measurements to persist in chlorobenzene solutions even at "infinite" dilution [7]. In the absence of *t*-butyl hydroperoxide and adventitious peroxides, solutions of the salt in the chlorobenzene/dioxane mixture used in the current work are the same deep blue colour, indicating that even in the presence of

When *t*-butyl hydroperoxide is added to a solution of cobalt(II) 2-ethylhexanoate in either chlorobenzene or the 5 : 1 chlorobenzene/dioxane mixture there is an immediate colour change from deep blue to deep green, presumably due to the formation of the oxo-bridged complex **9**. While three of the carboxylate anions in this species are still bridging, one is now unidentate.* In the subsequent catalytic cycle, at least two (for the species corresponding to **5** and **6**) of these three groups will probably remain bridging in all the dinuclear species involved. Several dinuclear cobalt complexes that correspond to structures **4** and **6** and which contain bridging acetate groups have had their structures determined by X-ray crystallography [22,27]. These include the cationic complex of type **6** referred to above. This dicobalt(II) complex was prepared, as a pyridine adduct, by the oxidation of cobalt(II) acetate with peracetic acid, and contains unidentate as well as bridging acetate groups [22].

It follows that the bridging nature of the carboxylate group will ensure that all the dinuclear species in the catalytic cycle derived from cobalt 2-ethylhexanoate are relatively stable with respect to dissociation, even in the presence of dioxane, and for this reason the rate of catalyst deactivation is low. The same explanation would apply, of course, to other cobalt(II) carboxylates for which high catalytic activities have been reported, e.g., the stearate [28] and, of course, the acetate (see, for example, [5]).

Compared with the 2-ethylhexanoate the acetylacetonate **1g** undergoes fairly rapid deactivation. In the solid state the anhydrous form of this complex is a tetramer [29] with the acetylacetonate anions acting as bridging ligands as shown in the partial structure, **10**; R′ = R^1 = Me.† This type of bridging is much

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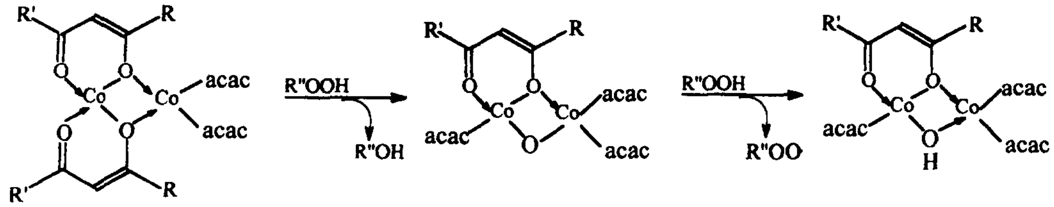
* An example of this type of transformation is provided by the reaction of the di-iron(II) ribonucleotide reductase R2 protein with molecular oxygen. The two iron(II) atoms are oxidised to an Fe(III)—O—Fe(III) system, while the associated glutamic acid residue, Glu238, which was originally bidentate and bridging becomes unidentate [26].

† For simplicity, only the central two cobalt atoms of the tetramer and two of the chelated acetylacetonate residues are shown in structure **10**. In the hydroperoxide decompositions the acetylacetonate was used as the dihydrate, which has the monomeric structure **2g**; L = H_2O [30]. This does not alter the validity of the argument concerning the strength of the intermonomeric bonding in a hydroxy-bridged dinuclear species such as **11** which, for convenience, is shown as being derived from **10**.



10

11

weaker than that exhibited by carboxylate anions, and even in non-coordinating solvents the tetrameric structure is retained only at relatively high concentrations and is broken down into smaller oligomers on dilution [31,32]. At 30×10^{-3} mol dm^{-3} virtually all the acetylacetonate is in the form of a monomer. It seems highly likely, therefore, that at the total catalyst concentration of 1.70×10^{-3} mol dm^{-3} used in the present work a dinuclear unit such as **11** would readily dissociate. This is particularly true when the solvent contains dioxane which, being a σ-donor, would facilitate the dissociation by solvating the monomeric forms.

