Laser Photochemistry. II.* Determination of the ORD and CD Spectra of Some Chromium(III) β-Diketonates

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An argon ion laser has been used to partially photoresolve the following tris(β-diketonato)chromium(III) complexes; Cr(acac)$_3$, Cr(3-X-acac)$_3$ (X=Cl$^-$, Br$^-$, I$^-$, and NO$_2^-$), Cr(tfac)$_3$, and Cr(bzac)$_3$, where the abbreviations are acac=acetylacetonate ion, 3-X-acac=γ-substituted acetylacetonate ion, tfac=trifluoroacetylacetonate ion, and bzac=benzoylacetonate ion. From the wavelength dependence of the steady state resolution yield, the method of photoresolution has been confirmed to allow the determination of the ORD and CD spectra of optically pure enantiomers. The ORD and CD spectra of the above-mentioned compounds are given.

Induction of optical activity into chemical systems without resort to any asymmetric chemical agent is a rather interesting but less investigated phenomenon. Only scattered examples have been known to date in which the effect of circularly polarized light (CPL) on chemical systems or reactions has been studied. The photochemistry with CPL has recently been reviewed by Buchardt.$^{1)}$ We may tentatively classify this field of research into three categories; "asymmetric photodecomposition" where the optical activity is introduced transiently by irradiating the light of circular polarization but is lost on long illumination due to photodecomposition, "total asymmetric synthesis" wherein optically inactive materials are allowed to react under the influence of CPL to produce optically active material(s), followed by the fading out of optical activity because of photodecomposition, and "partial photoresolution" which is similar in nature to the first category but different in that the material photoresolved does not lose its optical activity, except due to thermal racemization, even on long illumination. If we limit ourselves to metal compounds, a reported example of the first category may be, to our knowledge, only on potassium tris(oxalato)cobaltate(III).$^{2)}$ No example of asymmetric synthesis appears to be reported for metal complexes. Partial photoresolution has been effected successfully on [Cr(ox)$_3$]$^{3-}$,**$^{4,3)}$ Cr(acac)$_3$,$^{5)}$ and [Cr(ox)(phen)$_2$]$^+$, [Cr(ox)$_2$(phen)]$^-$, [Cr(bipy)$_3$]$^{3+6)}$ and several other cobalt(III) and chromium(III) complexes.$^{7,8)}$ A slight modification of this method has been utilized by Kane-Maguire *et al.*$^{9)}$ to achieve a partial resolution of [Cr(phen)$_3$]$^{3+}$ using an analogue of the Pfeiffer effect.

It is reported here that partial photoresolution of tris(β-diketonate)chromium(III) complexes can be made successfully by using the beam of an argon ion laser. This method of resolution is quite important in that it allows the otherwise impossible determination of the optical rotatory dispersion (ORD) and circular dichroism (CD) spectra of optically pure enantiomers.

Experimental

Material. Cr(acac)$_3$, Cr(tfac)$_3$, and Cr(bzac)$_3$ have been prepared by well established methods.$^{10-12)}$ The identity of the complexes has been confirmed by chemical analysis. Cr(tfac)$_3$, Found: C, 35.22; H, 2.42%. Calcd for CrC$_{15}$H$_{12}$O$_6$F$_9$: C, 35.24; H, 2.37%. Cr(bzac)$_3$, Found: C, 67.81; H, 5.19%. Calcd for CrC$_{30}$H$_{27}$O$_6$: C, 67.28; H, 5.08%. The γ-substituted acetylacetonates have been prepared from chromium acetylacetonate after the method of Collman and coworkers.$^{13)}$ Cr(3-I-acac)$_3$, Found: C, 25.43; H, 2.67%. Calcd for CrC$_{15}$H$_{18}$O$_6$I$_3$: C, 24.78; H, 2.50%. Cr(3-Br-acac)$_3$ has been obtained as chloroform solvate. Found: C, 27.77; H, 2.66%. Calcd for CrC$_{16}$H$_{19}$O$_6$Br$_3$Cl$_3$: C, 27.24; H, 2.71%. Cr(3-NO$_2$-acac)$_3$, Found: C, 36.74; H, 3.79; N, 8.34%. Calcd for CrC$_{15}$H$_{18}$O$_{12}$N$_3$: C, 37.20; H, 3.79; N, 8.68%.

