7.53; B, 36.72; Cl, 6.02; N, 9.51; P, 15.77. Found: C, 23.83; H, 7.95; B, 36.76; Cl, 7.43; N, 8.88; P, 14.16; mol wt (in chloroform), 598.

Reaction of *m*-$B_{10}H_9BrLi$ with PCl_3.—A solution of *m*-$B_{10}H_9$-BrC_2H_2[1] (22.3 g, 0.1 mole) in ether (100 ml) was added, with stirring and ice cooling, to a solution of butyllithium (0.25 mole) in hexane (170 ml) and ether (100 ml). The reaction mixture was stirred at 0° for 1 hr, then filtered. The insoluble dilithium salt was washed with ether, then slurried with 250 ml of ether, and added with ice cooling to a solution of PCl_3 (41.1 g, 0.3 mole) in 500 ml of ether. After stirring for 12 hr at ambient temperature, the resulting mixture was filtered, and then the filtrate was evaporated to dryness. Trituration of the residue with methanol afforded 25 g of polymer, mp 115–120° (starts to shrink at 105°).

Anal. Calcd for $C_{15}H_{63}B_{60}Br_6Cl_2O_3P_6$ (1712.1): C, 10.52; H, 3.71; B, 37.91; Cl, 6.21; Br, 28.00; P, 10.85. Found: C, 9.67; H, 3.68; B, 36.34; Cl, 6.21; Br, 28.00; P, 11.08; mol wt (in toluene at 39°), 1784.

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Tracer Experiments on the Oxidation of Methyl Esters of Oxalic Acid by Cerium(IV)

BY C. ANDRADE AND H. TAUBE

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The oxygen tracer experiments which we describe in this note were undertaken in trying to develop convenient methods for determining in solution the isotopic composition of the oxygen contained in CH_3-C_2O_4H and $CH_3C_2O_4CH_3$. The reactions proved not quite clean enough to meet our analytical requirements, but the results we obtained are sufficiently clear-cut to provide insight into the mechanism of oxidation of these species.

Experimental Section

Earlier work has shown that CO_2 generated in aqueous solution can be removed rapidly enough by a stream of inert gas so that little exchange with solvent takes place.[1] The oxidation was done by adding the ester solution to the solution containing Ce(IV) and $HClO_4$. Each of the solutions was enriched in O^{18} to the same extent. The stream of N_2 used to carry off the CO_2 served also to stir the solution. Carbon dioxide was trapped out of the N_2 stream using liquid N_2 as coolant, and CO_2 was collected for isotopic analysis after it was sublimed from a Dry Ice–methanol trap. The isotopic composition of the solvent was determined by equilibration with CO_2.

The reaction of Ce(IV) with the oxalate esters is rapid, the half-time being less than 1 min under our conditions. The time of reaction was chosen as 5 min. A matter of some concern is the extent of oxygen exchange between the esters and the solvent in the highly acidic reaction medium. The rate of exchange of the esters has been determined, and an upper limit can be set on the incorporation of solvent oxygen by exchange. The extent of exchange is small and is dealt with in the next section.

Results

The results of the tracer experiments are shown in Table I. The values of n (see footnotes to Table I) are calculated from the equation

$$n = \frac{2E_{CO_2} - 1}{E_{solv} - 1}$$

TABLE I

OXYGEN TRACER RESULTS ON THE OXIDATION OF $(CH_3)_2C_2O_4$ AND $KCH_3C_2O_4$ BY Ce(IV)[a]

~2.5 *M* $HClO_4$, ~0.20 *M* Ce(IV)

	E^b for		
Substrate,[a] *M*	Solvent	CO_2	n^c
	$(CH_3)_2C_2O_4$		
0.0423	5.378	3.266	1.03
0.0508	5.328	3.238	1.03
	$CH_3C_2O_4H$		
0.0352	5.183	2.192	0.57
0.0422	5.125	2.166	0.57

[a] Room temperature. [b] E = enrichment ratio, that is the isotopic composition in the sample in question compared to that of normal CO_2. [c] n = number of atoms of oxygen for each CO_2 formed which are derived from the solvent. Note that 2 moles of CO_2 results from the oxidation of each mole of ester.

Discussion

The values of n, slightly in excess of 1.00 for $(CH_3)_2$-C_2O_4 and slightly in excess of 0.50 for $CH_3C_2O_4$, are upper limits on the incorporation of solvent oxygen into CO_2 by the reaction itself. Exchange of oxygen between solvent and unreacted complex must be allowed for, as must ester hydrolysis and exchange between the CO_2 formed and the solvent. Using as the half-life for reaction the upper limit of 1 min, and results[2,3] on the rates of oxygen exchange, the rate of oxidation for the diester compared to exchange is 200 or greater and the incorporation of solvent oxygen per CO_2 by exchange is less than 0.005. Making a similar estimate for $CH_3C_2O_4H$, assuming that the rate of exchange of the three exchangeable oxygens is one-half that observed for $H_2C_2O_4$, the upper limit to the number of atoms incorporated is ~0.1. Ester hydrolysis competing with oxidation can at most account for 0.015 solvent atom per CO_2 in the case of $(CH_3)_2C_2O_4$ and even less in the case of $CH_3C_2O_4H$. Incorporation by exchange between CO_2 and solvent is less than 2%. This analysis indicates that the actual incorporation of solvent oxygen by oxidation is exactly 1.00 in the case of $(CH_3)_2C_2O_4$ and very nearly 0.50 in the case of CH_3-C_2O_4H.

