of −30.73070 (Cl_2), −20.83662 (S_2), and −46.76204 au (SO_2) for all the orientations listed in Table I. By comparison, method A gives a total energy of −21.99841 au for triplet state S_2 at all values of θ. Clearly, without the indicated modification, method B is unreliable for the theoretical investigation of molecular conformations and related problems.

Finally, we feel that attempts to improve second row CNDO theory are appropriate if it is to be widely used in theoretical investigations.

Acknowledgment. Partial support of this work by the donors of the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

Partial Photoresolution. III.
The Tris(acetylacetonato)chromium(III) System

Kenneth L. Stevenson

Contribution from the Department of Chemistry, Purdue University at Fort Wayne, Fort Wayne, Indiana 46805. *Received January 13, 1972*

Abstract: Tris(acetylacetonato)chromium(III) was partially resolved in circularly polarized light at 5461 Å in several organic solvents. The circular dichroism spectrum, normalized to that of pure enantiomer, yields a maximum at 420 nm and a minimum at 540 nm, with ($\epsilon_l - \epsilon_r$) having values of +1.7 and −4.3 M^{-1} cm^{-1}, respectively. Another maximum out of range of the CD machine occurs around 620–640 nm. Quantum yields for the photolytic inversion of enantiomers were measured in chlorobenzene solution as a function of wavelength and temperature. The results indicate that (1) the inversion is an order of magnitude less efficient than that of $Cr(C_2O_4)_3^{3-}$, (2) the photolysis is essentially wavelength independent in the visible region, and (3) the apparent activation energy is 2300 cal/mol at 5461 Å. Solvent studies indicate that the reaction is slightly more efficient in acetone and acetylacetone than in chlorobenzene, but that water inhibits the reaction slightly in acetone. A short discussion of mechanism is included.

Partial photoresolution, *i.e.*, the use of light in inducing optical activity in racemic mixtures through photolytic inversion of enantiomers, has been applied to several D_3 complexes of Cr(III) in aqueous solution.[1-3] When circularly polarized light is used, the degree of resolution is a direct function of the dissymmetry factor $g = (\epsilon_l - \epsilon_r)/\epsilon_{av}$, at the irradiating wavelength,[2] and hence such a partial resolution can be used to calculate the molar circular dichroism, $\epsilon_l - \epsilon_r$, without resorting to a complete, chemical resolution of optical isomers. Such experiments, coupled with photoracemization studies, can yield information about the photochemistry of the inversion process.

Tris(acetylacetonato)chromium(III) has been partially resolved[4] by column chromatography, most recently by Fay, *et al.*,[5] but the optical activity of pure enantiomer has not yet been determined. Moreover, its photochemistry in organic solvents might be expected to be different from that of Cr(III) complexes in aqueous solutions since the postulated mechanisms for the latter almost always involve water molecules. The purpose of this work, then, was (1) to determine the ORD and CD spectra of a pure enantiomer, and (2) to study the photolytic inversion of enantiomers in organic solvents through both photoresolution and photoracemization procedures.

Experimental Section

The complex, Cr(acac)$_3$, was prepared and purified according to established procedures.[6] *Anal.* Calcd for $Cr(C_5H_7O_2)_3$: C, 51.57; H, 6.06. Found: C, 51.66; H, 6.24.

Solutions of about 0.02 *M* were prepared and irradiated in constant-temperature cells made of glass or quartz thermostated to within 0.05° in an optical train described previously.[2] For photoracemization runs, the circular polarizer was removed from the train. At suitable time intervals the irradiation cell was transferred from the train to a Bendix Polarmatic 62 spectropolarimeter for ORD measurements. Twenty-five runs were made, and at the end of each the light intensity was measured using the potassium reineckate chemical actinometer.[7]

The solvents used were Spectroquality acetone, reagent grade chlorobenzene, and technical acetylacetone which had been triple distilled. None of the solutions were degassed because absorption spectra of irradiated samples were identical with those of fresh samples. Absorption spectra were taken on a Spectronic 505 spectrophotometer.

The circular dichroism spectrum of a partially resolved sample was made on a Cary 60 ORD-CD machine. A photoresolution run was made on trioxalatochromate(III) at 0° according to a previously described procedure[2] in order to determine its quantum yield for comparison purposes.

