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THE FORMATION OF A REVERSIBLE COMPLEX BETWEEN DIETHYLCADMIUM AND OXYGEN

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SUMMARY

From an investigation of the autoxidation of diethylcadmium (DEC) in n-heptane the formation of a reversible 1/2 DEC-oxygen complex has been established by a kinetic method.

Some properties of this complex have been studied, *viz.* its ability to undergo spontaneous and catalytic transformation into bis(ethylperoxy)cadmium and its ultraviolet and infrared absorption spectra.

The formation of reversible complexes with oxygen has been demonstrated for chelates of transition metals[1]. Such data are not available for organic compounds of the non-transition elements, for although a report has appeared suggesting the formation of such a complex in the autoxidation of tri-n-butyl-boron[2] this has subsequently been disproved[3]. In this present work, which involves an investigation of the kinetics of the autoxidation of DEC in n-heptane, the data obtained suggest the existence of a reversible 1/2 DEC–oxygen complex.

The autoxidation of DEC in n-heptane at ca. −40° is accompanied by the absorption of two moles of oxygen per mole of initial DEC. On completion of the absorption process the reaction mixture exists as a homogeneous colourless solution (I). A material which is insoluble in organic solvents and subsequently shown to be bis(ethylperoxy)cadmium is gradually precipitated from solution (I). The molar yield of this bis-peroxide corresponds to the consumption of one mole of the initial DEC and two moles of absorbed oxygen. The formation of bis(ethylperoxy)cadmium in (I) does not involve either the additional absorption of oxygen or the liberation of oxygen from the solution.

Heating solution (I) or the addition to it of very small amounts of water, ether, ionol, *o*-phenylenediamine or other compounds capable of acting as ligands (L) for DEC lead to an increased rate of formation of bis(ethylperoxy)cadmium in (I).

A similar effect is observed if these compounds are present in the DEC solution before oxidation of the latter. In this case, however, the formation of a homogeneous colourless solution is not observed and only a sediment of bis(ethylperoxy)cadmium is obtained.

On completion of oxygen uptake, (I) contains no peroxide compound and the oxygen absorbed may at this point be removed from the reaction mixture by evacuation*. In so doing solution (I) is transformed into the initial reaction solution, *i.e.* a solution of DEC in n-heptane. Subsequent further addition of oxygen once again leads to the absorption of two moles of oxygen per mole of DEC. Successive oxidation of DEC to solution (I), regeneration of the initial solution and subsequent oxidation back to solution (I) has been repeatedly performed. The regeneration of the initial solution from solution (I) by evacuation of the latter has been convincingly demonstrated by spectrophotometry.

By differential spectrophotometry of (I), the ultraviolet absorption spectrum of the complex $Et_2Cd \cdot 2O_2$ has been shown to contain an intense absorption band at 276 nm (Fig. 1). Regeneration of the initial solution from solution (I) by the method described above causes the disappearance of this band but on subsequent oxidation of DEC back to (I) the absorption band reappears.

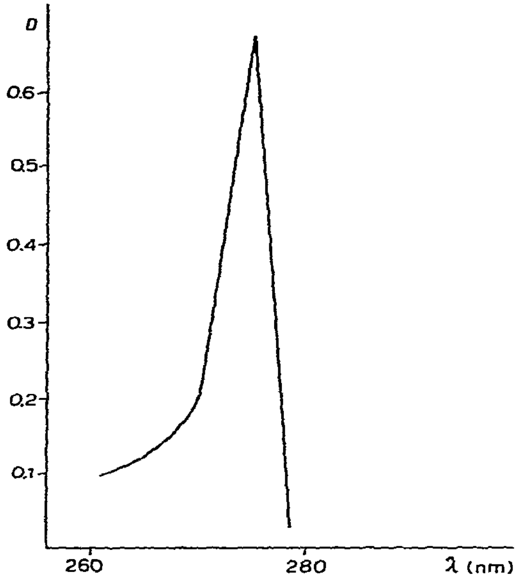

Fig. 1. The ultraviolet absorption spectrum of the complex $Et_2Cd \cdot 2O_2$.

The infrared spectrum of solution (I) differs from that of the initial DEC solution in n-heptane by the appearance of an additional band at 790 cm^{-1} (Fig. 2).

