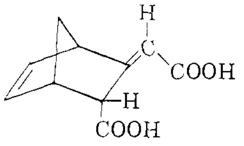
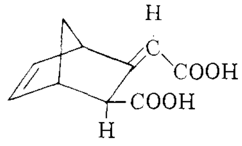
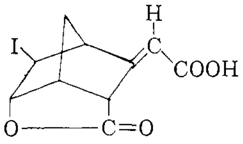
Since the lower melting compound (VII) yielded an iodolactone[11] (IX, infrared split lactone carbonyl band 5.54, 5.58 μ; acid carbonyl band 5.89 μ; double bond 6.01 μ) on treatment with iodine and sodium bicarbonate,[12] the carboxyl participating in this reaction must possess the *endo* configuration shown. Further, the stereochemistry of the α,β-unsaturated acid grouping must be as indicated, since treatment of the diacid with warm acetic anhydride gave a monomeric anhydride[11] (X, infrared carbonyl bands 5.54, 5.71 μ). The anhydride was hydrolyzed back to VII in good yield by warming with aqueous dioxane. These facts and consideration of the reaction sequence leading to VI serve to establish structure VII for the lower melting adduct. Although we have done little work with the higher melting Diels–Alder product, we may say that it probably has structure VIII, since its reaction with iodine and bicarbonate gives no iodolactone, but treatment with acetic anhydride does afford X.[13]



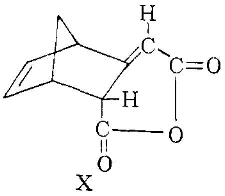
VII



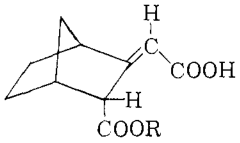
VIII



IX



X

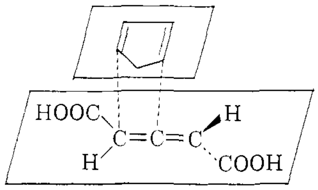


XI, R = H
XII, R = CH_3

Adduct VII absorbed one mole of hydrogen rapidly in methanol over palladium on carbon to furnish the dihydrodiacid XI[11] (one vinyl proton in n.m.r. spectrum), which then was esterified with diazomethane to XII.[11] This ester was successively ozonized at −60°, treated with potassium iodide–acetic acid,[14] and hydrolyzed and decarboxylated with hot concentrated hydrochloric acid.[15] The resulting crude product was converted directly into norcamphor dinitrophenylhydrazone (VI),[16] the identity of which was confirmed by comparison with an authentic sample.

To obtain optically active material a sample of glutinic acid was resolved partially with brucine; the dextrorotatory allene ($[\alpha]_D$ 2.4°) thus obtained condensed with cyclopentadiene to give optically active VII. The dinitrophenylhydrazone formed on degradation of this adduct was found to be dextrorotatory ($[\alpha]_D$ 2.2°).

Now, Berson's work[9] has demonstrated the absolute configuration implied in VI for (+)norcamphor itself, and the dinitrophenylhydrazone prepared from his ketone is also dextrorotatory. We can, therefore, assign structure VI in the absolute sense to the material formed on degradation of VII and accept the absolute stereochemistry of structure VII for the original optically active adduct. This requires in turn that (+)pentadiendioic acid have the absolute configuration shown in V. (The steric relationship between V and VII is depicted in XIII.) We may note finally that VII is the adduct predicted by the Alder–Stein rules[10,17] in conjunction with simple steric considerations. Formation of either of the possible, unobserved adducts (alternative *cis–trans* isomer of the α,β-unsaturated acid) would require approach of cyclopentadiene to V directly over a carboxyl group rather than a hydrogen atom (*cf.* XIII).



XIII

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[12] (a) E. E. van Tamelen and M. Shamma, *J. Am. Chem. Soc.*, **76**, 2315 (1954); (b) C. S. Rondestvedt, Jr., and C. D. Ver Nooy, *ibid.*, **77**, 4878 (1955).

[13] The epimerization implied in the transformation of both VII and VIII to X requires no comment, as X is a glutaconic anhydride. As might be expected (ref. 10), the compound does appear to exist in the form written; its solution infrared spectrum shows no trace of hydroxyl absorption.

[14] P. S. Bailey, *Chem. Ber.*, **88**, 795 (1955).

[15] L. Ruzicka, *Helv. Chim. Acta*, **3**, 748 (1920).

[16] K. Alder, H. K. Schäfer, H. Esser, H. Krieger, and R. Reubke, *Ann.*, **593**, 23 (1955).

[17] K. Alder and G. Stein, *Ann.*, **514**, 1 (1934); *Angew. Chem.*, **50**, 510 (1937).