Solvents are of special grade, purchased from Katayama Chemical Co., and used without further purification.

Apparatus and Measurements. The experimental arrangement used in this work is essentially similar to that reported in the literature.$^{3)}$ The light source is a NEC GLG-2023 argon ion laser operating at either 514.5, 501.7, 496.5, 488.0, 476.5, or 457.9 nm(in single mode). The light of linear polarization emitted from the laser is passed through a quartz quarter-wave plate matched for the wavelength of the irradiating light to produce CPL. The light of circular polarization is then incident on a 1 cm quartz cell containing the solution to be illuminated. The diameter of the beam is approximately 8 mm. The ellipticity of CPL has been confirmed to be small enough to be neglected from measurement of the light intensity passing through a linear polarizer situated beyond the quarter-wave plate. An approximate value of the light intensity incident on the sample solution is monitored by measuring the current induced in a photovoltaic CdS cell, which is precalibrated.

The ORD and CD spectra have been recorded on a JASCO Model ORD/UV-5 spectrometer with a CD attachment. Some CD spectra have been measured also on a JASCO Model J-2 spectrometer. The process of photoresolution has been traced by checking at suitable time intervals the optical rotation of the sample solution with the aid of a Union Giken PM-71 digital polarimeter. Absorption spectra are taken on a Shimadzu double beam spectrophotometer Model UV-200.

Unless otherwise stated, all solutions have been made to 5.0×10^{-3} mol/l in benzene and irradiated at room temperature.

Principles

The principle of photoresolution is the preferential isomerization of one enantiomer over the other, which

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* Part I: H. Yoneda, Y. Nakashima, and U. Sakaguchi, *Chem. Lett.*, **1973**, 1343.

** The following abbreviations are used in this paper; ox=oxalate ion, phen=phenanthroline, bipy=bipyridyl, oxine=8-hydroxyquinolinate ion, dbzm=dibenzoylmethanate ion, TTA=thenoyltrifluoroacetonate ion, FTA=furoyltrifluoroacetonate ion, and DTC=diethyldithiocarbamate ion.

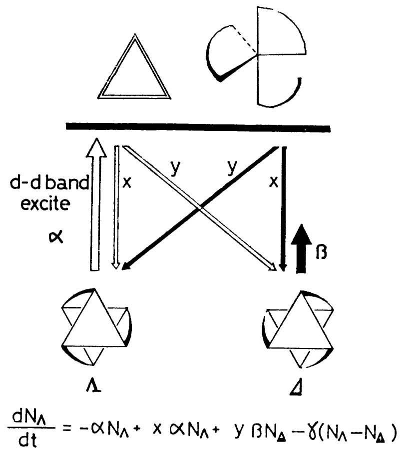

Fig. 1. Schematic illustration of a possible mechanism of photoresolution.

is a mere consequence of the differential absorptivities of the two enantiomers in a CPL (circular dichroism). Thus, the efficiency of photoresolution is expected to be a function of the asymmetric factor g.

We consider a racemic mixture of some metal complex. If right-CPL, whose intensity is I_0, is incident on the system, the complex absorbs the power ΔI. According to the Lambert-Beer's law

$$\Delta I = I_0[1-10^{-(\varepsilon_\Delta c_\Delta+\varepsilon_\Lambda c_\Lambda)d}] \tag{1}$$

where ε_Δ and c_Δ are the absorption coefficient and the concentration of the Δ-isomer and d the length of the optical path.