Results and Discussion

I. Optical Activity. The results of a 200-hr irradiation in circularly polarized, 5461 Å, light at 25° are shown in Figure 1. The parameter of optical activity observed was the difference between the maximum and minimum in the ORD Cotton effect curve, $\alpha_{max} - \alpha_{min}$. The steady-state optical activity has a slight positive slope because of small evaporation of solvent from the stoppered cell over long time periods. The

---

[1] K. L. Stevenson and J. F. Verdieck, *J. Amer. Chem. Soc.*, 90, 2974 (1968).

[2] K. L. Stevenson and J. F. Verdieck, *Mol. Photochem.*, 1, 271 (1969).

[3] N. A. P. Kane-Maquire, B. Dunlop, and C. H. Langford, *J. Amer. Chem. Soc.*, 93, 6293 (1971).

[4] T. Moeller and E. Gulyas, *J. Inorg. Nucl. Chem.*, 5, 245 (1958).

[5] R. C. Fay, A. Y. Girgis, and U. Klabunde, *J. Amer. Chem. Soc.*, 92, 7056 (1970).

[6] W. C. Fernelius and J. E. Blanch, *Inorg. Syn.*, 5, 130 (1957).

[7] E. E. Wegner and A. W. Adamson, *J. Amer. Chem. Soc.*, 88, 394 (1966).

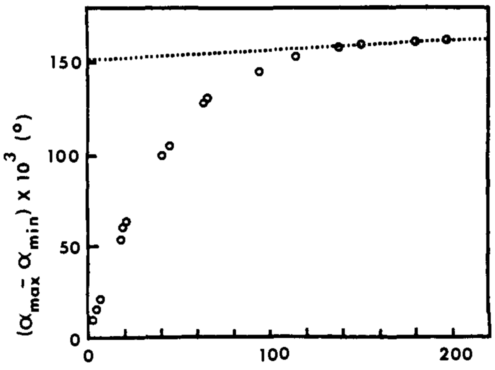

Figure 1. Amplitude of visible ORD curve induced in 0.0200 *M* $Cr(acac)_3$ solution by irradiating with circularly polarized light at 25°, 5461 Å, in chlorobenzene.

steady-state optical activity was thus found by extrapolation back to zero time.

The ORD and CD curves, normalized to pure enantiomer having a negative optical rotation at the sodium D line, are shown in Figure 2, along with the visible absorption spectrum and the dependence of the dissymmetry factor, *g*, on wavelength. The normalization was accomplished by using the expression[2]

$$(A_l - A_r)_{pss} = c(g/2)(\epsilon_l - \epsilon_r)$$

where pss represents the photostationary-state value and *c* is the molar concentration. This differential absorption was obtained from the photostationary-state value of $\alpha_{max} - \alpha_{min}$ in Figure 1 using the conversion for this complex: $\alpha_{max} - \alpha_{min} = 58(A_l - A_r)$ at 5461 Å. The circular dichroism spectrum shows a minimum of −4.3 at 540 nm and a maximum of 1.7 at 420 nm, which is clearly the $^4A_{2g} \rightarrow {}^4T_{1g}$ transition which lies hidden under the long-wavelength tail of the ligand band in the absorption spectrum. Another maximum probably occurs around 620–640 nm, but this was out of the range of the Cary 60. The ORD results indicate that Fay, *et al.*,[5] achieved about 24% resolution by their chromatography procedure.

The CD spectrum is very similar to that of $Cr(ox)_3{}^{3-}$ which has maxima or minima at 417, 550, and 625 nm.[2] However the value of $|g|_{max}$ is 0.048 for $Cr(ox)_3{}^{3-}$ compared to 0.078 for $Cr(acac)_3$. One might have expected, by reason of a ring-size effect,[8] that the acetylacetonato complex, with a six-membered ligand-metal ring, would have shown a smaller dissymmetry factor than the oxalato complex, with a five-membered ring. For example, the tris(malonato)chromate(III) ion, which also has a six-membered ring, has a dissymmetry factor of 0.008,[9] or about one-sixth that of the oxalato complex. However, there is chemical[10] and spectroscopic[11,12] evidence which suggests that the acetylacetonatochromium ring is more highly conjugated than that of the oxalato complex, and the effects of such a conjugation on the rotational strength may more than offset any ring-size effect.