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RECEIVED JULY 24, 1961

ROTATORY DISPERSION STUDIES OF COORDINATION COMPOUNDS. I. ABSORPTION SPECTRA AND ELLIPTICITY OF OPTICALLY ACTIVE DIHEDRAL COBALT(III) COMPLEXES

Sir:

From a study of the rotatory dispersion in the visible absorption bands of the $[Co(en)_3]^{3+}$ dihedral complex ion, Moffitt[1] suggested that the rotational strengths of the $^1A_{1g} \rightarrow {}^1T_{1g}$ inverse transition could be attributed to an admixture of the 4p with the 3d orbitals due to the trigonal component associated with the system. However, Sugano[2] has shown, from symmetry arguments alone, that Moffitt's first order theory cannot account for the rotational strengths and has suggested that different mechanisms operate for rotations and visible absorption. Sugano's symmetry arguments are applicable to strictly dihedral systems but for slightly distorted dihedral systems, which include most of the optically active cobalt(III) complexes, the argument cannot be applied precisely. We wish to point out some experimental evidence in support of Sugano's argument that a different

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[1] W. Moffitt, *J. Chem. Phys.*, **25**, 1189 (1956).

[2] S. Sugano, *ibid.*, **33**, 1883 (1960).

TABLE I

ABSORPTION AND ELLIPTICITY DATA FOR *cis*-$[Co(en)_2(NH_3)X]t^+$ COMPLEXES

Complex	$^1A_{1g} \rightarrow {}^1Eg$ Absorption ϵ	Absorption Maximum	Ellipticity Maximum	Δ	$^1A_{1g} \rightarrow {}^1A_{1g}$ ($\Delta \cong 0$) Absorption ϵ	Absorption Maximum	Ellipticity Maximum
cis-$[Co(en)_2(NH_3)H_2O](NO_3)_3$	60	(19,800) cm.$^{-1}$	19,200 cm.$^{-1}$	600 cm.$^{-1}$	42	(22,000) cm.$^{-1}$	(22,000) cm.$^{-1}$
cis-$[Co(en)_2(NH_3)Cl]Cl_2$	57	(18,500)	18,000	500	40	(20,800)	20,800
cis-$[Co(en)_2(NH_3, Br]Cl_2$	60	(18,200)	17,700	500	40	(20,600)	20,600

mechanism operates for molecular inverse dispersion than for visible absorption.

The experimental quantities dealt with here are the molar extinction coefficient (ϵ) and the molar ellipticity ($[\theta]$).[3]

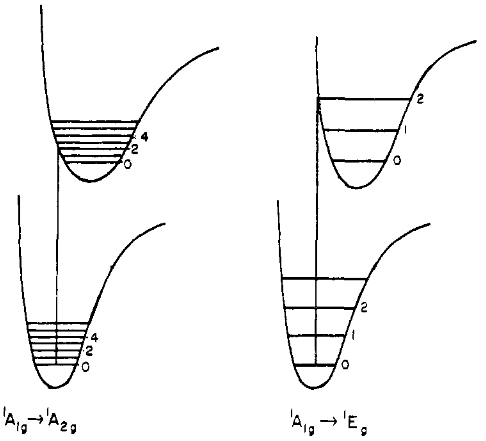

Fig. 1.—Potential energy curves representing the two transitions.

The molar ellipticity when plotted against wave length gives rise to a Gaussian band, similar to the plot of molar extinction coefficient *versus* wave length. If these two experimental quantities are plotted on the same graph one can compare differences in the wave length of the maxima, the half-width, and the peak height. In many cases the wave length of maximum absorption does not coincide with the wave length of maximum ellipticity, a phenomenon observed some time ago by Kuhn and Gore.[4]

Our interest is in the electronic contribution to the molar ellipiticity and we shall use the same terminology in describing the optically active electronic transitions that is used to describe the related visible absorption band.[2] There is no doubt that the same electronic transitions are involved in both the absorption spectra and the ellipticity.

We shall consider complexes of the type *cis*-$[Co(en)_2(NH_3)X]^{n+}$ ($X = Cl^-$, Br^-, and H_2O). Their molecular symmetry is no higher than C_1, but their absorption spectra and ellipticity show that their effective symmetry is really much higher and approaches D_{4h}.[5] Absorption and ellipticity data for these complexes are given in Table I.

From Table I it can be seen that for the $^1A_{1g} \rightarrow {}^1A_{2g}$ electronic transitions the maxima for both absorption and ellipticity coincide. For each of the $^1A_{1g} \rightarrow {}^1E_g$ transitions the maximum for absorption falls at a shorter wave-length than that for the ellipticity.