Oxidation in the three cases studied thus far results in bond breaking as indicated below.

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(1) R. M. Milburn and H. Taube, *J. Am. Chem. Soc.*, **81**, 3515 (1959).

(2) C. Andrade, Ph.D. Dissertation, University of Chicago, 1964.

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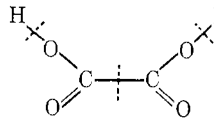

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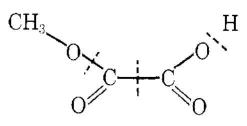

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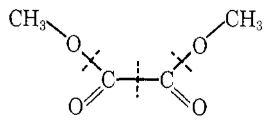

present work

In none of the cases is HCO_3^- or H_2CO_3 formed as an intermediate stage in the oxidation. Much of course remains to be said on the detailed sequence of events in these reactions.

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Polarized Crystal Spectra of the *trans*-Dihalobis(ethylenediamine)cobalt(III) Ion

BY R. A. D. WENTWORTH

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Recently the implications of both crystal field and molecular orbital calculations for tetragonal amine complexes of cobalt(III) have received renewed interest.[1,2] Of fundamental importance was the discovery that the splitting of the $^1T_1$ band in the tetragonal field could be readily interpreted in terms of $\delta\Delta$, the difference in the crystal field stabilization energies of the axial and in-plane ligands. However, a complete knowledge of the one-electron energy levels of a tetragonal complex has been hindered by a lack of experimental information concerning the splitting of the $^1T_2$ band. Using data from solution spectra, it was previously shown[2] that the position of the band maximum of the apparently unsplit $^1T_2$ band varied almost linearly with $\delta\Delta$. With an empirical molecular orbital model as a basis, it was shown that accompanying a monotonic decrease in the field strength of the axial ligand there was an apparent monotonic increase in π bonding. Furthermore, it appeared that for π-bonding ligands of relatively weak field strength such as chloride and bromide ions, the crystal spectra of the *trans* disubstituted complexes should reveal splitting of this band if, indeed, splitting is to be found. However, Yamada, Nakahara, Shimura, and Tsuchida[3] (hereafter YNST), who measured the polarized crystal spectra of *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ and *trans*-$[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$, found no more information in this regard than that afforded from solution spectra. Consequently, a low-temperature investigation of the polarized crystal spectra of these compounds was undertaken.

Experimental Section

The insolubility of *trans*-$[Co(en)_2X_2]X \cdot HX \cdot 2H_2O$ (X = Cl or Br) precluded the growth of spectroscopically suitable crystals by direct methods. However, this situation was avoided by effecting the hydrolysis of these compounds in hot aqueous solution to form $Co(en)_2(H_2O)_2^{3+}$, which is extremely soluble in the presence of halide ion, followed by the addition of the appropriate hydrohalic acid to the cooled solution. Crystals of the desired compound began to appear in several days and could be grown as large as 1 cm on edge and 3 to 4 mm thick. If a large crystallizing dish was used, very thin plates of large surface area could be invariably obtained from the sides of the dish. These were suitable for spectroscopy using ordinary techniques since the optical density of the d–d spectrum never exceeded 1.5 absorbancy units. Moreover, the large surface area ensured that slit widths remained below 0.08 mm.

Both of these compounds are unstable to loss of HX and H_2O, which leads to opacity within several hours. The application of a rubber cement (transparent between 5000 and 30,000 cm^{-1}), which was diluted with acetone, effectively prevented this occurrence. Spectra taken on coated and uncoated crystals were identical.

The crystallographic axes were located with a polarizing microscope using the excellent descriptions of the crystal habit and dichroism of these compounds which are contained in the reports of their crystal structures.[4,5] Spectra were then recorded with the incident light polarized perpendicular and parallel to the *c* axis. To ensure the best alignment of the electric vector with this axis, the spectrum of the region between 14,000 and 17,000 cm^{-1} was recorded at 2° intervals until the absorbancy reached a maximum, where the electric vector was truly parallel to the *c* axis. The perpendicular spectra were then obtained by rotating the polarizer through 90°. Extinction coefficients in M^{-1} cm^{-1} were computed from the known density,[4,5] formula weight, and thickness of a crystal which was measured with a micrometer.

The experimental apparatus has been previously described[6] with one exception. In the present work, the Cary spectrophotometer was equipped with its accessory high-intensity source.

Results and Discussion

The results at both room and liquid nitrogen temperatures are listed in Table I. Average extinction coefficients were obtained from the spectra of ten crystals of each compound with a precision of 10%, and these are compared in the table to the earlier room temperature results of YNST. Good agreement can be seen in both cases below 24,000 cm^{-1}. The polarizations are referred to the crystallographic *c* axis, which is nearly coincident with the halide–cobalt–halide bonds.[4,5] Resolution of the perpendicular and parallel components into the true σ and π spectra was not necessary since the differences between the observed and resolved spectra were much too small to be meaningful.

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