Note that the wavelength of the CPL corresponds to the electronic excitation of the metal compounds. Thus, absorption of the light by metal racemate induces some form of electronic excitation; metal d–d transition and/or charge transfer excitation, *etc.* (see Fig. 1). In Fig. 1 the horizontal bar is assumed to represent some excited state wherein the structure of the complex may be trigonally twisted or bond-ruptured. The transition probabilities from the excited Δ-isomer to the ground state Δ- and Λ-isomers are denoted by x and y, respectively. By symmetry the probabilities from the excited Λ-isomer to the ground state Λ- and Δ-molecules should be x and y. The values of x and y are related to the quantum yield for photoresolution and may be determined by the mechanisms of electronic relaxation and/or vibrational relaxation. Irrespective of these relaxation mechanisms, the following identity holds.

$$x+y=1 \tag{2}$$

The change with time in the number of Λ-molecule will be governed by the kinetic equation.

$$\frac{dN_\Lambda}{dt} = -\alpha N_\Lambda + x\alpha N_\Lambda + y\beta N_\Delta \tag{3}$$

Similarly, for Δ-molecules

$$\frac{dN_\Delta}{dt} = -\beta N_\Delta + x\beta N_\Delta + y\alpha N_\Lambda \tag{4}$$

αN_Λ and βN_Δ are the numbers of Λ and Δ isomers excited by the CPL and are defined by

$$\alpha N_\Lambda = \frac{\Delta I}{h\nu}\,\frac{\varepsilon_\Lambda c_\Lambda}{\varepsilon_\Delta c_\Delta+\varepsilon_\Lambda c_\Lambda} \tag{5}$$

$$\beta N_\Delta = \frac{\Delta I}{h\nu}\,\frac{\varepsilon_\Delta c_\Delta}{\varepsilon_\Delta c_\Delta+\varepsilon_\Lambda c_\Lambda} \tag{6}$$

Since the difference between ε_Δ and ε_Λ are small as compared with ε and the best yield attainable by this method is rather low (see below), we can safely regard the coefficients α and β as the time-independent constants. To this approximation the rate of photoresolution is given by $y(\alpha+\beta)$. The photostationary state (PSS) is defined by the condition $dN_\Delta/dt=0$ and $dN_\Lambda/dt=0$. This condition leads us to the ratio of N_Λ to N_Δ as given by

$$\frac{N_\Lambda}{N_\Delta} = \frac{\beta}{\alpha} \tag{7}$$

From Eqs. (5) and (6), we obtain

$$\frac{N_\Lambda}{N_\Delta} = \frac{\varepsilon_\Delta}{\varepsilon_\Lambda} \tag{8}$$

Equation (8) holds exactly irrespective of the approximation made above. Therefore the yield of partial photoresolution is expressed in terms of the asymmetric factor g as follows.

$$\frac{N_\Lambda-N_\Delta}{N_\Lambda+N_\Delta} = \frac{g}{2} \tag{9}$$

where $g=(\varepsilon_\Delta-\varepsilon_\Lambda)/\varepsilon$. Thus, it is readily seen that the sample solution partially photoresolved will show the optical rotation at PSS

$$\theta_{\mathrm{PSS}} = (g/2)\,\theta \tag{10}$$

and the CD proportional to

$$(g/2)\ (g\varepsilon c_0 d) \tag{11}$$

Here, θ and $(g\varepsilon c_0 d)$ are the optical rotation and the CD values, both at the wavelength used for the resolution, and expected for the optically pure enantiomer whose concentration is c_0. Note that the yield does not depend on the individual values of x and y and is determined only by the asymmetric factor g. Equations (10) and (11) hold also for the irradiation of the left-CPL, if we replace $(g/2)$ by $-(g/2)$ in both equations.