The $^1A_{1g} \rightarrow {}^1A_{2g}$ transition of the visible spectrum is allowed only with simultaneous excitation of the e_u vibrational mode.[6,7] Transitions to the ^1E_g state may occur with the aid of e_u and a_{2u} vibrational modes. The e_u vibrational mode corresponds to a "rocking mode" and makes a minimum disturbance of the ligand framework. The a_{2u} vibration corresponds to stretching and compressing the chelate rings, causing a greater disturbance in the ligand framework. Since the intensity of absorption increases with the amplitude of the perturbing vibration we expect the molar extinction coefficient for the $^1A_{1g} \rightarrow {}^1E_g$ band to be larger than that for the $^1A_{1g} \rightarrow {}^1A_{2g}$ band and this is what is found in Table I.[8,9] At present, no temperature dependent studies of intensity have been carried out on these systems, but we can predict that the $^1A_{1g} \rightarrow {}^1E_g$ band will be more temperature dependent than the $A_{1g} \rightarrow A_{2g}$ band.

The vibrational spacing in the $^1A_{2g}$ state (e_u excited) will be small compared to the vibrational spacing in the ^1E_g state (e_u and a_{2u} excited). For the Franck–Condon transitions of $^1A_{1g} \rightarrow {}^1A_{2g}$ the 0,0 and the n,0 bands will lie close together, but for the $^1A_{1g} \rightarrow {}^1E_g$ transitions the 0,0 and then, 0 bands will be relatively further apart, with the n,0 band displaced to shorter wave lengths. This is illustrated in Fig. 1. If the visible absorption and the ellipticity were brought about by the same mechanism, then one would expect the maxima of both to coincide for both transitions. The coincidence of the maxima of the visible absorption and the ellipticity for the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition where the vibrational spacing is small suggests that the ellipticity involves the 0,0 transition. The displacement of the absorption maximum toward shorter wave lengths for the $^1A_{1g} \rightarrow {}^1E_g$ transition suggests that the ellipticity maximum corresponds to the 0,0 transition whereas the absorption maximum corresponds to an n,0 transi-

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(3) A. Moscowitz in C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., N. Y., 1960, pp. 150–177. $[\theta] = \frac{\theta\ 18\ M}{\pi C'}$, where $\theta = \frac{1}{4}(k_d - k_l)$, k_d, k_l = absorption coefficients for *dextro* and *levo* circularly polarized light, M = molecular weight, and C' = concentration in g/cm^3 of optically active material.

(4) W. Kuhn and E. Gore, *Z. physik. Chem.* (Leipzig), **B12**, 389 (1931).

(5) Complexes with crystal field symmetry C_{4v}, will have the same spectra as those with D_4h, but with only one half the splitting. See W. Moffitt and C. J. Ballhausen, *Ann. Rev. Phys. Chem.*, **7**, 107 (1956).

(6) These values were obtained from graphs published by J. P. Mathieu, *Bull. soc. chim.*, (5) **3**, 463, 476 (1936). The values in parentheses were obtained by Gaussian analysis, the others could be obtained directly. The error involved in obtaining the values from the curves is probably of the order of 100 cm.$^{-1}$.

(7) C. J. Ballhausen in "Progress in Inorganic Chemistry," Vol. 2, F. A. Cotton, Ed., Interscience Publishers Inc., New York, N. Y., 1960, pp. 251–265.

(8) C. J. Ballhausen and C. K. Jorgensen, *Kgl. danske vidensk Selsk. Mat. fys. medd.*, **29**, (14) (1955).

(9) F. Basolo, C. J. Ballhausen and J. Bjerrum, *Acta chem. scand.* **9**, 810 (1955).

tion. These experimental results suggest that the ellipticity does not arise from vibronic coupling. The vibronic mechanism was also ruled out by Sugano[3] using symmetry arguments.

Data are available for other complexes and these data are consistent with the above interpretation. The use of ellipticity data in the analysis of optical rotatory dispersion curves of coördination compounds will be developed in more detailed publications.

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RECEIVED NOVEMBER 17, 1961

THERMAL DECOMPOSITION KINETICS OF CARBON SUBOXIDE[1]

Sir:

Recently, Bayes[2] has reported on some experiments in which carbon suboxide, C_3O_2, was photolyzed with 2537 Å. radiation in the presence of added hydrocarbons. He suggests that the primary act is C–C bond breakage: $C_3O_2 \rightarrow C_2O + CO$. We wish to report some results for the pyrolysis of C_3O_2 which appear to have bearing on this question.

The pyrolysis has been performed with an annular flow system into which C_3O_2 is carried by a large excess of helium. The C_3O_2 is prepared by the method of Stock and Stoltzenburg,[3] with slight modification, and is stored at −80° or lower to avoid polymerization. Its infrared spectrum is essentially identical with that reported by Long, Murfin and Williams,[4] but it shows two additional bands reported by Lord and Wright[5] that probably are attributable to use of a higher concentration and longer path length than those employed by Long, *et al.* No bands are present that can be attributed to impurities.