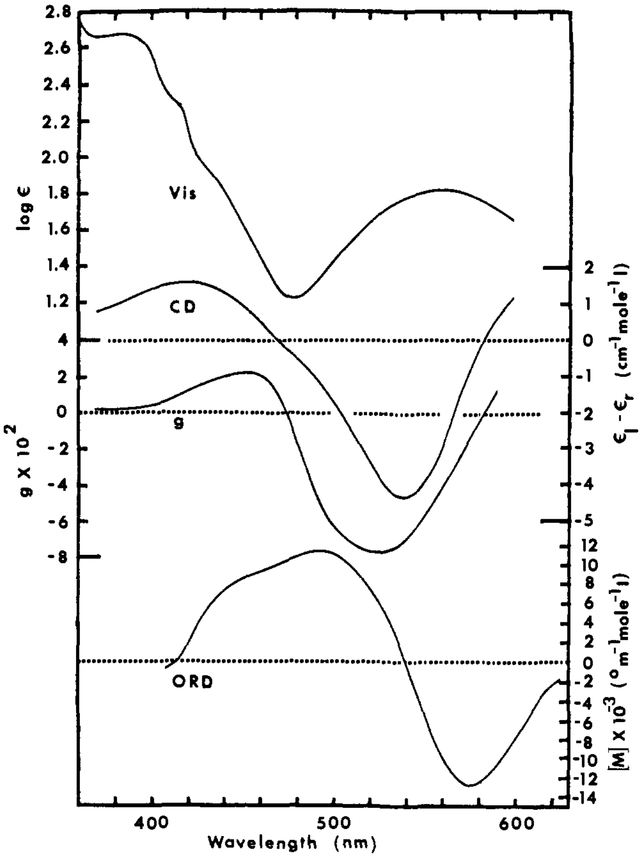

Figure 2. Visible absorption, circular dichroism, dissymmetry factor, and ORD spectra for (−)-$Cr(acac)_3$ in chlorobenzene.

II. Photokinetics. In determining the quantum yield, ϕ, for the inversion process

$$D \xrightarrow{h\nu} L$$

both photoresolution and photoracemization runs were performed. At 5461 Å all runs were photoresolutions since $|g|$ is large. These partially resolved samples were then used for photoracemizations at other wavelengths. Since there is negligible thermal racemization at these temperatures, it can be shown[2] that for photoresolution a plot of ln $(1 - (\Delta\alpha/\Delta\alpha_{pss}))$ *vs.* *t* yields a slope given by

$$-2\phi I_0(1 - 10^{-\epsilon cl})(S/V)/c$$

where $\Delta\alpha$ is $\alpha_{max} - \alpha_{min}$ and pss has the same meaning as before, I_0 is the light intensity in einsteins cm^{-2} sec^{-1}, ϵ is the molar extinction coefficient at the irradiating wavelength, *c* is molar concentration, *S* is the cross section of the beam in cm^2, and *V* is the volume of solution in liters. A plot of ln $\Delta\alpha$ *vs.* *t* for photoracemization gives the same expression for the slope.

Table I shows the dependence of ϕ on wavelength at 25° in chlorobenzene solution. The results indicate that the photolytic inversion is essentially wavelength independent, a result expected since quantum yields for phosphorescence and photochemical reactions for other complexes of Cr(III) of O_h symmetry display the same type of behavior.[13,14] Such behavior means that the excited states must decay very rapidly to the

---

[8] F. Woldbye, *Proc. Roy. Soc., Ser. A*, 297, 78 (1967).

[9] A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).

[10] J. P. Collman, R. P. Blair, R. L. Marshall, and L. Slade, *Inorg. Chem.*, 2, 576 (1963).

[11] K. DeArmond and L. S. Forster, *Spectrochim. Acta*, **19**, 1403 (1963).

[12] A. M. Fatta and R. L. Lintvedt, *Inorg. Chem.*, 10, 478 (1971).

[13] D. Valentine, Jr., *Advan. Photochem.*, 6, 123 (1968).

[14] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970, p 100.