In order to explain the higher rates of catalyst deactivation observed with the fluorinated complexes **1h** and **1i**, the reasoning above requires that the dinuclear structures that are involved in the corresponding catalytic cycles are held together by bonds that are weaker than those in the corresponding species derived from the acetylacetonate **1g**. This is almost certainly the case. With pyridine and primary amines the acetylacetonate **1g** forms monomeric adducts **2g**; L = amine, which in non-coordinating solvents partly dissociate and exist in equilibrium with the free amine and the various oligomeric forms of the parent acetylacetonate [31,33]. In contrast, the corresponding amine adducts obtained from cobalt(II) trifluoroacetylacetonate **1h** are stable with respect to dissociation [34]. In benzene, cobalt(II) trifluoroacetylacetonate is entirely monomeric [35], whereas the acetylacetonate is oligomeric.

These differences may be ascribed to electron-withdrawal by the trifluoromethyl group. This decreases the basicity and σ-donor strength of the two oxygen atoms in the coordinated diketonate anions, and consequently, the Co—O → Co bonds that hold the monomeric units together in oligomers such as **10** are weaker. The same explanation has already been advanced to account for the lower thermal stability of the anhydrous form of the hexafluoroacetylacetonate **1i**, relative to that of the anhydrous form of the trifluoro complex **1h** [36].

The same electronic effect also explains the observed order of deactivation, **1a** < **1g** < **1f**, for the pK_a values of the three parent 1,3-dicarbonyl compounds (in dimethylformamide) are 12.6, 11.7, and 7.4 respectively [37]. As these values reflect the relative basicity of the corresponding anions, it follows that the strength of the intermonomeric bonds in dinuclear species such as **11** will decrease in the order **1a** > **1g** > **1f**. The fact that **1d** is deactivated at a slower rate than the isomer **1f** may be explained similarly, for the reduction in the basicity of the anion that is caused by the electron-withdrawing effect of a 2,2,2-trifluoroethyl group is not as great as the reduction caused by a trifluoromethyl group.

Initially the lower rate of deactivation of the *t*-butyl ester complex **1b** compared with that of the ethyl ester **1a** suggests that an increase in the size of the alkoxy group increases the stability of the dinuclear species derived from these complexes. If this were correct, it would be rather difficult to explain. However, an inspection of molecular models of the dinuclear units **10** and **11** based on the published crystal structure for the tetrameric form of **1g** [29] shows that while an increase in the size of both of the groups R and R′ causes severe steric interactions between the two individual monomeric units, any interactions which might result from an increase in the size of only one of the groups can easily be avoided. This suggests that the lower rate of deactivation of the *t*-butyl ester **1b** is probably electronic rather than steric in origin, but unfortunately there appears to be no published data which enables the basicity of the anions of the ethyl and the *t*-butyl esters of acetoacetic acid to be compared. It should be noted that the interactions referred to above explain why in non-coordinating solvents the β-diketone complex **1j**, with its two *t*-butyl groups, exists entirely as the monomer, even at the high concentrations where the acetylacetonate **1g** exists largely as trimers and tetramers [32].

EXPERIMENTAL

IR spectra were measured on a Perkin Elmer 1600 Series Fourier Transform spectrometer using Nujol mulls. Chlorobenzene and dioxane were purified by the standard methods [38].

t-Butyl hydroperoxide was purchased from Aldrich Chemical Company as a solution in 2,2,4-trimethylpentane. The presence of approximately 5% (by volume) of this solvent in the hydroperoxide decomposition mixtures is ignored in all the discussion above. The preparation of the parent β-keto ester required for the complex **1c** has already been described [39]. The β-keto ester required for **1d** was prepared as described in the literature [40], and afforded ^{1}H NMR data consistent with structure. All other 1,3-dicarbonyl compounds were obtained from commercial sources and were used as received.

