642. *Peroxides of Elements other than Carbon. Part V.*[1] *The Formation of Cadmium Peroxides by Autoxidation and by Nucleophilic Substitution.*

By Alwyn G. Davies and J. E. Packer.

Alkylperoxycadmium compounds can be prepared by the reaction of cadmium alkyls with molecular oxygen, or with alkyl hydroperoxides.

Similar reaction with hydrogen peroxide gives products containing the Cd·O·O·Cd group.

The only peroxides of cadmium so far reported are compounds of indefinite composition, usually prepared by treating cadmium hydroxide with aqueous hydrogen peroxide.[2] We have now investigated the autoxidation of cadmium alkyls, and their nucleophilic substitution by alkyl hydroperoxides and by anhydrous hydrogen peroxide, as routes to the peroxides of cadmium.

Autoxidation of Cadmium Alkyls.—Dimethylcadmium in air absorbed oxygen, giving a glass which exploded when touched. In cyclohexane, approximately 1 mol. of oxygen was absorbed slowly at room temperature, giving a product containing 1 mol. of peroxide. The reaction appeared to be catalysed by a trace of pyridine, and was slower in ether but faster in anisole.

Diethylcadmium and dibutylcadmium are much more reactive. In ether, approximately 2 mol. of oxygen were absorbed, essentially all forming peroxide. A white solid separated after 1 mol. of oxygen had been taken up. In cyclohexane, rather less oxygen was absorbed, giving a deficiency of peroxide in the case of diethylcadmium.

It would therefore appear that these cadmium alkyls undergo autoxidation in a manner (and perhaps by a mechanism) similar to that of the Grignard reagents [3] and boron alkyls,[4,1] *i.e.*:

$$R_2Cd \xrightarrow{O_2} \underset{(I)}{RCd{\cdot}O{\cdot}OR} \xrightarrow{O_2} \underset{(II)}{Cd(O{\cdot}OR)_2} \quad . \; . \; . \; . \quad (1)$$

Dimethylcadmium gives the peroxide (I; R = Me), whereas diethyl- and dibutylcadmium are more reactive and form the insoluble peroxides (II; R = Et or Bu). To confirm this structure, the precipitate obtained by autoxidation of diethylcadmium was treated with terephthaloyl chloride; diethyl diperoxyterephthalate [5] was isolated, confirming the presence of the ethylperoxy-group. Similarly, in the hydrolysate of the autoxidation product of dibutylcadmium (II; R = Bu), butyl hydroperoxide was identified by gas–liquid chromatography.[6,4]

When diethylcadmium was allowed to absorb 1 mol. of oxygen, the product (I; R = Et) was stable. This suggests that when the amount of peroxide formed is less than the amount of oxygen taken up, the reduction occurs intermolecularly between dialkylcadmium and an alkylperoxycadmium group.

Reaction of Cadmium Alkyls with Hydroperoxides.—Whereas boron alkyls do not react with protic reagents, cadmium alkyls undergo nucleophilic substitution, liberating the alkane. A possible route to the cadmium peroxides might therefore be of the type:

$$R'O{\cdot}OH + RCd{\cdot} \longrightarrow R'O{\cdot}OCd{\cdot} + RH \quad . \; . \; . \; . \; . \quad (2)$$

Reduction of the peroxide by the alkyl cadmium might complicate this simple picture.

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[1] Part IV, Davies and Hare, *J.*, 1959, 438.

[2] Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., London, 1923, Vol. IV, p. 532.

[3] Walling and Buckler, *J. Amer. Chem. Soc.*, 1955, **77**, 6032.

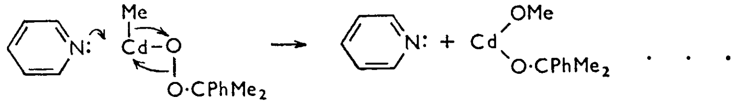
[4] Part III, Abraham and Davies, *J.*, 1959, 429.

[5] Baeyer and Villiger, *Ber.*, 1901, **34**, 738.

[6] Abraham, Davies, Llewellyn, and Thain, *Analyt. Chim. Acta*, 1957, **17**, 499.

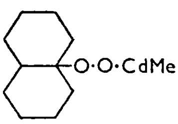
Treatment of dimethylcadmium in cyclohexane * with 1 mol. of decahydro-9-naphthyl hydroperoxide caused evolution of 1 mol. of methane and separation of 9-decalylperoxymethylcadmium (III), which did not melt without decomposition. It could not be redissolved in any aprotic solvent, and with acetic acid rapidly liberated 1 mol. of methane.