The effect of thermal racemization can be taken into account by introducing a term $-\gamma(N_\Lambda-N_\Delta)$, γ being the rate of thermal racemization. In this situation, the PSS should render the (N_Λ/N_Δ) value as given by

$$\frac{N_\Lambda}{N_\Delta} = \frac{\beta+2\gamma}{\alpha+2\gamma} \tag{12}$$

This equation indicates that as thermal racemization becomes faster, the optical activity of the sample solution at PSS are expected to decrease. The effect has really been observed and reported in some cases.[3,4)]

Results and Discussion

Wavelength Dependence. Stevenson[5)] has investigated the wavelength dependence of the kinetic behavior of the photoresolution process of $Cr(acac)_3$ but the effect of wavelength on the PSS yield has not been stated explicitly. Norden[4)] and Stevenson and Ver-

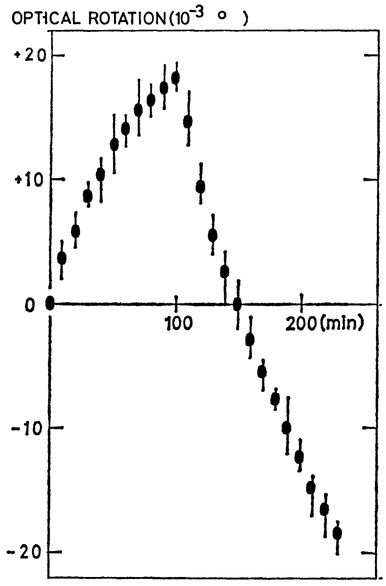

Fig. 2. The time-evolution of the optical rotation of $Cr(acac)_3$ accompanying the photoresolution.

dieck[3] have attained an apparent PSS for $[Cr(ox)_3]^{3-}$. However, it can readily be seen that the process of photoresolution is competitive with thermal or dark racemization, resulting in the optical activity much lower than that expected from Eqs. (10) and (11).

Fay *et al.*[14] have separated $Cr(acac)_3$ partially into its optical antipodes by passing through a chromatographic column containing D(+)-lactose. The first- and the second-eluted fractions have been slowly recrystallized from benzene–hexane, which gave rise to racemic crystals and resulted in an approximately tenfold enhancement in the optical rotation of the solution left uncrystallized. Molecular rotations after this partial recrystallization treatment are reported to amount to +3600° and −5240° for the first- and the second-elutions, respectively. These methods cannot, however, lead to a complete resolution and the ORD and CD curves given by them do not correspond to the optically pure enantiomers.

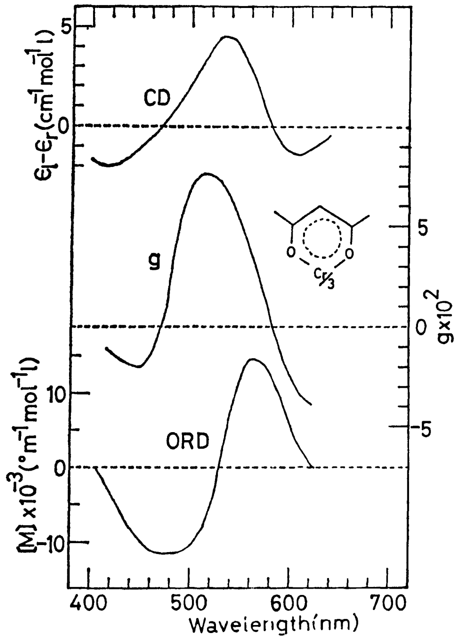

Fig. 3. The ORD, CD, and *g* curves of the optically pure $(+)_{589}$-$Cr(acac)_3$ in benzene solution.

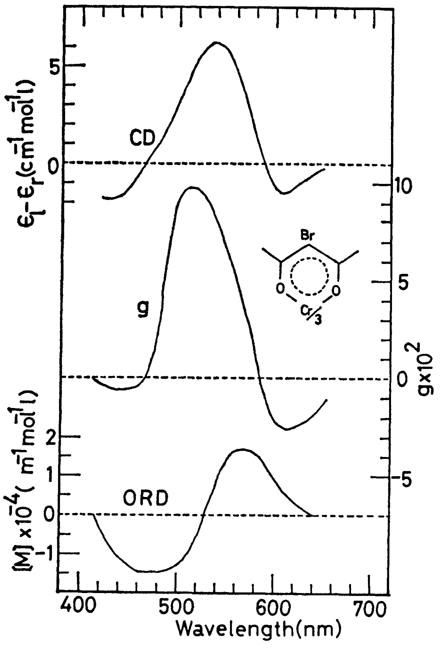

Fig. 4. The ORD, CD, and *g* curves of $(+)_{589}$-Cr-(3-Br-acac)$_3$.