Table I. Dependence of Quantum Yield for Inversion of Cr(acac)$_3$ on Wavelength, at 25°, Chlorobenzene Solution

λ, Å	ϕ	Inversion mode	Concn, *M*
3650	0.0063	Photoracemization	0.0206
4047	0.0045	Photoracemization	0.0235
4358	0.0049	Photoracemization	0.0199
5000	0.0060[a]	Photoracemization	0.0188
5461	0.0054	Photoresolution	0.0195
5770	0.0045	Photoracemization	0.0202
6505	0.0099[a]	Photoracemization	0.0195

[a] These values have a high uncertainty because of low lamp output and low absorbance of sample. Other values are ±5%.

lower $^4T_{2g}$ or ^2E_g states, where reaction occurs. Recent work[15–17] suggests that the quartet state may be the chemically reactive one.

The solvent dependence data are shown in Table II.

Table II. Effect of Solvent on Photolytic Inversion of Cr(acac)$_3$ at 5461 Å, 31.4°

Solvent	ϕ	Concn, *M*
Acetylacetone (2,4-pentanedione)	0.0068	0.0187
Acetone	0.0098	0.0185
Acetone + H_2O (4:1 by vol)	0.0086	0.0185
Chlorobenzene[a]	0.0055	0.0195

[a] Determined at 35.8°.

The changes in quantum yield may be the result of the differing abilities of solvent molecules to effect competing thermal deactivation of the excited, reactive state. Since water inhibits the reaction in acetone, it is assumed that the inversion mechanism does not involve water molecules.

Table III. Dependence of Quantum Yield for Inversion of Cr(acac)$_3$ on Temperature, 5461 Å, Chlorobenzene Solution

Temp, °C	ϕ	Concn, *M*
25.0	0.0055	0.0217
35.8	0.0055	0.0195
41.3	0.0057	0.0146
41.3	0.0059	0.0195
46.5	0.0062	0.0195
52.3	0.0073	0.0195
58.5	0.0078	0.0195
61.8	0.0082	0.0195
69.7	0.0091	0.0195

Table III shows the temperature dependence of quantum yield at 5461 Å. An Arrhenius plot yields an apparent activation energy of 2300 cal/mol. The quantum yield for photolytic inversion of Cr(ox)$_3{}^{3-}$ in aqueous solution was measured in this work. The value obtained at 5461 Å, 0°, was 0.040, which is half that obtained by Spees and Adamson.[18] This is not inconsistent since their photoracemization quantum yields were defined as initial photoracemization rate divided by light absorption rate, which turns out to be twice as great as the quantum yield for photolytic inversion of enantiomers. The important point is that it is larger than the inversion quantum yield of Cr(acac)$_3$ by a factor of about 10. This difference may merely reflect differing thermal deactivation efficiencies in the two solvent systems. It could also be the result of rather different mechanisms. For trioxalatochromate(III), Spees and Adamson[18] have suggested a hydrolysis mechanism occurring for both the photo and thermal racemization, for which the activation energy is 15 kcal. The thermal racemization of Cr(acac)$_3$ has an activation energy of 34.9 kcal,[5] which is considerably larger than that found for chromium–oxygen ligand exchange reactions in aqueous solution. Because the nature of the solvent seems to preclude any solvolysis in the Cr(acac)$_3$ system, it is reasonable to suggest either a monomolecular ligand dissociation leading to a five-coordinate intermediate or a six-coordinate twist mechanism as the slow step in the inversion for both the thermal and photochemical reactions.

Acknowledgments. This research was supported by a grant from the Petroleum Research Fund of the American Chemical Society. The author thanks Mr. William Carl of Purdue's Lafayette campus for taking the circular dichroism spectrum.

---

(15) S. N. Chen and G. B. Porter, *J. Amer. Chem. Soc.*, **92**, 2189 (1970).

(16) G. B. Porter, S. N. Chen, H. L. Schlafer, and H. Gausmann, *Theor. Chim. Acta*, **20**, 81 (1971).

(17) N. A. P. Kane-Maquire and C. H. Langford, *J. Chem. Soc. D*, 895 (1971).

(18) S. T. Spees and A. W. Adamson, *Inorg. Chem.*, **1**, 531 (1962).