(αα-Dimethylbenzylperoxy)-methylcadmium (IV) was prepared similarly from αα-dimethylbenzyl hydroperoxide, and showed similar properties. When it was kept at 50° overnight with a trace of pyridine, the peroxide content fell by three quarters with an equivalent loss of CdMe groups (as measured by the evolution of methane by acetic acid). This can reasonably be interpreted as involving nucleophilic migration of an alkyl group from the metal to oxygen (eqn. 3) as we have postulated for similar boron [4,1] and silicon peroxides.[7]



. . . (3)

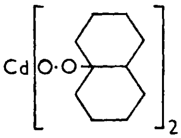
The reaction of diethyl- and dibutyl-cadmium with hydroperoxides was more vigorous. Both alkyl groups tended to be displaced, though some active alkyl groups were lost in reduction of the peroxide. For example, 2 mol. of 9-decalyl hydroperoxide with diethylcadmium gave 1·8 mol. of ethane, and 0·2 mol. of peroxide was reduced. As we observed in the autoxidation reactions, precipitation of the dialkylperoxycadmium compounds started as soon as the second alkylperoxy-group was introduced. From the reaction of 9-decalyl hydroperoxide with diethylcadmium and with dibutylcadmium, partially reduced bisdecalylperoxycadmium (V) was obtained as an amorphous white powder; it was insoluble in all unreactive solvents. On hydrolysis, 9-decalyl hydroperoxide was isolated.



(III)

$MeCd{\cdot}O{\cdot}O{\cdot}CPhMe_2$

(IV)



(V)

Similar reaction between cadmium dialkyls and anhydrous hydrogen peroxide in inert solvents might provide a route to cadmium peroxides, such as $RCd{\cdot}O{\cdot}O{\cdot}CdR$ and CdO_2. By this type of reaction, Perkins [8] obtained from diethylcadmium a compound which he supposed to have the composition $3CdO,H_2O_2$, and which exploded under reduced pressure.

Dimethylcadmium (2 mol.) and hydrogen peroxide (1 mol.) in ether liberated approximately 2 mol. of methane; the product gave a further 2 mol. of methane with acetic acid. The compound $MeCd{\cdot}O{\cdot}O{\cdot}CdMe$ is thus apparently being formed, but no attempt was made to isolate it.

The reaction between equimolecular amounts of hydrogen peroxide and diethyl- or dimethyl-cadmium in ether was complete in a few seconds, and in different experiments, between 1·2 and 1·6 mol. of alkane were collected. A white solid separated, with a peroxidic oxygen : cadmium ratio of up to 0·84 : 1. It appears then that these products contain a substantial amount of cadmium peroxide, CdO_2, but that the substitution reaction is accompanied by some reductive rearrangement of the alkyl group. An attempt was made to minimise this by conducting the reaction at −20°. The product from one such reaction decomposed violently under vacuum, giving brown cadmium oxide; from a second reaction a compound with a peroxidic oxygen : cadmium ratio of 0·78 : 1 was isolated.

* It was found that nitromethane reacts with dimethylcadmium according to the equation: $2CH_3{\cdot}NO_2 + Me_2Cd \longrightarrow 2MeH + Cd(CH_2{\cdot}NO_2)_2$. The dry product is explosive.

[7] Part I, Buncel and Davies, *J.*, 1958, 1550.

[8] Perkins, *J.*, 1929, 1687.

An attempt was made to cause reaction between hydroperoxides and cadmium salts in an inert solvent; the above type of reduction could not then occur. Anhydrous sodium αα-dimethylbenzyl peroxide in toluene could be obtained by adding the hydroperoxide to sodium methoxide in toluene and removing methanol under reduced pressure. Attempts to prepare alkylperoxycadmium compounds by treating this peroxide with a cadmium salt, particularly the iodide or acetate, were unsuccessful.

EXPERIMENTAL

The usual explosion precautions were observed in reactions involving peroxides.[7] Cadmium peroxides were handled in an anhydrous atmosphere in a glove box.

Analysis.—Peroxidic oxygen. Organoperoxides were determined iodometrically in propan-2-ol,[7] and hydrogen peroxide and other non-organic peroxides similarly but in aqueous solution.