To ascertain whether or not the optical activity at PSS is in actuality coincident with that given by Eqs. (10) and (11), we examined the wavelength dependence of the PSS yield using $Cr(acac)_3$ as an example. A necessary prerequisite to this experiment is that the rate of thermal racemization is much smaller than that of photoresolution. For this compound, the thermal racemization rate is reported at $k=0.134\times10^{-5}\,s^{-1}$ (96.1 °C) so that we can neglect its effect completely. Figure 2 shows the time-evolution of the optical rotation of $Cr(acac)_3$ accompanying the photoresoution. Irradiating wavelength is 514.5 nm and the incident power is approximately 150 mW. At time $t=100$ min, the sense of the circular polarization is inverted by rotating the quarter-wave plate through 90 °. The fact that no measurable photodecomposition has occured is confirmed spectrophotometrically. This plot clearly shows that the process of photoresolution is reversible. When the light intensity incident on the sample solution is approximately 200 mW, the PSS can be reached in 3 to 4 hr. In this experiment, $Cr(acac)_3$ has been partially resolved by irradiating

Table 1. The $\Delta\varepsilon$ values of the optically pure $Cr(acac)_3$ photoresolved at four different wavelengths

λ (nm) irrad.	$\Delta\varepsilon$ at 530 nm
514.5	4.49
501.7	4.37
496.5	4.30
488.0	4.49

Table 2. Summary of data obtained in this work
[M] in units of $^\circ \mathrm{m}^{-1}\mathrm{M}^{-1}$ and $\Delta\varepsilon$ in $\mathrm{cm}^{-1}\mathrm{M}^{-1}$

Complex	ORD		CD		g	
	$\lambda_{\max}$	$[\mathrm{M}]\times 10^{-3}$	$\lambda_{\max}$	$\Delta\varepsilon$	$\lambda_{\max}$	$g\times 10^2$
$(+)_{589}$-Cr(acac)$_3$	480	−11.24	415	−2.00	450	−1.90
	562	+14.18	535	+4.50	515	+7.60
			610	−1.44	650	−4.40
$(-)_{589}$-Cr(3-Cl-acac)$_3$	480	+16.95	540	−5.64	530	−9.00
	570	−17.82	610	+1.96		
$(+)_{589}$-Cr(3-Br-acac)$_3$	470	−15.0	430	−1.82	440	−0.64
	570	+17.0	538	+6.20	515	+9.70
			610	−1.44	614	−2.60
$(-)_{589}$-Cr(3-I-acac)$_3$	485	+27.5	540	−8.67	542	−8.10
	575	−25.5	620	+2.48		
$(+)_{589}$-Cr(3-NO$_2$-acac)$_3$	475	−13.94	534	+5.60	450	−2.20
	560	+16.83	610	−1.83	518	+8.00
$(+)_{589}$-Cr(tfac)$_3$	470	−12.0	420	−2.52	460	−2.40
	560	+10.0	540	+3.65	530	+6.80
	650	−5.0	610	−2.14		
$(-)_{589}$-Cr(bzac)$_3$	495	+10.48	535	−4.40	520	−5.72
	565	−16.46	605	+1.65		