Preparation of the 1,3-*dicarbonyl complexes*

The dihydrate of **1g** and the hydrated forms of **1h** and **1i** were prepared from the parent ligands and cobalt(II) acetate as described in the literature [16,17]. For **1g**, $2H_2O$, Found: C, 40.8, H, 6.0. $C_{10}H_{18}CoO_6$ requires C, 41.0, H, 6.1%. For **1h**, 2.5 H_2O, Found: C, 28.7, H, 3.2. $C_{10}H_{11}CoF_6O_{6.5}$ requires C, 29.3, H, 3.2%. For **1i**, 2.5 H_2O, Found: C, 22.05, H, 1.45. $C_{10}H_5CoF_{12}O_{6.5}$ requires C, 23.2, H, 1.35%.

Bis(*ethyl acetoacetato*)*cobalt*(*II*), **1a**. Cobalt(II) acetate tetrahydrate (5.0 g, 0.02 mol) was dissolved in water (15 cm^3) and the solution was added to ethyl acetoacetate (5.2 g, 0.04 mol) in methanol (10 cm^3). Triethylamine (4.04 g, 0.04 mol) in methanol (10 cm^3) was then added dropwise with stirring, and the solid was filtered off, washed with cold methanol (*ca* 50 cm^3) and rapidly crystallised from water-free methanol to give the complex **1a** as pink feathers (3.1 g, 49%), m.p. 220°C (lit. [13] m.p. 207°C). Found: C, 45.5; H, 5.6. $C_{12}H_{18}CoO_6$ requires C, 45.4; H, 5.7%. IR (1700–1500 cm^{-1}): 1630s, 1520m. Prolonged heating of the complex in methanol afforded the methoxy complex Co(eaa)(OMe)(MeOH), which crystallised from the cooled solution as pink needles, m.p. >300°C. Found: C, 38.5, H, 6.4. $C_8H_{16}CoO_5$ requires C, 38.3, H, 6.4%. IR: 3450m, 1630s, 1520m.

The complexes **1**; **b–f** were prepared in a similar manner. Data were as follows:

1b, m.p. 124–126°C. Found: C, 51.2, H, 6.7. $C_{16}H_{26}CoO_6$ requires C, 51.5, H, 7.0%; ν_{max} 1625s and 1540 cm^{-1}.

1c, 2MeOH, m.p. 87–89°C. Found: C, 60.5, H, 8.7. $C_{30}H_{56}CoO_8$ requires C, 59.7, H, 9.35%; ν_{max} 3450m, 1640s and 1535m cm^{-1}.

1d, $2H_2O$, m.p. 160–164°C. Found: C, 31.3, H, 3.5. $C_{12}H_{16}CoF_6O_8$ requires C, 31.25, H, 3.5%; ν_{max} 3160m, 1650s, 1615m and 1525m cm^{-1}.

1e, m.p. 104–106°C. Found: C, 30.2, H, 2.1. $C_{10}H_8CoF_6O_6$ requires C, 30.25, H, 2.0%; ν_{max} 1660s and 1585m cm^{-1}.

1f, m.p. 112–114°C. Found: C, 33.8, H, 2.7. $C_{12}H_{12}CoF_6O_6$ requires C, 33.9, H, 2.8%; ν_{max} 1650s and 1575m cm^{-1}.

Hydroperoxide decompositions

The cobalt compound (3.57×10^{-5} mol) was dissolved in the chlorobenzene/dioxane mixture (20 cm^3) and dry, purified nitrogen was bubbled through the solution for 10 min. A 1 cm^3 portion of the solution of *t*-butyl hydroperoxide in 2,2,4-trimethylpentane was added with swirling, the flask was flushed with nitrogen, stoppered, and immersed in a water bath maintained at 25 ± 0.2°C. Aliquots (4 cm^3) of the mixture were removed at intervals and added to a 9 : 1 (v/v) mixture of 2-propanol and acetic acid (20 cm^3), and then aqueous potassium iodide (4.8 M, 2 cm^3) was added immediately. The mixture was heated in a boiling water bath for exactly 3 min, cooled to room temperature and titrated against standardised aqueous sodium thiosulfate (0.1 M). The titre obtained when the cobalt compound was omitted from this procedure showed that the concentration of hydroperoxide in the reaction mixtures was 0.142 mol dm^{-3}.

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