Cadmium. The sample was added to an excess of a standard solution of disodium dihydrogen ethylenediaminetetra-acetate, and the excess determined by titration of the solution, buffered to pH 10, with a standard Zn^{++} solution, Eriochrome Black T being used as indicator.[9]

Alkylcadmium groups. MeCd and EtCd groups were estimated by hydrolysis with acetic acid; the paraffin was evolved quantitatively, and its volume measured in the gas burette (see Fig. 2, Part III [4]). When appropriate, the capsules were broken into the solvent containing acetic acid by the technique described previously, or the acetic acid was added *via* the tap *C*; [4] anisole (saturated with the appropriate paraffin) was a convenient solvent because it can readily be dried and has a low vapour pressure.

Preparation of Materials.—The cadmium dialkyls were prepared by treating the appropriate Grignard reagent with anhydrous cadmium chloride, and the products isolated by distillation and stored under nitrogen in glass capsules (see Part III [4]) at low temperature. All the compounds fumed violently, but did not ignite, when exposed to air.

Dimethylcadmium (72% yield), b. p. 63°/205 mm., is difficult to separate from the last traces of ether. Analysis for cadmium showed it to be 94·4% pure. It was stored at −20°, no decomposition occurring during 6 months. With an excess of butanol in cyclohexane, 1·09 mol. of methane were evolved in 3 hr., and a compound presumably MeCd·OBu formed in solution; acetic acid liberated a further 0·96 mol. of methane.

Autoxidation of cadmium alkyls.

Solvent	Time (hr.)	O_2 absorbed (mol.)	Peroxide formed (mol.)	Solvent	Time (hr.)	O_2 absorbed (mol.)	Peroxide formed (mol.)
	Dimethylcadmium				*Diethylcadmium*		
Et_2O	16	0·00	—	Et_2O	1	1·90	1·97
Et_2O	5	[a]	0·58	cyclo-C_6H_{12}	0·75	1·74	1·52
cyclo-C_6H_{12}	20	1·12	1·02				
cyclo-C_6H_{12} [b]	2	1·18	1·13		*Dibutylcadmium* [d]		
PhOMe	1	1·0 [c]	—	Et_2O	1	2·00	1·93
				cyclo-C_6H_{12}	1	1·63 [e]	1·58

[a] Oxygen was dispersed through a sintered-glass plate into the solution. [b] In the presence of one drop of pyridine. [c] More oxygen was absorbed slowly at 60°. [d] Assumed to be 83% pure. [e] This reaction may be incomplete because a bulky gelatinous precipitate prevented stirring.

Diethylcadmium, mixed with ether, was distilled at 1 mm. into a trap cooled in liquid nitrogen from the reaction mixture in a bath slowly heated to 120°. The ether was removed into a second cold trap. At room temperature the diethylcadmium (55% yield) slowly deposited grey cadmium. It was stored at −80°, and no further decomposition occurred. Quantitative hydrolysis showed it to be 96·5% pure; it catalysed the polymerisation of methyl methacrylate both in the presence and in the absence of oxygen.

Dibutylcadmium (12% yield), extracted similarly, also decomposed at room temperature but not at −80°. It was not analysed because the evolution of butane could not be accurately measured and because an analysis for cadmium would have yielded no useful information. A lower limit to the purity of 83% can be derived from the maximum values of the oxygen absorbed and the peroxide formed, during autoxidation.

Pentane, cyclohexane, and ether were dried over sodium wire and distilled immediately

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[9] Schwarzenbach, " Complexometric Titrations," (trans. Irving) Methuen, London, 1957, p. 83.

before use. Anisole and toluene were heated under reflux with molten sodium for 3 hr., then distilled as required.

Reaction of Cadmium Alkyls with Oxygen.—Thin glass capsules containing 0·2—0·8 g. of the appropriate cadmium alkyl were broken in solvent (*ca.* 50 c.c.) under oxygen in the apparatus described in Fig. 2, Part III.[4] Typical experiments are listed in the Table; others are described individually below. In all solvents used, a precipitate appeared as soon as more than 1 mol. of oxygen was absorbed.

Dimethylcadmium with no solvent. A capsule of the cadmium alkyl was broken in air in the gas burette. A glassy solid was deposited on the walls of the flask; when it was touched with the stirrer, it exploded, breaking the apparatus.