The bond between the two components in the complex $Et_2Cd \cdot 2O_2$ is weak as confirmed by the ready removal of oxygen from the system on evacuation. This is supported by the fact that neither the intensity of the absorption bands corresponding to the C–Cd stretching vibrations nor a shift in the maxima of these bands occurs in the infrared spectrum on conversion of free Et_2Cd to $Et_2Cd \cdot 2O_2$ and vice-versa. However, it should be noted that even in the comparatively stable complexes formed between organozinc and organocadmium compounds and dioxane and ethers the

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* The best results have been achieved by evacuating the solution while the latter is simultaneously frozen and melted two or three times. Prior introduction of glass fragments into the solution facilitates this process.

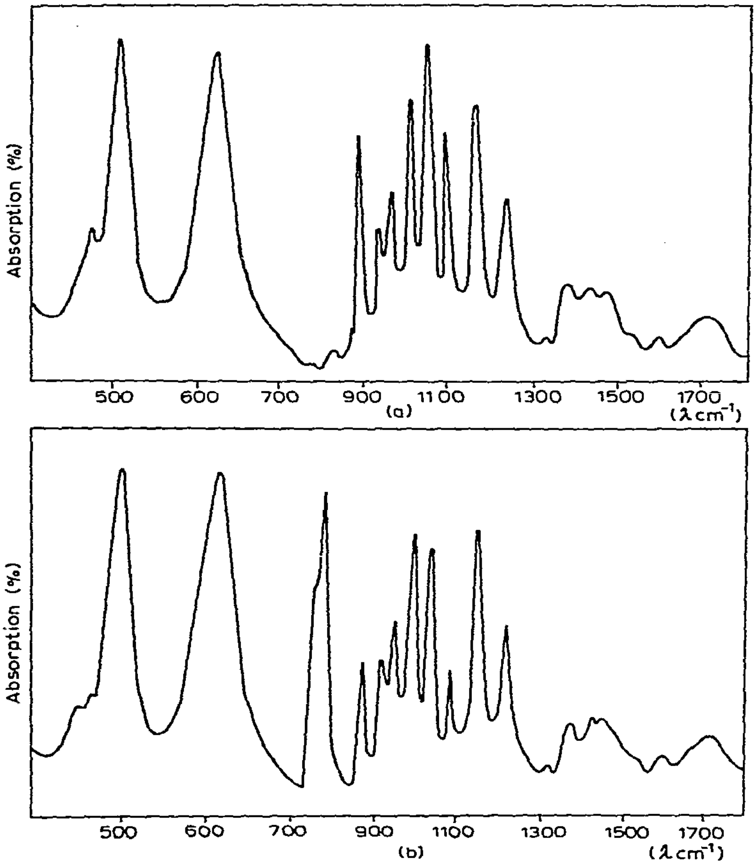


Fig. 2. The infrared absorption spectra of (a) Et_2Cd solution in n-heptane and (b) the complex $Et_2Cd \cdot 2O_2$ in n-heptane.

shifts in the maxima of the absorption bands corresponding to the C–Zn and C–Cd bond stretching vibrations only amounts[4] to 5–15 cm^{-1}.

The results of this work indicate the formation of a reversible complex between DEC and oxygen during the oxidation of Et_2Cd with the subsequent transformation of this complex into bis(ethylperoxy)cadmium:

$$Et_2Cd + 2O_2 \rightleftharpoons Et_2Cd \cdot 2O_2 \qquad (1)$$

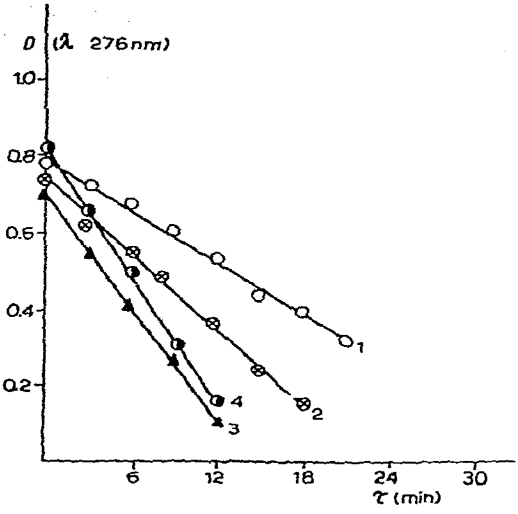
$$Et_2Cd \cdot 2O_2 \rightarrow EtOOCdOOEt \qquad (2)$$

It should be noted that the purity of the initial reactants used has a profound effect on the reproducibility of the results obtained.