The rate of decomposition of C_3O_2 is measured by following the deposition of film carbon on a specified length of the glazed porcelain rod that forms the inner boundary of the annular flow system. In another publication[6] we have described in detail the mathematical analysis by means of which the carbon deposition rate is related to the rate of disappearance of C_3O_2 in the gas phase.

C_3O_2 decomposition was studied between 900 and 1025°K. at 1 atmosphere total pressure. Concentrations of C_3O_2 ranged between about 0.1 and 0.5 mole per cent. in the helium. The effluent gas from the reactor contained only He, CO, and unreacted C_3O_2, as analyzed by means of a Beckman GC-1 chromatograph. Studies in a static system confirm that the stoichiometry of the decomposition at these temperatures is essentially $C_3O_2 \rightarrow C(s) + 2CO$.

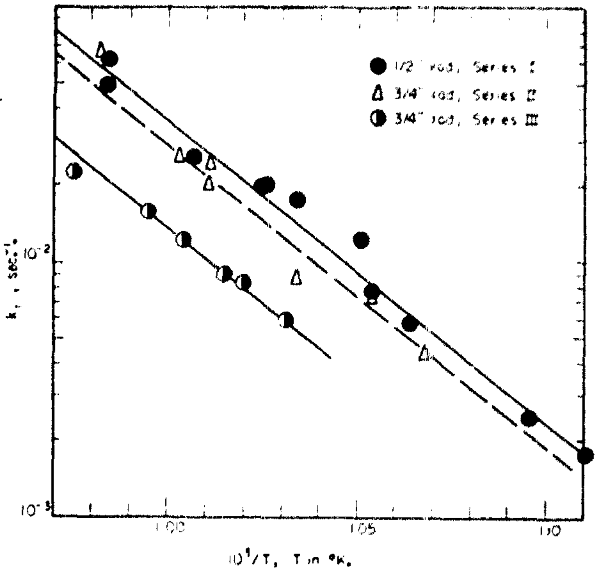

Fig. 1.

The gas-phase rate constant results for three series of runs are presented as an Arrhenius plot in Fig. 1. The slopes are quite well defined and yield an activation energy of 54 kcal., with an uncertainty of about ± 2 kcal. The range of experimental frequency factors is from 7.7×10^{14} cc./mole sec. to 2.05×10^{15} cc./mole sec., for an assumed second-order reaction. The reaction was proved first-order in $[C_3O_2]$ by variation of the suboxide concentration; however, we do not know the order in helium. The variation in the experimental frequency factor from series to series is perhaps attributable to differences in the flow characteristics, caused by minor differences in surface configurations of the three central rods employed. Agreement between Series I and Series II lends weight to the higher value for the frequency factor.

Unless decomposition of C_2O on the surface to give C(s) and CO is very slow, the 54 kcal. figure is almost certainly the activation energy for $C_3O_2 \rightarrow C_2O + CO$. A rough estimate of the ΔH for the only alternative gas-phase reaction, the splitting off of an O atom, puts it at some 183 kcal. endothermic.

By drawing analogies between polyatomic carbon molecules and the oxides of carbon (except CO), as Pitzer and Clementi have done,[7] we have estimated the ΔH of the primary reaction to be 46 ± 10 kcal./mole. In making these estimates, the figure −8.3 kcal./mole has been used for the heat of formation of gaseous C_3O_2.[8]

The estimates plus the experimental activation energy indicate that the back reaction between CO and C_2O has a probable activation energy on the order of 8 kcal., but with large uncertainty. They also indicate that the reaction $C_2O \rightarrow C(g) + CO$ is about 79 kcal. endothermic. Thus Bayes' suggestion that this reaction is occurring thermally at a rapid rate in his system seems to us an unlikely possibility. On the other hand, 2537 Å. photolysis

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[1] Work supported by the U. S. Atomic Energy Commission under contract AT(30-1)-1710.

[2] K. Bayes, *J. Am. Chem. Soc.*, **83**, 3712 (1961).

[3] A. Stock and H. Stoltzenburg, *Ber.*, **50**, 498 (1917).

[4] D. A. Long, F. S. Murfin, and R. L. Williams, *Proc. Roy. Soc. (London)*, **A223**, 251 (1954).

[5] R. C. Lord and N. Wright, *J. Chem. Phys.*, **5**, 642 (1937).

[6] T. J. Hirt and H. B. Palmer, "Proceedings of the Fifth Conference on Carbon," Pergamon Press, New York, in press.

[7] K. S. Pitzer and E. Clementi, *J. Am. Chem. Soc.*, **81**, 4477 (1959).

[8] This figure is an estimate from the JANAF Interim Thermochemical Tables (Dow Chemical Company), communicated to us by Dr. C. H. Shomate, U.S.N.O.T.S., China Lake, Calif.