Diethylcadmium: identification of the ethylperoxy-group. Diethylcadmium (0·7736 g.) was autoxidised in ether, and the solid was allowed to settle. The ether was decanted, and the solid shaken with terephthaloyl chloride (0·5 g.) in benzene (20 c.c.) until the yellow colour of the acid chloride disappeared. The cadmium chloride and the excess of diethylperoxycadmium were filtered off, and the benzene was removed from the filtrate under reduced pressure, leaving an oil which was crystallised twice from light petroleum giving diethyl diperoxyterephthalate, m. p. 31·5—32·5° (Found: C, 57·6; H, 5·9. Calc. for $C_{12}H_{14}O_6$: C, 56·7; H, 5·55%). Baeyer and Villiger[5] give m. p. 37°; our sample probably contained some monoperoxy- or nonperoxy-ester as impurity.

Diethylcadmium: oxygen in limited supply. By using two burettes to circulate air through the flask, diethylcadmium (0·5421 g.) was allowed to absorb 0·91 mol. of oxygen; the supply of gas was then discontinued; 0·69 mol. of peroxide had been formed, and persisted for 42 hr. at room temperature, even in the presence of a trace of pyridine. If it is assumed that the difference between the amount of oxygen absorbed and that of the peroxide formed is due to the reaction $\text{EtCd}\cdot + \text{EtO·OCd}\cdot \longrightarrow 2\text{EtO·Cd}\cdot$, it follows that diethylcadmium must be the reducing agent, and that the molecular balance of the various groups present is EtCd, 0·87; EtO·OCd, 0·69; EtO·Cd, 0·44.

Dibutylcadmium: identification of the butylperoxy-group. Oxygen was passed through an ethereal solution of dibutylcadmium (0·65 g.) for 1 hr., a white solid being precipitated. The product was hydrolysed with 4N-hydrochloric acid (25 c.c.) for 2 hr., and the ethereal layer washed and dried. The ether was removed and the residual liquid analysed by gas–liquid chromatography.[6,4] n-Butyl hydroperoxide was identified by comparison with an authentic specimen.

Reaction of Cadmium Alkyls with Hydroperoxides.—Capsules of the cadmium alkyl were broken in a solvent containing the hydroperoxide and saturated with the appropriate alkane. The volume of alkane evolved was measured, and the amount of peroxide estimated iodometrically. The amount of RCd group remaining could be determined by measuring the further evolution of alkane with acetic acid.

Dimethylcadmium and 9-decalyl hydroperoxide. In cyclohexane, 1 mol. of dimethylcadmium with an excess of the hydroperoxide gave 1 mol. of methane. A second mol. was evolved when acetic acid was added. When the reaction was conducted in pentane, crystals separated during 3 hr. Next day they were washed with pentane and dried *in vacuo*, giving 9-decalylperoxymethylcadmium; it became brown at *ca.* 93°, and sintered at *ca.* 150°, but did not melt (Found: C, 43·3; H, 7·0; Cd, 36·8; peroxidic O, 9·9. Calc. for $C_{11}H_{20}O_2Cd$: C, 44·5; H, 6·8; Cd, 37·9; peroxidic O, 10·8%). It could not be dissolved in any aprotic solvent, and no further purification was possible.

Dimethylcadmium and αα-dimethylbenzyl hydroperoxide. Dimethylcadmium with 2 mol. of the hydroperoxide in cyclohexane similarly gave 1·25 mol. of methane, without loss, even after 24 hr., of peroxide; acetic acid yielded a further 0·75 mol. of methane. With 1 mol. of the hydroperoxide in cyclohexane, 1·07, 1·09, and 1·08 mol. of methane were evolved in different experiments. The solvent was removed under reduced pressure, giving methyl-(αα-dimethylbenzylperoxy)cadmium as white crystals which were washed with cyclohexane and dried; they became brown at *ca.* 150°, but did not melt below 240°. Again no solvent could be found for recrystallisation (Found: C, 40·0; H, 4·9; Cd, 36·8; peroxidic O, 11·3. Calc. for $C_{10}H_{14}O_2Cd$; C, 43·1; H, 5·0; Cd, 40·3; peroxidic O, 11·5%). At 50° in the presence of a trace of pyridine the peroxide content fell by three-quarters overnight, with an equivalent loss of MeCd groups.

Diethylcadmium and αα-dimethylbenzyl hydroperoxide. With 2 mol. of the hydroperoxide, 1·51 mol. of ethane were evolved and 0·53 mol. of peroxide was reduced.