As mentioned above, this fact is related to the ability of a whole range of compounds for acting as effective catalysts for reaction (2) above.

$$Et_2Cd \cdot 2O_2 \longrightarrow (EtOO)_2Cd \qquad (3)$$

Some kinetic data have been obtained relating to reaction (2). Thus the rate of conversion of $EtCd \cdot 2O_2$ into bis(ethylperoxy)cadmium in n-heptane in a quartz



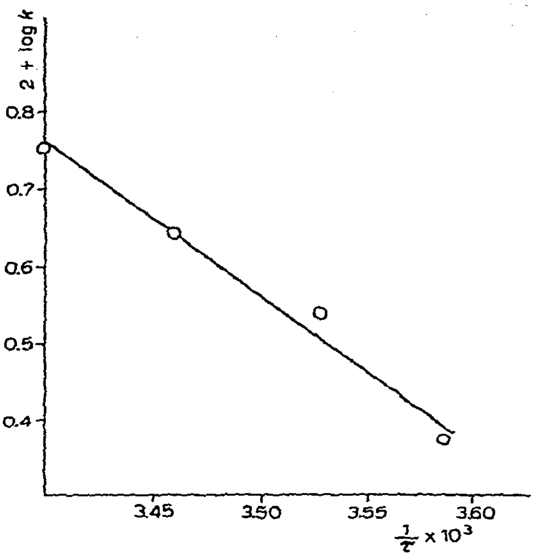


Fig. 3. Kinetic analysis of the conversion of $Et_2Cd \cdot 2O_2$ into bis(ethylperoxy)cadmium at 6, 11, 16 and 21° (corresponding to the curves 1–4) respectively.

Fig. 4. The temperature dependence of the rate constant for the conversion of $Et_2Cd \cdot 2O_2$ into bis(ethylperoxy)cadmium.

reaction vessel* is constant up to high degrees of conversion (Fig. 3) indicating that reaction (2) is zero order under the conditions employed. This result may apparently be attributed to the heterogeneous nature of this reaction which occurs on the walls of the reaction vessel.

The influence of temperature on the rate constant (k) for the conversion of $Et_2Cd \cdot 2O_2$ into bis(ethylperoxy)cadmium is shown in Fig. 4; under the above conditions this dependence may be expressed by the following equation:

$$k = 10^{14.15} \exp\{-8700/RT\} \qquad (\text{mole} \cdot l^{-1} \cdot s^{-1})$$

EXPERIMENTAL

DEC was prepared by the reaction of a Grignard reagent with cadmium bromide[5]. The resulting compound was purified by two distillations and recondensation under a pressure of 0.5 mmHg.

Oxygen was prepared by heating potassium permanganate and dried by passing over phosphorus pentoxide and through a trap cooled in liquid nitrogen.

Heptane of "standard" grade was purified further by the method previously described[6].

The oxidation experiments were carried out in a circulatory vacuum apparatus; the techniques employed have been discussed previously[7].

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* The kinetics of reaction (2) was studied spectrophotometrically (by following the absorption band at 276 nm) by thermostatting solution (I) in quartz cells.

Quantitative determination of bis(ethylperoxy)cadmium was undertaken by iodometric titration in acetic acid solution.

The ultraviolet spectrum was measured using a quartz vacuum cell ($l=0.7$ mm) while the infrared spectra were measured using a KBr cell in an atmosphere of dry argon.

REFERENCES

1 L. H. Vogt, N. M. Faigenbaum and S. E. Wiberley, *Chem. Rev.*, 63 (1963) 269.
2 L. Zutty and F. I. Welch, *J. Org. Chem.*, 25 (1960) 861.
3 A. G. Davies, D. G. Hare and O. R. Khan, *J. Chem. Soc.*, (1963) 1125.
4 A. N. Rodionov, I. E. Paleeva, D. N. Shigorin, I. Sheverdina and K. A. Kotcheshov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 5 (1967) 1031.
5 I. Sheverdina and K. A. Kotcheshov, *The methods of element organic chemistry: Zinc. Cadmium*, Nauka, Moscow, 1964, pp. 145, 150–151.
6 A. Weissberger, E. S. Proskauer, J. A. Riddick and E. E. Toops, *Organic solvents, Physical properties and method of purification*, Interscience Publ., Inc., New York, 2nd. Ed., 1955.
7 G. A. Razuvaev, Yu. A. Alexandrov, V. N. Glushakova and G. N. Figurova, *J. Organometal. Chem.*, 14 (1968) 339.