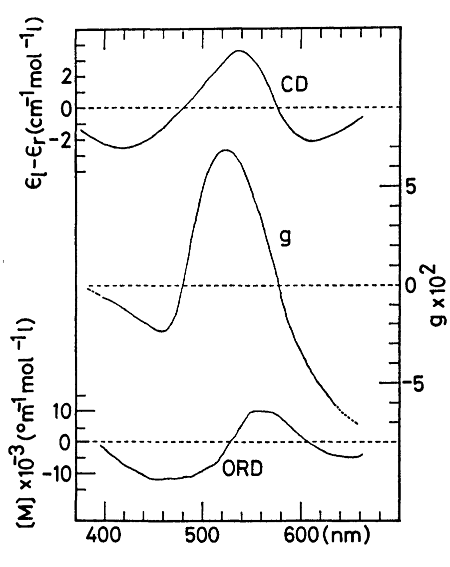

Fig. 5. $(+)_{589}$-Cr(tfac)$_3$.

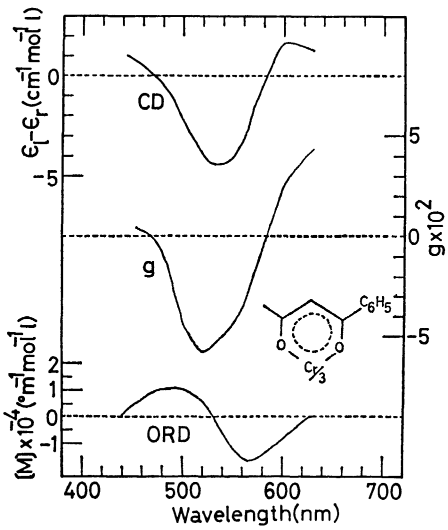

Fig. 6. $(-)_{589}$-Cr(bzac)$_3$ in 5×10^{-3} M chlorobenzene solution. Photoresolved at about 70 °C.

CPL at four different wavelengths, 514.5, 501.7, 496.5, and 488.0 nm. The ORD and CD spectra of the optically pure enantiomer have been calculated by using Eqs. (10) and (11). If these equations are correct, these four CD spectra should coincide with each other. As seen from Table 1, the $\Delta\varepsilon$ values at the CD peak position (530 nm) are equal well within experimental uncertainties. This method of justification appears to be somewhat round-about indeed but inevitable since no other method for determining ORD and CD curves has been available at present.[15]

ORD and CD Spectra. As mentioned previously, the optical resolution with CPL has one distinctive advantage over other chemical methods of resolution in that it enables one to determine the ORD and CD spectra of the optically pure enantiomers. This is especially the case with those complexes which have no formal charge. The ORD and CD spectra and the asymmetric factor g of the optically pure $(-)_{589}$-Cr(acac)$_3$ are depicted in Fig. 3. Spectra of the other complexes are given in Figs. 4—6. Numerical values for all the compounds investigated in this work are summarized in Table 2. Cr(acac)$_3$ has been partially resolved by Stevenson[5] using a high pressure mercury lamp in more than 200 hr. Our results for this complex are in good agreement with those given by him. All the asymmetric factors listed in Table 2 fall in the range from 5.7 to 9.7×10^{-2} around the wavelength of 514.5 nm. These values correspond to the photoresolution efficiency of 2.85 to 4.85%.

Interesting is the case with Cr(bzac)$_3$, where the compound has been dissolved in chlorobenzene and photoresolution examined. However, no optical activity was detected at room temperature even on long irradiation (5 to 8 hr at 514.5 nm). Thus, experiments have been made at elevated temperatures and the PSS has been achieved in less than 3 hr at about 70 °C. This result, along with the fact that all the complexes photoresolved in this work and so far racemize thermally, suggests that photoresolution can be effected, if possible at all, on those compounds which racemize thermally and in addition at some adequate rates.

We have tried in vain to photoresolve some complexes of chromium(III). These include $Cr(dbzm)_3$, $Cr(TTA)_3$, $Cr(FTA)_3$, $Cr(oxine)_3$, and $Cr(DTC)_3$. The first three compounds seem to have precluded the resolution for kinetic reasons mentioned just above because it is unrealistic that the asymmetric factors for these compounds differ greatly from that of $Cr(acac)_3$.

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