Diethylcadmium and 9-*decalyl hydroperoxide.* With 2 mol. of the hydroperoxide in cyclohexane, 1·83 mol. of ethane were evolved, and partially reduced di-9-decalylperoxycadmium was obtained as a white powder (Found: Cd, 25·6; peroxidic O, 11·1. Calc. for $C_{20}H_{34}O_4Cd$; Cd, 25·0; peroxidic O, 14·2%). Hydrolysis with 2N-sulphuric acid liberated 9-decalyl hydroperoxide, m. p. and mixed m. p. 84—86°.

Diethylcadmium and t-butyl hydroperoxide. With 2 mol. of the hydroperoxide in anisole, 1·54 mol. of ethane were evolved slowly, and a further 0·30 mol. on the addition of acetic acid.

Dibutylcadmium and αα-dimethylbenzyl hydroperoxide Because of the high solubility of butane in organic solvents (up to 1 l. of gas per 50 c.c. of solvent) and its sensitivity to temperature variations, measurement of the volume of butane evolved during reaction was not possible.

Dibutylcadmium in pentane containing αα-dimethylbenzyl hydroperoxide under nitrogen gave a precipitate within 5 min. After 3 hr. the solvent was removed under reduced pressure, and the residue hydrolysed with aqueous acetic acid. No butane was evolved, showing that no BuCd groups remained.

Dibutylcadmium and 9-*decalyl hydroperoxide.* From the reaction between dibutylcadmium and the hydroperoxide (2 mol.), partially reduced bis-9-decalylperoxycadmium was obtained (Found: Cd, 26·5; peroxidic O, 11·7%).

Aliquot portions of a similar mixture were analysed periodically for peroxide, the mixture being stirred vigorously during sampling after solid had separated (30 min.). The results were as follows:

Time (min.)	0	10	21	32	87	Next day
Peroxide (mol.)	2·00	1·85	1·78	1·71	1·66	1·44

Reaction of Cadmium Alkyls with Hydrogen Peroxide.—The powdered dry urea–hydrogen peroxide complex was kept at 60°/1 mm., and 98% hydrogen peroxide was collected in a trap at −40°.

Dimethylcadmium. With dimethylcadmium (1 mol.), hydrogen peroxide in ether gave 1·60 mol. of methane within 5 sec., and a white precipitate separated (Found: Cd, 74·2; peroxidic O, 16·5. Calc. for CdO_2: Cd, 77·8; peroxidic O, 22·2%).

In an attempt to minimise the amount of reduction, the experiment was repeated at low temperature. Reaction occurred when the cold mixture was allowed to warm to −20°. The precipitate was separated, but decomposed violently under reduced pressure in the desiccator, giving clouds of a fine brown powder, presumably cadmium oxide. When dried in a stream of air, the solid could be analysed (Found: peroxidic O, 15·9%).

Diethylcadmium. The reaction between diethylcadmium and hydrogen peroxide (1 mol.) in ether was again very fast, and 1·2 mol. of ethane were evolved. The white precipitate was washed and dried (Found: Cd, 59·8; peroxidic O, 14·2%).

Preparation of Anhydrous Sodium αα-Dimethylbenzyl Peroxide in Toluene.—The sodium salt, prepared by treating the hydroperoxide with aqueous sodium hydroxide, is hydrated. The following method of preparing the salt in toluene may be useful when the anhydrous reagent is required.

Sodium was dissolved in toluene by adding the minimum possible amount of methanol. The hydroperoxide (1 mol. with respect to sodium) was then added, and the methanol removed by concentrating the solution to half volume under reduced pressure. A peroxide determination shows that about 5% of the peroxide is decomposed in this process.

Attempts to prepare alkylperoxycadmium compounds by treating this solution with anhydrous cadmium salt, particularly the iodide or acetate, were not successful.

The Reaction between Dimethylcadmium and Nitromethane.—A capsule of dimethylcadmium was broken in nitromethane. After about 10 min., methane (2 mol.) was evolved and a yellow solid separated. The dry solid detonated whilst being handled in the glove box; with careful manipulation it could be analysed [Found: Cd, 45·2. Calc. for $Cd(CH_2{\cdot}NO_2)_2$: Cd, 48·3%]. The same compound was apparently formed when an attempt was made to recrystallise (αα-dimethylbenzylperoxy)methylcadmium from nitromethane.

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